JV TASK 13 – ENVIRONMENTAL EVALUATION FOR UTILIZATION OF ASH IN SOIL STABILIZATION

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EXECUTIVE SUMMARY

Coal combustion by-products (CCBs) are produced in large volumes at coal-fired power plants. CCBs include fly ash, bottom ash, boiler slag, and flue gas desulfurization materials, and these materials have been shown to have advantageous properties for engineering, construction, and manufacturing applications [1,2,3, 4]. As indicated by the 1993 decision by the U.S. Environmental Protection Agency (EPA), CCBs do not warrant hazardous waste regulation under the Resource Conservation and Recovery Act (RCRA). While this decision places the regulation of CCBs in the jurisdiction of individual states that EPA "encouraged the utilization of CCBs and supported State efforts to promote utilization in an environmentally beneficial manner." The utilization of CCBs has been demonstrated in numerous applications, including concrete, soil stabilization, controlled low-strength materials, highway road base and subgrade, soil amendments for agricultural uses, waste stabilization, extenders in plastics and paints, and the manufacture of products such as cement, insulating materials, lightweight building block, brick, and other construction materials. Some utilization applications, such as their use as a mineral admixture in concrete, have gained full commercial status. Work continues to demonstrate the effectiveness of CCBs in several applications, as is the case with the use of CCBs for soil stabilization.

CCBs, especially fly ash, have properties that are beneficial in soil stabilization applications such as soil drying, soil amendments to enhance subgrade support capacities for pavements and floor slabs, reduction of shrink—swell properties of soils, and stabilizers in aggregate road base construction and asphalt recycling. Six percent of the fly ash utilized and 20% of the bottom ash utilized were in road base and subbase applications in 1999, down slightly from 7% of fly ash in 1997 and 1998 and 25% and 31% of bottom ash in 1997 and 1998, respectively [5,6,7]. EPRI and the U.S. Department of Energy (DOE) realize that both the engineering and environmental performance of CCBs must be demonstrated and documented for CCBs to be fully accepted as a commercially viable option for soil stabilization applications. These entities provided support to the University of North Dakota Energy & Environmental Research Center (EERC) and the University of Minnesota Department of Soil, Water, and Climate to perform a laboratory and field investigation on the environmental performance of regionally available fly ash for soil stabilization.

This effort was designed to evaluate the environmental performance of regional coal fly ash in typical soil stabilization applications, with an emphasis on addressing issues raised by the regulatory community. To determine the types of environmental risk associated with the use of coal combustion fly ash in soil stabilization, the effort included laboratory evaluations of fly ash composition, a field demonstration to evaluate runoff quality, and laboratory leaching of stabilized soil samples from full-scale soil stabilization projects. Xcel Energy and Mineral

Solutions, Inc., suppliers of coal fly ash, selected eleven commercial sites for demonstration of the use of five regional fly ash samples to stabilize soils in various applications ranging from road subgrade to backfilling in a utility trench. Typical of most soil stabilization applications, the stabilized soil in these applications was surfaced or covered as part of the overall construction project. The fly ash addition, based on the engineering performance required, was 12 or 14 parts fly ash added to 100 parts soil.

Samples of background soil, fly ash used, background water sample (where used), and stabilized soil were collected at each site and submitted for laboratory evaluations including bulk composition and leaching characteristics of the stabilized soils. Similar samples from the runoff demonstration (Site 12) were collected and subjected to the same laboratory evaluations. The runoff demonstration was accomplished using equipment to simulate a rainfall event and compared runoff quantity and quality from test sections of unstabilized soil, lime-stabilized soil, and fly ash-stabilized soil.

Solid materials, laboratory generated leachates, and runoff samples were evaluated for a predetermined list of parameters recommended by the Minnesota Pollution Control Agency (MPCA). These included antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, iron, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, vanadium, zinc, and sulfate. Many of these elements are environmentally significant and have been shown to be present in CCBs. CCB leachate concentrations of most of these elements are typically below environmental and health limits. The analytical LLO (lower limit of quantitation) used in this study was at or below the LLQ required by MPCA, which in nearly all cases was lower than any regulatory limits. The laboratory leaching methods were also selected to address MPCA recommendations. These were the SPLP (synthetic precipitation leaching procedure), an 18-hour procedure using a dilute sulfuric acid leaching solution, and American Society for Testing and Materials (ASTM) D3987, an 18-hour procedure using distilled, deionized water as the leaching solution. Additionally, long-term leaching was performed using the same leachant as the ASTM D3987 procedure but using extended equilibration times of 30 and 60 days. Long-term leaching results can demonstrate an increase or decrease in the mobility of the constituents of interest with respect to time. Under static laboratory batch-leaching conditions, these changes are dependent on chemical and mineralogical changes rather than on dilution or dispersion. Secondary mineralization of CCBs has been shown to play an important role in the mobility of constituents from CCBs and CCBs combined with other materials [13,14,15]. These reactions frequently take extended periods of time and may occur over days or even months, so the use of long-term laboratory leaching procedures can facilitate an understanding of potential field performance of CCBs.

Results of the laboratory evaluations indicated that the range of concentrations of most parameters were higher for the fly ash samples than the soil samples (Table ES-1). One source of fly ash was used at seven of the eleven commercial demonstration sites, and it was noted that the concentration range of this material over the course of the project was similar to the overall range of elemental concentrations in all fly ash samples in the study.

Table ES-1 Summary of Solids Data Ranges, μg/g

Parameter	Fly Ash Data Range	Soil Data Range	Parameter	Fly Ash Data Range	Soil Data Range
Sb	2.3–3.8	0.3–2.5	Mn	139–558	212–1337
As	11.9–19.0	3.5–9.7	Hg	0.015-0.600	0.011-0.480
Ва	134–6870	263–679	Мо	7.6–25.0	0.2–3.2
Ве	1.5–5.3	0.3–1.2	Ni	16–165	8–108
В	480–1392	< 4–39	Se	15.1–25.2	1.3–11.6
Cd	0.55–1.99	0.11–1.06	Ag	1.18–1.94	0.10-1.14
Cr	35–95	11–46	TI	0.37–0.68	0.20-0.67
Co	13.0–29.9	9.0–18.0	V	56–312	16–103
Fe	24,825–44,666	13,830–22,502	Zn	50–175	26–174
Pb	21.1–54.5	9.0–16.8			

For 12 of the 20 leachate parameters analyzed, more than 75% of the 43 leachates exhibited concentrations less than the LLQ required by MPCA. This information is summarized in Table ES-2. The lowest and highest detectable leachate concentrations obtained for each parameter are also shown in Table ES-2. Leachate concentrations were compared to several regulatory limits for drinking water and groundwater, and the comparison indicated that the ash—soil leachates generally do not exceed these limits of concern by the regulatory community.

The short- and long-term leaching results were very similar, but some long-term results did indicate changes in the leachate concentrations over time. Decreasing concentrations in long-term leachates were noted in several cases for arsenic, barium, boron, selenium, and sulfate. These results are consistent with leaching profiles obtained from fly ash and other moderate-to high-calcium CCBs. These reductions in leachate concentration can be attributed to precipitation reactions such as the formation of barium sulfate and the formation of secondary hydrated phases that have been shown to incorporate several of the elements into the phase structure. The relatively high leachate alkalinity, demonstrated by the leachate pH range of 8.8 to 11.3 was consistent with these proposed mechanisms for reduced leaching potential.

Interpretation of the leaching results included calculating the maximum leaching potential of the elements evaluated. This calculated value was obtained using the total bulk concentration of each element in the ash–soil mixture and assuming that the maximum leachate concentration would be represented by 100% dissolution of that element. Using the same liquid-to-solid ratio used in all the leaching tests, the potential maximum leachate concentration of each element was calculated.

Table ES-2 Summary of Ash–Soil Leachate Results, ug/L

Parameter	Values below LLQ (of 43)	Low (detectable)	High	Parameter	Values below LLQ (of 43)	Low (detectable)	High
Sb	all <3			Mn	42 values <5		8
As	22 values <4	4.4	14	Hg	29 values < 0.01	0.0013	0.066
Ва	0 values <10	42	296	Мо	1 value <2	2.5	82.4
Ве	all <1			Ni	34 values <4	4.3	10
В	0 values <200	260	1400	Se	9 values <2	2.1	7.1
Cd	42 values < 0.3		0.96	Ag	34 values < 0.3	0.34	5.3
Cr	4 values <1	4.2	131	TI	37 values <1	1.01	1.38
Со	41 values <2	2.2	2.3	V	14 values <40	43	340
Fe	39 values <10	11	24	Zn	all <30		
Pb	42 values <2		9.2	SO ₄ ²⁻	0 values <1000	16,400	295,000

In every case, the actual leachate concentrations were much lower than the calculated maximum. In most cases, the actual leachate concentrations were less than 10% of the calculated maximum, but in a few limited cases the actual leachate concentrations ranged from 10% to 40% of the calculated maximum leachate value. This is evidence of the low mobility of constituents from the stabilized soil.

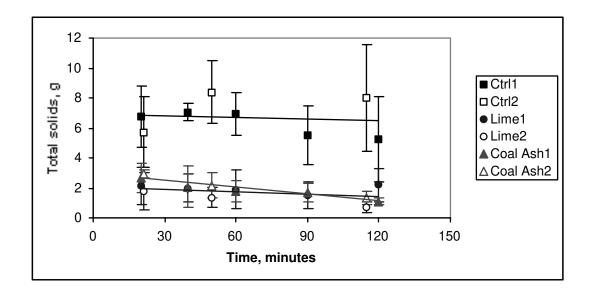
Solid samples (soil, fly ash, lime, and stabilized soil cores) and water from the simulated rainfall event were all incorporated into the laboratory evaluations already discussed, and the results from the fly ash and ash—soil samples were similar to the samples collected at the commercial demonstration sites. Lime—soil stabilization was included in the simulated rainfall event because lime is a typical stabilizing agent used for soils. Results from the lime-soil samples were generally in the same ranges as those from the ash—soil samples.

The primary goal of the simulated rainfall test was to evaluate the runoff from stabilized surfaces to address the issue of storm water runoff, which always needs to be addressed in construction activities. Replicate test sections of soil-only, a lime-soil mixture, and a fly ash-soil mixture were placed, and the simulated rainfall event was initiated. The soil-only and lime-soil mixtures were included for comparison with the ash-soil mixture. Runoff samples were collected during two simulated rainfall events, and these samples were evaluated for the parameters noted. The cementation of the soil due to the addition of ash or lime greatly reduced total solids (TS) in the runoff. The runoff from the lime and fly ash treatments contained less than one-third as much TS

as the control soil treatment (Figure ES-1). The data clearly show that the cementation due to lime and ash additions was effective in reducing the rate of detachment of soil particles from soil surface.

Figure ES-1

Total solids in runoff over the time of two rainfall events



The runoff solutions contained dissolved salts as well as suspended solids. However, the salt concentrations were small, and the total solids (TS) obtained by drying the samples closely approximated the concentration of total suspended solids (TSS). The greatest salt concentrations were in the runoff from the fly ash treatment but made little difference in the TS and TSS concentrations.

The total elemental concentrations of the runoff as collected (with suspended solids) and the concentration of dissolved components were determined. These data were compared with MPCA discharge water quality standards, and none of the elemental concentrations exceeded these water quality standards.

The relative mobility per unit concentration in the soil or soil mixes of the elements of interest varied in the ash–soil runoff samples. In some cases the mobility of an element was determined to be lower from the ash than from the soil resulting in a lower concentration of that element than predicted with a simple mixing model. These elements included Ag, Be, Co, Fe, Hg, Mn, Pb, Ni, Sb, and Tl. All of the elements of interest except B, Mo, S, and V were mostly associated with the suspended solids.

The data assembled from the laboratory and field efforts for this project support the conclusion that the environmental performance of fly ash in soil stabilization applications is environmentally viable. The limited leachability of the constituents in laboratory tests and the quality of the simulated field runoff indicated that fly ash used in this application is environmentally

appropriate and even offers advantages in limiting potential runoff in soil stabilization projects. The reactive type of fly ash that is most suited to fulfill the engineering performance requirements for soil stabilization also tends to provide leachate-limiting mechanisms that recommend these materials as an environmentally sound choice. Laboratory evaluations can be used to qualify CCBs but cannot predict field behavior. For the type of soil stabilization applications evaluated in this project, the engineering design limits the potential for water to contact the stabilized soil. The results presented support previous works showing little-to-negligible impact on water quality. This and past work indicates that soil stabilization is an environmentally beneficial CCB utilization application as encouraged by the EPA. This project addressed the environmental aspect of fly ash use for soil stabilization, but the demonstrated engineering performance and economic advantages also indicate that the use of CCBs in soil stabilization can and should become an accepted engineering option, promoted by state and industrial sectors.

REPORT SUMMARY

The Minnesota Pollution Control Agency (MPCA) approved the use of coal ash in soil stabilization, indicating that environmental data needed to be generated. An effort was funded by EPRI and the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL), with involvement from Xcel Energy (formerly Northern States Power Company), Mineral Solutions, Inc. (MSI), the University of North Dakota Energy & Environmental Research Center (EERC), and the University of Minnesota Department of Soil, Water, and Climate. The overall project goal was to evaluate the potential for release of constituents into the environment from ash used in soil stabilization projects.

Background

Coal combustion by-products (CCBs) are produced in large volumes at coal-fired power plants. CCBs include fly ash, bottom ash, boiler slag, and flue gas desulfurization materials, and these materials have been shown to have advantageous properties for engineering, construction, and manufacturing applications [1,2,3,4]. CCBs, especially fly ash, have properties that are beneficial in soil stabilization applications such as soil amendments to enhance subgrade support capacities for pavements and floor slabs, reduction of shrink–swell properties of soils, and stabilizers in aggregate road base construction and asphalt recycling. The EPRI and DOE realize that both the engineering and environmental performance of CCBs must be demonstrated and documented for CCBs to be fully accepted as a commercially viable option for soil stabilization applications. These entities provided support for a laboratory and field investigation on the environmental performance of regionally available fly ash for soil stabilization.

Objectives

The overall project goal is to evaluate the potential for release of constituents into the environment from ash used in soil stabilization projects. Supporting objectives are:

- To ensure sample integrity through implementation of a sample collection, preservation, and storage protocol to avoid analyte concentration or loss.
- To evaluate the potential of each component (ash, soil, water) of the stabilized soil to contribute to environmental release of analytes of interest.
- To use laboratory leaching methods to evaluate the potential for release of constituents to the environment.
- To facilitate collection of and to evaluate samples from a field runoff demonstration effort.

Approach

The EERC provided project management for the overall effort and performed the laboratory efforts to determine the composition of the bulk materials and the laboratory leaching studies on field-collected cores as reported in Chapter 1. Under subcontract to the EERC, the University of Minnesota Department of Soil, Water, and Climate performed a simulated rainfall event, associated sample collection of runoff, and analytical testing of the runoff samples reported in Chapter 2. The project was designed to evaluate the environmental performance of regional coal fly ash in typical soil stabilization applications with an emphasis on addressing issues raised by the regulatory community. To determine the types of environmental risk associated with the use of coal combustion fly ash in soil stabilization, the effort included laboratory evaluations of fly ash composition, a field demonstration to evaluate runoff quality, and laboratory leaching of stabilized soil samples from full-scale soil stabilization projects. Xcel Energy and MSI chose eleven commercial sites and one field-scale demonstration site to demonstrate the environmental and engineering performance of ash in soil stabilization. Leachate generation was performed in the laboratory using several leaching protocols, including both short- and long-term batch shakeleaching procedures. A field demonstration of soil stabilization was used to collect runoff samples generated from a simulated rainfall event. Data generated was compared to appropriate regulatory limits, with input from the MPCA.

Results

The results of this study indicated limited mobility of the coal combustion fly ash constituents in laboratory tests and the field runoff samples. The results presented support previous work showing little to negligible impact on water quality. This and past work indicates that soil stabilization is an environmentally beneficial CCB utilization application as encouraged by the U.S. Environmental Protection Agency. This project addressed the regulatory-driven environmental aspect of fly ash use for soil stabilization, but the demonstrated engineering performance and economic advantages also indicate that the use of CCBs in soil stabilization can and should become an accepted engineering option.

EPRI Perspective

(EPRI provides this when it goes to Publishing)

Keywords

Soil stabilization coal combustion by-products (CCBs) fly ash trace elements environmental impact

ABSTRACT

The Minnesota Pollution Control Agency approved the use of coal ash in soil stabilization, indicating that environmental data needed to be generated. An effort was funded by EPRI and the U.S. Department of Energy, with involvement from Xcel Energy (formerly Northern States Power Company), Mineral Solutions, Inc. (MSI), the University of North Dakota Energy & Environmental Research Center, and the University of Minnesota Department of Soil, Water, and Climate. The overall project goal was to evaluate the potential for release of constituents into the environment from ash used in soil stabilization projects.

Xcel Energy and MSI chose twelve sites to demonstrate the environmental and engineering performance of ash in soil stabilization. One site was a simulated rainfall event used to evaluate the potential for runoff and to determine the composition of the runoff collected.

The objective of this trace element project was to determine the environmental performance of the use of fly ash in soil stabilization. The objective was met by determining trace element transport from stabilized sites in both runoff and leachate generation. Leachate generation was performed in the laboratory using several leaching protocols, including the U.S. Environmental Protection Agency 1312 synthetic acid precipitation leaching procedure. The other procedure was an American Society for Testing and Materials (ASTM) D3987 shake leach procedure with long-term leaching components of 30 and 60 days. This modified ASTM leaching test is called the synthetic groundwater leaching procedure. Both leaching procedures are batch leaching protocols utilizing a 20:1 liquid-to-solid ratio.

The results of the testing protocols all indicate that the use of fly ash for soil stabilization can be done in an environmentally sound manner and with good engineering performance. The tests also demonstrate that there can be some variability between different fly ash samples, although few leachate trace element concentrations were above any problematic levels.

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1 ENVIRONMENTAL EVALUATION FOR UTILIZATION OF ASH IN SOIL STABILIZATION

Chapter 1 was prepared by Loreal V. Heebink and David J. Hassett of the University of North Dakota Energy & Environmental Research Center.

1.1 Introduction

Many coal combustion by-products (CCBs) have advantageous properties for engineering, construction, and manufacturing applications [1,2,3,4]. CCB utilization applications include concrete, soil stabilization, controlled low-strength materials, highway road base and subgrade, highway embankments, soil amendments for agricultural uses, waste stabilization, extenders in plastics and paints, and the manufacture of products such as cement, insulating materials, lightweight building block, brick, and other construction materials. CCBs have properties that are beneficial in soil stabilization applications such as soil drying, a soil amendment to enhance subgrade support capacities for pavements and floor slabs, reduction of shrink–swell properties of soils, and a stabilizer in aggregate road base construction and asphalt recycling.

Approximately 31% of all U.S. CCBs produced in 1999 were utilized, which is up from 28% and 29% in 1997 and 1998, respectively [5,6,7]. These CCBs included fly ash, bottom ash, boiler slag, and flue gas desulfurization materials. Six percent of the utilized fly ash and 20% of the utilized bottom ash were used in road base and subbase applications in 1999, down slightly from 7% of fly ash in 1997 and 1998 and 25% and 31% of bottom ash in 1997 and 1998, respectively [5,6,7]. The typical usage rate of CCBs for soil stabilization applications is 6%–15%, although this varies on the basis of engineering performance in prescribed laboratory tests.

Laboratory batch leaching tests have been utilized to determine the potential impact of CCBs on the environment, based on numerous articles in the literature. The most common laboratory leaching tests are 1) the toxicity characteristic leaching procedure (TCLP), U.S. Environmental Protection Agency (EPA) Method 1311 [8]; 2) the synthetic precipitation leaching procedure (SPLP), EPA Method 1312 [9]; and 3) the American Society for Testing and Materials (ASTM) D3987 leaching procedure [10]. TCLP is generally not a suitable leaching test for the evaluation of field behavior of CCBs, as it was designed for the evaluation of leaching of wastes when codisposed in a sanitary landfill. SPLP and ASTM D3987 are more appropriate for evaluating the environmental performance of CCBs. Field evaluations of ground and surface water have been performed to determine the impact of CCB use [11,12]. The use of CCBs in various applications, including paving, embankments, and road base, resulted in little-to-negligible impact on water quality, as shown in these reports.

Although field leaching behavior cannot be accurately duplicated with laboratory leaching, the mobility of constituents in materials to be placed in the environment can be estimated. The Minnesota Pollution Control Agency (MPCA) recommended the use of SPLP and a pH-neutral leaching test. The ASTM D3987 leaching procedure was chosen as the pH-neutral test, using distilled, deionized water for the leachate. These short-term, 18-hour tests do not allow adequate time for secondary mineralization to occur with the subsequent change in the materials controlling long-term behavior. The use of long-term leaching (LTL), typically 30- and 60-day equilibration times at the Energy & Environmental Research Center (EERC), can demonstrate an increase or decrease in the mobility of the constituents of interest with respect to time. Under static laboratory batch leaching conditions, these changes are dependent on chemical and mineralogical changes rather than on dilution or dispersion.

Secondary mineralization of CCBs has been shown to play an important role in the mobility of constituents from CCBs and CCBs combined with other materials [13,14,15]. These reactions frequently take extended periods of time and may occur over days or even months. Ettringite, a mineral having the nominal composition Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O, is an example of a secondary hydrated mineral. Ettringite is also the family name for a series of related compounds. Ettringite is a primary hydration product that forms when coal ash and water combine under alkaline conditions with a nominal pH between 11.5 and 12.5. The formation of ettringite and other secondary minerals can benefit the physical and engineering performance of stabilized soils. Ettringite formation acts to "dry" wet sites by incorporating large amounts of water into the CCB as it hydrates and improves handling properties of the soils as well as adds strength and reduces permeability. The secondary mineralization of field samples must occur prior to or during laboratory testing, so that laboratory results can best simulate real-world conditions.

Ettringite has characteristic structural features that are fairly unique. The structure consists of columns of calcium aluminate $(Ca_6Al_2[OH]_{12} \cdot 24H_2O)^{6+}$, with the channels between these columns containing the other components, which include an oxyanion such as sulfate with hydroxide and water $([SO_4]_{2-4}[OH]_{0-4}[H_2O]_{0-6})^{6^\circ}$. Ettringite is unique in that several elements that exist as oxyanions in aqueous solutions can substitute for the sulfate in the structure. These elements include, but are not limited to, arsenic, boron, chromium, molybdenum, selenium, and vanadium. Additionally, a decrease in the concentrations of major cations and anions such as calcium, aluminum, and sulfate often occurs. Ettringite is also responsible for strength development in products (such as concrete and controlled low-strength material) that contain CCBs. Ettringite has been shown to form in several types of CCBs, including fly ash generated from the combustion of subbituminous and lignite coal [13,14]. Many fly ashes meet the requirements for ettringite, which are soluble calcium, aluminum, sulfate, alkaline pH, and adequate water.

Leachate concentrations in this report are compared to Minnesota groundwater standards, national drinking water standards, and leaching regulations. The Minnesota groundwater standards are the Health Risk Limit (HRL) and the Health Based Values (HBV) set by the Minnesota Department of Health. An HRL is the concentration of groundwater contaminant, or a mixture of contaminants, that can be safely consumed daily for a lifetime. HBV are derived by the same methodology as HRL but may or may not have the same level of confidence. HRLs are promulgated by rule whereas HBVs are not. The national drinking water standards used are

EPA's Maximum Contaminant Level (MCL), Maximum Contaminant Level Goal (MCLG), and Secondary Drinking Water Regulations (SDWR). The MCL is the highest level of a contaminant that EPA allows in drinking water. The MCL of lead is listed as a treatment technique (TT), which is a required process intended to reduce the level of contaminant in drinking water. It is then given an action level, which if exceeded in over 10% of the homes tested triggers treatment. An MCLG is the level of a contaminant in drinking water at which there would be no risk to human health; this is a nonenforceable level. The SDWR are nonenforceable federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water [16]. The leaching regulations are the Resource Conservation and Recovery Act (RCRA) and Universal Treatment Standards (UTS) levels, which have been historically based on TCLP tests but can be used as a guideline when analyzing results from other leaching tests. UTS are constituent-specific treatment standards.

The hierarchy of values utilized in Minnesota is HRL, HBV, and MCL. The MPCA required leachate lower limit of quantitation (LLQ) for beryllium and thallium is higher than a few water regulations. The beryllium LLQ of 1 μ g/L is greater than the HRL of 0.08 μ g/L. The thallium LLQ of 1 μ g/L is greater than the HRL of 0.6 μ g/L and the SDWR of 0.5 μ g/L. Since the LLQs for Be and Tl are above the HRLs, MPCA desired comparisons will not be possible.

1.2 Experimental

Xcel Energy (formerly Northern States Power Company) and Mineral Solutions, Inc., chose twelve sites to demonstrate the environmental and engineering performance of fly ash in soil stabilization. One site was a simulated rainfall demonstration used to determine the potential for trace element mobility of runoff collected during the simulated rainfall event.

1.2.1 Sample Description

A description of the type of soil stabilization for each site is listed in Table 1-1. Sites 3–6 consisted of a 2-mile stretch of road, with each one-half mile stabilized with different fly ashes. The simulated rainfall demonstration site is split into three because a control plot and two types of stabilized soil plots were compared and contrasted for runoff effects.

Table 1-2 indicates the addition rate of ash, the source of fly ash used, and the blend method at each site. The addition rate indicates 12 or 14 parts fly ash (or five parts lime) added to 100 parts soil. Fly ash from all five of Xcel's Minnesota coal-fired power plants was utilized in the project. Eagan Class C fly ash is a blend of fly ash from the Black Dog and High Bridge plants. Riverside Unit 7 is a Class C fly ash. Sherco is short for Sherburne County Generating plant. Riverside Unit 8 and Allen S. King are cyclone boiler units that burn 5%–10% petroleum coke. At Site 12, plots were stabilized with either Allen S. King fly ash or lime to compare and contrast runoff effects. A mixture of Sherco Unit 3 and Riverside Unit 7 fly ashes produces Pozzolite, which is sold only to masonry producers.

Table 1-1
Type of Fly Ash Soil Stabilization Project at Each Site

Site	Description
1	Subgrade stabilization beneath arena floor prior to placement of sand base and concrete floor
2	Subdivision street subgrade stabilization prior to placement of base course and wear surface
3	Road subgrade
4	Road subgrade
5	Road subgrade
6	Road subgrade
7	Street subgrade stabilization prior to placement of base course and wear surface
8	Water main trench backfill (soil and fly ash mixed, backfilled into the trench and compacted)
9	Subgrade stabilization inside building prior to placement of sand base and concrete floor
10	Subgrade stabilization beneath basketball arena parking lots prior to placement of base course and wear surface
11	Subgrade stabilization beneath parking lots prior to placement of base course and wear surface
12a	Simulated rainfall demonstration test plot (fly ash)
12b	Simulated rainfall demonstration test plot (agricultural lime)
12c	Simulated rainfall demonstration test plot (control)

1.2.2 Sample Collection

Samples collected from each site included a background soil sample, an ash sample, a background water sample (only where needed to aid in the soil stabilization process), and stabilized soil samples (collected in core tubes). One 350-mL sample of unstabilized soil and of fly ash from the delivery truck was collected. Three samples of soil stabilized with fly ash were collected using 12-inch-long zero contamination stainless steel shelby tubes. Liquid samples were preserved by the addition of 2% hydrochloric acid. All samples were transported to the lab in coolers at 4°C. The core tubes were stored sealed under controlled conditions (18°–20°C) for at least 7 days. This allowed for strength development and accompanying mineralogical transformations to occur.

Additional samples collected at the simulated rainfall demonstration included a lime sample, a background water sample at the point of release, runoff samples from the stabilized soil plots, and a background runoff sample.

Table 1-2
Addition Rates of Ash, Ash Sources, and Blend Methods Used in the Project

Site	Addition Rate and Source of Ash	Blend Method
1	12 parts Eagan Class C fly ash	Rotary tiller
2	12 parts Eagan Class C fly ash	Motor grader
3	14 parts Riverside Unit 7 Class C fly ash	Pulvomixer
4	14 parts mix: 2/3 Sherco Unit 3, 1/3 Riverside Unit 8 fly ash	Pulvomixer
5	14 parts Sherco Unit 3 fly ash	Pulvomixer
6	14 parts mix: 2/3 Sherco Unit 3, 1/3 Riverside Unit 7 Class C fly ash	Pulvomixer
7	12 parts Eagan Class C fly ash	Motor grader
8	12 parts Eagan Class C fly ash	Disk
9	14 parts Eagan Class C fly ash	Rotary tiller
10	12 parts Eagan Class C fly ash	Disk
11	12 parts Eagan Class C fly ash	Pulvomixer
12a	12 parts Allen S. King fly ash	Rototiller
12b	5 parts lime	Rototiller
12c	Control (only soil)	_

1.2.3 Bulk Composition

The raw materials (fly ash, lime, soil, and water) from the sites were analyzed for bulk composition at the Xcel Energy Environmental Laboratory. Fly ash and soil were tested for all sites; lime was tested for Site 12b; and water was tested for Sites 3–6. The elements required in MPCA Permit SW-532 are listed in Table 1-3, as well as the LLQ required by the MPCA. The soil samples were air-dried at $104^{\circ}F$ and ground in a tungsten carbide mill. The samples were digested with nitric, hydrochloric, and hydrofluoric acids in closed Teflon microwave vessels. The test methods used to determine the concentration of these elements were inductively coupled plasma (ICP), inductively coupled plasma/mass spectroscopy (ICP/MS), cold-vapor atomic absorption (CVAA), and thermal decomposition, amalgamation, and atomic absorption spectrophotometry (TDA/AAS) (listed in Table 1-4). EPA Method 245.1 was first used to measure the concentration of Hg in the solids. The solids that yielded a concentration of less than the method detection limit (MDL) of $0.06~\mu g/g$ were retested using EPA Method 7473 to achieve the required LLQ of $0.001~\mu g/g$.

Table 1-3 **MPCA Required Lower Limit of Quantitation**

Parameters	Solids, µg/g	Runoff and Leachates, µg/L	Parameters	Solids, μg/g	Runoff and Leachates, µg/L		
Sb	0.3	3	Mn	0.5	5		
As	0.4	4	Hg	0.001	0.01		
Ва	1.0	10	Мо	0.2	2		
Be	0.5	5 ª	Ni	0.4	4		
В	20	200	Se	0.2	2		
Cd	0.03	0.3	Ag	0.03	0.3		
Cr	0.1	1	SO ₄ ^{2°}	_	1000		
Со	0.2	2	TI	0.3	3ª		
Fe	1.0	10	V	4	40		
Pb	0.2	2	Zn	3	30		
^a The LLQ was lowered to 1 μg/L at the EERC.							

Table 1-4 **Test Methods Used to Analyze Solids**

Test Method	Element(s) tested
EPA 200.7	Ba, B, Fe, V (ICP)
EPA 200.8	Sb, As, Be, Cd, Cr, Co, Pb, Mn, Mo, Ni, Se, Ag, Tl, Zn (ICP/MS)
EPA 245.1	Hg (CVAA, manual) (MDL of 0.06 μg/g)
EPA 7473	Hg (TDA/AAS) (MDL of 0.001 μg/g)

1.2.4 Leaching

Leaching was performed on fly ash-stabilized soil composites. Duplicate fly ash-stabilized soil core tubes were received from several locations at each site. One core from each of the locations was disaggregated and used to make a composite for each site. Each composite was subjected to SPLP, ASTM D3987, and LTL tests.

The ASTM D3987 and SPLP leaching had an equilibration time of 18 hours. The SPLP extraction fluid was prepared by adding a 60/40 weight percent H_2SO_4 –HNO3 solution to distilled, deionized water until a pH of 5.00 ± 0.05 was reached, which is used to determine the leachability of soil for sites west of the Mississippi River. A pH of 5.03 was achieved. The ASTM D3987, referred to hereafter as the 18-hour test, and LTLs used distilled, deionized water. The equilibration time for the LTL of the composites was 30 and 60 days. Four separate leachings were done for each sample. A 20:1 liquid-to-solid ratio with end-over-end rotation at 30 rpm was used for all leachings. The leachates were filtered through a 0.45- μ m filter, and the pH of the filtered solution was recorded. The solutions were preserved with nitric acid to pH less than 2.

All leachates were analyzed at the EERC for the parameters in Table 1-4. The instrumental methods used were graphite furnace atomic absorption (GFAA), inductively coupled argon plasma (ICAP), CVAA, gaseous hydride atomic absorption, and ion chromatography (IC) (Table 1-5). Minnesota Valley Testing Laboratories, Inc., in Bismarck, North Dakota, performed the turbidimetric determination of sulfate.

Table 1-5
Test Methods Used to Analyze Leachates

Test Method	Element(s) Tested	Test Method	Element(s) Tested
EPA 200.7	Ba, Be, B, Fe, Mn, V, Zn (ICAP)	EPA 249.2	Ni (GFAA)
EPA 204.2	Sb (GFAA)	EPA 272.2	Ag (GFAA)
EPA 206.2	As (GFAA)	EPA 245.1	Hg (CVAA)
EPA 213.2	Cd (GFAA)	EPA 270.3	Se (gaseous hydride AA)
EPA 218.2	Cr (GFAA)	EPA 279.2	TI (GFAA)
EPA 219.2	Co (GFAA)	EPA 300.0	Sulfate (IC)
EPA 239.2	Pb (GFAA)	EPA 375.4	Sulfate (turbidimetric)
EPA 246.2	Mo (GFAA)		

1.2.5 Simulated Rainfall Demonstration

The simulated rainfall demonstration was conducted at the University of Minnesota Rosemount Research and Outreach Center. Composites were made of the four control (soil only) plots, of the four fly ash–stabilized soil plots, and of the four lime-stabilized soil plots. The stabilized soil composites were leached in the same manner as was done for the core composites. Runoff from the study is evaluated in Chapter 2.

1.2.6 Biotoxicity

On July 28, 2000, a report entitled *Relative Toxicity of Soil, Soil/Lime, and Soil/Fly Ash Leachates* was sent to Xcel Energy by Environmental Toxicity Control, Inc., as a part of a study conducted by the University of Minnesota to determine water quality of runoff from stabilized soils. The following is a short summary of methods and findings from this report, which is included as Appendix K.

There were two stabilized soils tested along with an unstabilized control:

- 1. Soil from the runoff site
- 2. Soil + 5% lime
- 3. Soil + 12% fly ash from the Allen S. King power plant

The levels of treatment are taken from the test plan used in the runoff demonstration. Five test species were used in the toxicity testing.

- 1. Fathead minnow, Pimephales promelas
- 2. Water flea, Ceriodaphnia dubia
- 3. Algae, Selenastrum capricornutum
- 4. Frog embryo, Xenopus laevis
- 5. Earthworm, Eisenia foetida

Leachates were prepared from the three test materials described above.

1.3 Results and Discussion

Table 1-6 gives the MPCA LLQs and state and federal regulatory limits. The hierarchy of values utilized in Minnesota is HRL, HBV, and MCL. In this report, SDWR, RCRA, and UTS regulatory limits are also included in comparisons.

Results from Sites 1–11 and the simulated rainfall demonstration are reported separately.

1.3.1 Bulk Composition

A summary of the range of data on the bulk composition of the solids from Sites 1–11 is presented in Table 1-7. The results for the solids from the simulated rainfall demonstration are presented later. All bulk composition values can be seen in Appendix A. Mercury values obtained using EPA Method 7473 are denoted in Appendix A.

Table 1-6 Leachate and Runoff MPCA Lower Limits of Quantitation and Minnesota State and National Regulatory Limits, $\mu g/L$

		Minnesota		National I	Regulation	าร
		Groundwater	Drinking Water		Leachates	
Parameter	Leachate and Runoff LLQ	HRL / HBV	MCL	SDWR	RCRA	UTS
Sb	3	6	6			1500
As	4		50		5000	5000
Ва	10	2000	2000		10,000	2100
Ве	5ª	0.08	4			1220
В	200	600				
Cd	0.3	4	5			
Cr	1	100	100		5000	600
Co	2	30				
Fe	10			300		
Pb	2		15 ^⁵		5000	75
Mn	5	100		50		
Hg	0.01		2		200	25
Мо	2	30				
Ni	4	100				11,000
Se	2	30	50		1000	5700
Ag	0.3	30		100	5000	140
TI	3ª	0.6	2	0.5°		20
V	40	50				1600
Zn	30	2000		5000		4300
SO ₄ ²⁻	1000			250,000		
^a Lowered to	1 μg/L at the EEF	RC. b TT action lev	/el. ° MC	LG. ^d Cr III.		

It can be seen that the fly ashes and soils are quite different in composition. Generally, the concentration of the trace elements determined is higher in the fly ash than in the soil. The stabilized soil chemistry is mostly dependent upon the interaction between the fly ash and soil. These hydration reactions that the fly ash can undergo and possible ash sediment interactions can take time to occur and are dependent on water contact and chemistry of both the ash and the soil.

Table 1-7 Summary of Solids Bulk Composition Data Ranges for Sites 1–11, μg/g

Parameter	Fly Ash Data Range	Soil Data Range	Parameter	Fly Ash Data Range	Soil Data Range
Sb	2.3–3.8	0.3–2.5	Mn	129–558	212–1337
As	11.9–19.0	3.5–9.7	Hg	0.015-0.600	0.011-0.480
Ва	134–6870	263–679	Мо	7.6–25.0	0.2–3.2
Be	1.5–5.3	0.3–1.2	Ni	16–165	8–108
В	480–1392	< 4–39	Se	15.1–25.2	1.3–11.6
Cd	0.55–1.99	0.11–1.06	Ag	1.18–1.94	0.10-1.14
Cr	35–95	11–46	TI	0.37–0.68	0.20-0.67
Со	13.0–29.9	9.0–18.0	V	56–312	16–103
Fe	24,825–44,666	13,830–22,502	Zn	50–175	26–174
Pb	21.1–54.5	9.0–16.8			

Table 1-8 shows the data range of the bulk elemental composition in the Eagan Class C fly ashes. Eagan fly ash is a blend of fly ash from two different sources and is more of a marketing source than an originating source. Eagan fly ash was used as the additive in Sites 1, 2, and 7–11. Other sources of fly ash were used for Sites 3–6. Eagan Class C fly ash is comparable to the other fly ashes used in the study.

Table 1-9 shows the range for the soil in Sites 3–6. These sites consist of four one-half mile stretches of a road. The numbers are fairly consistent, as expected.

Water was used at Sites 3–6 to aid in the soil stabilization process. The elemental composition results are shown in Table 1-10. The concentrations are compared to Minnesota HRLs and HBVs and national drinking water regulations, as these are the highest in the MPCA hierarchical order. All concentrations of this background water are lower than the Minnesota required limits. However, the certainty of the Be comparison to the HRL is unclear since the LLQ is higher than the HRL, but it is lower than the MCL.

1.3.2 Leaching

The range of all leaching results for the soil stabilization composites from Sites 1–11 is shown in Table 1-11 (43 leachings total) and compared to regulatory limits. A 30-day leaching of Site 2 was not performed because of a lack of material. The results for the leachates from the simulated rainfall demonstration are presented later. The number in the column labeled "Low" is the lowest reported value above the LLQ. All leachate values can be found in Appendix B.

Table 1-8 Eagan Class C Fly Ash Bulk Elemental Composition, $\mu g/g$

Parameter	Data Range	Parameter	Data Range
Sb	2.3–2.7	Mn	129–162
As	11.9–19.0	Hg	0.162-0.600
Ва	4747–6870	Мо	7.6–10.2
Ве	1.5–5.3	Ni	16–98
В	480–1084	Se	15.1–25.2
Cd	1.17–1.99	Ag	1.44–1.94
Cr	37–95	TI	0.40-0.68
Со	13.0–29.9	V	160–202
Fe	30,989–44,666	Zn	54–175
Pb	46.1–54.5		

Table 1-9 Bulk Elemental Composition of Soil from Sites 3–6, $\mu g/g$

Parameter	Data Range	Parameter	Data Range
Sb	0.61–0.84	Mn	648–1337
As	7.3–8.0	Hg	0.14-0.2
Ва	628–655	Мо	0.9–1.9
Be	1.11–1.23	Ni	21.6–36.0
В	<4–8	Se	1.3–3.0
Cd	0.22–0.48	Ag	0.33-0.38
Cr	26.7–45.7	TI	0.46–0.61
Со	10.1–13.3	V	81–103
Fe	18,387–22,502	Zn	64–69
Pb	13.1–15.9		

Table 1-10
Bulk Composition Results of Water Used for Sites 3–6, μg/L

Parameter	Concentration	HRL / HBV	MCL / SDWR			
Sb	<0.04	6	6			
As	1		50			
Ва	42	2000	2000			
Be	<0.1	0.08	4			
В	360	600				
Cd	<0.1	4	5			
Cr	13	100	100			
Со	0.75	30				
Fe	259		300			
Pb	2.1		15ª			
Mn	96	100	50			
Hg	<0.02		2			
Мо	0.7	30				
Ni	1.4	100				
Se	<1	30	50			
Ag	<0.1	30	100			
TI	<0.01	0.6	2 / 0.5 ^b			
V	1	50				
Zn	12	2000	5000			
SO ₄ ²⁻	101,000		250,000			
^a TT action level. ^b MCLG.						

Few values were noted for Cd, Co, Fe, Pb, Mn, and Hg, and no values above the required MPCA LLQs were seen for Sb, Be, Tl, or Zn in any of the leaching tests performed. Since a detection limit below the MCL for Be and Tl was achievable, the LLQ was set to $1 \mu g/L$ at the EERC, which showed actual Tl values but no Be values. All leachate values were well below RCRA and UTS regulatory levels. Concentrations above the HRL or HBV limits were noted for B, Mo, Tl, and/or V in several sites. Three chromium values were slightly above the HRL and MCL limit. No other concentrations were above MCL levels.

The leaching values of the fly ash-stabilized soil composites varied between sites because of the differences in fly ash and bulk soil compositions, as well as because of potential geochemical changes induced through ash–sediment interactions and hydration reactions of the fly ash.

Comparisons of the results from the four leaching tests are displayed graphically by site in Appendix C. Only those elements with detected values are depicted in the figures. The number of elements detected for each site ranged from five to twelve, excluding sulfate. Sulfate is not included in the individual site figures in Appendix C because the values are much higher than those of any other element. The higher values made graphic presentation difficult. A dotted line indicates a separation between the right and left axes, both of which are in units of μ g/L. The SPLP value was, in many cases, higher than the 18-hour ASTM D3987 leachate value although

Table 1-11 Comparison of Leachate Concentrations to MPCA LLQs and Regulatory Limits, $\mu g/L$

Parameter	Values below LLQ (of 43)	Low (detected)	High	HRL / HBV	MCL / SDWR	RCRA	UTS
Sb	all <3	,		6	6		1500
As	22 values <4	4.4	14		50	5000	5000
Ва	0 values <10	42	296	2000	2000	10,000	2100
Be	all <1			0.08	4		1220
В	0 values <200	260	1400	600			
Cd	42 values < 0.3		0.96	4	5		
Cr	4 values <1	4.2	131	100	100	5000	600
Со	41 values <2	2.2	2.3	30			
Fe	39 values <10	11	24		300		
Pb	42 values <2		9.2		15ª	5000	75
Mn	42 values <5		8	100	50		
Hg	17 values <0.01	0.0013	0.066		2	200	25
Мо	1 value <2	2.5	82.4	30			
Ni	34 values <4	4.3	10	100			11,000
Se	9 values <2	2.1	7.1	30	50	1000	5700
Ag	34 values < 0.3	0.34	5.3	30	100	5000	140
TI	37 values <1	1.01	1.38	0.6	2 / 0.5°		20
V	14 values <40	43	340	50			1600
Zn	all <30			2000	5000		4300
SO ₄ ²⁻	0 values <1000	16,400	295,000		250,000		
^a TT action le	vel. ^b MCLG.	-1	1	1	ı	ı	

Each was an 18-hour test. This is most likely due to the instantaneous effect of the acidic pH leaching solution.

1.3.2.1 Calculated Maximum of Leachability

A calculated maximum level of leachability was determined for each element at each site for the fly ash (or lime) and the soil using Eq 1. Maximums were not determined for sulfate because it was not part of the bulk elemental testing of the solids. Maximum calculated concentration assumes total solubility of the material of interest or total release of analyte. A 20:1 liquid-to-solid ratio was used in the leachings. The calculated maximum values were determined for the fly ash and soil to show what could possibly leach if either solid were in an unstabilized environment.

CalcMax (ppb) =
$$\frac{\text{bulk elemental composition } (\mu g/g) \times \text{sample size } (g)}{\text{volume of leaching solution } (L)}$$
 [Eq. 1]

A core composite calculated maximum of leachability was determined by applying the ash application rate for each site (Table 1-2) to Eq 2. Each sample consisted of 100 + x parts, where x is the application rate. The calculated maximum assumes that the addition rate was accurate. The maximum was in all cases much higher than the actual leachate values for Sites 1°11. Figures of the leachate values plotted against the core composite calculated maximum values can be found in Appendix F. The core maximum generally mimicked that of the soil.

The core composite calculated maximum of leachability was also used to determine the percentage of possible leachability that actually occurred. For these calculations, the percentage was found by dividing the actual leachate result by the stabilized composite calculated maximum of leachability. Most of what did leach was less than 10% of the calculated maximum. Some leaching did occur between 10% and approximately 40%.

1.3.2.2 pH

Indirect evidence of ettringite formation is seen in some of the composite samples. This is in evidence because of decreasing concentrations of key indicator elements such as arsenic, boron, chromium, molybdenum, selenium, and vanadium. These trace elements and other elements known to exist as oxyanions in aqueous solution are known to form partially and/or fully substituted ettringites. It is also known that ettringite is the primary secondary hydration product formed when alkaline coal ash reacts with water. If the proper ingredients: aluminum, calcium, sulfate, and alkalinity are present, ettringite forms [17]. Optimal pH levels for ettringite formation are 11.5 to 12.5. Although this optimal pH range is required for ettringite formation, the bulk pH of samples may be below this limit and ettringite can still form. This is because of localized high pH at the ash granule—water interface. Evidence of ettringite formation has been

seen in samples with bulk pH values of between 9 and 10. Several trends of decreasing concentrations of trace elements can be seen in the elements arsenic, barium, boron, selenium, and sulfate. The decreasing concentration seen in barium is likely due to precipitation as barium sulfate where the others, which are oxyanions in aqueous solution, may likely be due to ettringite formation as well as to various other less likely precipitation reactions.

The final pH levels of all the filtered fly ash—soil-stabilized composite leachates are alkaline (see Figure 1-1). Table 1-12 shows the final pH levels of all leachates.

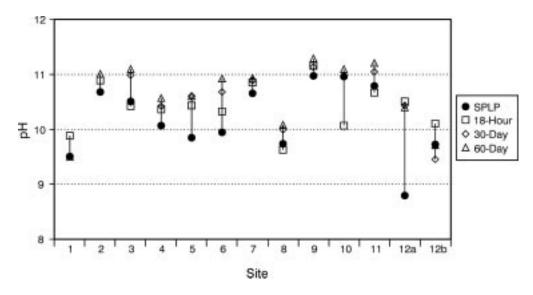


Figure 1-1
Final pH Levels of Fly Ash–Stabilized Soil Composite Leachates

It can be seen that the pH values for most of the samples were higher with distilled, deionized water and lower for an acidic leaching solution, as would be expected. The minor discrepancies for Samples 3, 8, 10, and 11, between the two 18-hour tests, are likely due to slight nonhomogeneity of the samples and are (for Samples 3, 8, and 11) also within experimental error for field samples of this type. The pH for 30- and 60-day leachings appears to increase with most of the fly ash-modified samples. Although the SPLP was an acidic leaching solution, the actual amount of acidity in a low ionic strength and unbuffered solution of this type is very low when compared to the available alkalinity of ash and buffering capacity of soil—ash systems. Differences in trace element concentrations and pH because of the use of an initially acidic solution, such as that used in SPLP leaching, may be due to an initial and near instantaneous effect of the acidic solution at the moment of first contact with sediment-ash systems. The general observation for these pH determinations is that, except for the low pH Sample12a with acidic leaching solution, all of the mixtures were potentially capable of ettringite formation. Even Sample 12a may have formed some ettringite. Direct evidence for ettringite formation can be obtained using x-ray diffraction but only at levels of greater than 1%. Because of the low loading of ash used in these projects, it would have been problematic to directly determine if ettringite had formed. The reduction of boron concentrations as well as decreases in concentrations of other oxyanionic element species with extended equilibration times in LTL,

however, is fairly good indirect evidence for ettringite formation given the high solubility of most boron compounds and minerals and because of the resistance of boron to sorptive removal.

Table 1-12 Final pH Levels of All Leachates

Site	SPLP pH	ASTM D3987 pH	30-day pH	60-day pH			
1	9.50	9.88	9.51	9.50			
2	10.68	10.89	NT	11.01			
3	10.51	10.42	10.99	11.10			
4	10.07	10.36	10.42	10.57			
5	9.85	10.43	10.60	10.61			
6	9.94	10.32	10.68	10.92			
7	10.65	10.85	10.89	10.93			
8	9.74	9.63	10.00	10.08			
9	10.97	11.15	11.13	11.29			
10	10.96	10.07	10.97	11.09			
11	10.79	10.67	11.05	11.20			
12a	8.79	10.51	10.44	10.40			
12b	9.73	10.11	9.45	9.71			
NT: No	NT: Not tested.						

Because ettringite formation can result in very efficient removal of select oxyanionic species (>99%), its formation in ash projects is highly desirable [18].

1.3.3 Simulated Rainfall Demonstration

1.3.3.1 Bulk Composition

Table 1-13 compares the solids used in the simulated rainfall demonstration test plots. A vast difference is seen in the concentrations of the elements among the three solids. The elemental concentrations are higher, in most cases much higher, in the fly ash than in the lime. It should be noted again that the fly ash utilized in this demonstration was from the Allen S. King plant, which is a cyclone boiler unit that burns 10% petroleum coke. Therefore, higher leachate

concentrations can be expected for Mo, Ni, V, and other trace elements that can be associated with petroleum coke.

Table 1-13 Comparison of Simulated Rainfall Demonstration Solids, $\mu g/g$

Parameter	Fly Ash	Lime	Soil	Soil Parameter		Lime	Soil
Sb	6.6	0.10	0.7	Mn	321	106	468
As	26.3	6.2	5.4 Hg		0.810	<0.00 1	0.190
Ва	432	5	514	Мо	105.1	0.2	1.2
Be	3.6	0.12	1.2	Ni	979	7.1	24
В	2005	38	<4	Se	29.4	24.6	1.8
Cd	1.90	0.06	0.18	Ag	1.87	0.06	0.38
Cr	78	4.3	38	TI	0.41	<0.01	0.52
Со	32.4	12.8	11.9	V	1537	3	80
Fe	43,885	1022	17,925	Zn	160	10	57
Pb	68.8	0.4	14.7				

Many of the King fly ash elemental concentrations are also higher than the concentrations of the other fly ashes in the project. The lime trace element concentrations were much lower than the concentrations in any fly ash samples, with the exceptions of cobalt and selenium. The soil is very similar elementally to the other soils in the project. Bulk composition results can be found in Appendix A.

1.3.3.2 Leaching

Table 1-14 compares the leachate ranges for each element to the regulatory limits. In most, but not all, cases, the leachate values for the fly ash–soil composite are higher than the leachate values for the lime–soil composite. The numbers do not directly correlate back to the bulk composition of the elements. In the fly ash–soil leachates, the B values are two times higher than the HRL. The Mo and V values are high in Site 12a, which is expected because of the 10% petroleum coke used in the firing of the coal. The Mo values are seven to nine times higher than the HBV in the fly ash-soil leachates. The V values are five to nine times higher than the HRL but still below the UTS level. A high silver value is seen in a lime–soil leachate, which is possibly an anomaly. The leachate values are found in Appendix B and are displayed graphically in Appendix G.

Calculated maximums of leachability were determined for the fly ash, lime, and soil using Eq. 1 and for the fly ash and lime-stabilized test plots using Eq. 2. The calculated maximum was determined using a 12-part addition of fly ash for Site 12a and a 5-part addition of lime for

Table 1-14 Comparison of Simulated Rainfall Demonstration Leachate Data Range to Regulatory Limits, $\mu g/L$

Parameter	Fly Ash–Soil Data Range	Lime–Soil Data Range	HRL / HBV	MCL / SDWR	RCRA	UTS		
Sb	all <3	all <3	6	6		1500		
As	<4-7.4	6–12		50	5000	5000		
Ва	86–97	<10–13	2000	2000	10,000	2100		
Ве	all <1	all <1	0.08	4		1220		
В	1200–1300	all <200	600					
Cd	<0.3–0.45	all <0.3	4	5				
Cr	2.4–3.6	<1–1.4	100	100	5000	600		
Со	all <2	<2-2.4	30					
Fe	all <10	all <10		300				
Pb	all <2	<2-2.6		15ª	5000	75		
Mn	all <5	all <5	100	50				
Hg	<0.01-0.0236	<0.01- 0.0306		2	200	25		
Мо	216–285	<2-4.7	30					
Ni	all <4	8.4–11	100			11,000		
Se	<2-5.2	all <2	30	50	1000	5700		
Ag	<0.3–5.2	<0.3–26	30	100	5000	140		
TI	all <1	all <1	0.6	2 / 0.5°		20		
V	270–417	<40-42	50			1600		
Zn	all <30	all <30	2000	5000		4300		
SO ₄ ^{2°}	19,000– 227,000	2900– 17,800		250,000				
^a TT action le	^a TT action level. ^b MCLG.							

Site 12b. The composite calculated maximum was, in most cases, much higher than the actual leachate values. In the samples where leaching above the LLQs did occur, the percentage of maximum leachability that occurred ranged from 0.045% to 46.22% for all of the elements. The highest percentages were for molybdenum. The 60-day silver leachate for Site 12b was higher than the estimated calculated maximum and is not included in the percentage range. This

represents some source of contamination, but because of the low bulk silver levels and low leachability, the source of silver contamination was not identified, and further investigation was considered to be beyond the scope of this project. The percentage values can be found in Appendix G.

1.3.4 Quality Assurance/Quality Control

The stabilized soil of five samples from four of the sites was leached again. Samples were included from Sites 1, 3, 4, and both stabilized soils from Site 12. These samples were chosen for duplicate leaching for the range of values to be tested. Sites 1, 3, and 4 had the most low, medium, and high values, respectively, overall. Sites 12a and 12b were chosen to further compare/contrast the values. Leachings performed were the deionized leachings: ASTM D3987 and the 30- and 60-day LTLs. Tables 1-15 and 1-16 show the changes in the data ranges with the duplicate results. Blank spots indicate no changes.

Table 1-15 Changes in Data Ranges for Duplicate Deionized Leachings of Sites 1, 3, and 4, $\mu g/L$

Element	Site 1	Site 1D	Site 3	Site 3D	Site 4	Site 4D
As			<4–11	6.2–7.4	5.9–14	6.7–7.4
Ва	68–93	69–147	42–234	59–115	59–222	89–227
В	260–360	250-400	640–920	1200–1600	420–570	970–1300
Cr	13.1–20.3	9.3–17.1	14.7–67	20.7–46.5	5.4–11.4	3.5–9.1
Co			<2	<2–2.8		
Fe			<10	<10–42	<10	<10–20
Mn					<5–8	<5
Мо	<2–5.7	3–11	10–22	21.7–35.4	49.7–72	76.5–118
Ni			<4–8.3	<4-4.7	<4–10	5.0-6.3
Se			2.2-4.8	5.3–6.4	3.2-5.6	5.0-6.4
SO ₄ ^{2°}	26,900– 32,900	44,500– 49,600	35,900– 63,600	83,200– 109,000	182,000– 284,000	332,000– 640,000
TI	<1–1.38	<1	<1–1.27	<1	<1–1.14	<1
V			56–97	45–110	180–340	190–320

Changes in the data ranges for 13 elements were noticed in Sites 1, 3, and 4. Generally, increases over previous concentrations were seen in boron, molybdenum, selenium, and sulfate; decreases were seen in arsenic, chromium, and nickel. Mixed results were seen for barium and vanadium. A few values were seen for cobalt and iron where no values had previously been seen above the LLQs. Values above the LLQs were no longer seen for manganese and thallium.

The changes in concentrations of the elements for Sites 12a and 12b varied. Arsenic, barium, selenium, and vanadium concentrations increased over the previous values for both samples; chromium and sulfate concentrations were lower. The boron changes were mixed and the molybdenum concentrations increased for Sample 12a. The cobalt, molybdenum, and nickel concentrations for Sample 12b varied. Values above the LLQs were no longer seen for cadmium and silver. The disappearance of silver confirms the suspicion that the original 60-day leaching result of $26 \,\mu\text{g/g}$ for Site 12b was likely due to contamination.

Table 1-16
Changes in Data Ranges for Duplicate Leachings of Sites 12a and 12b, μg/L

Element	Site 12a	Site 12aD	Site 12b	Site 12bD
As	<4–7.4	6.5–9.4	6–12	12–16
Ва	86–92	96–102	<10–11	12–14
В	1250–1300	1200–1500		
Cd	<0.3-0.45	<0.3		
Cr	2.6–3.6	2.0-3.2	<1–1.4	<1
Co			<2–2.4	<2-2.9
Мо	216–225	252–278	2.2–4.7	<2-2.9
Ni			8.4–11	5.7–11
Se	<2-5.2	5.0-6.2	<2	2.2–2.6
Ag	<0.3–5.3	<0.3	<0.3–26	<0.3
SO ₄ ^{2°}	194,000–227,000	202,000–210,000	3700–17,800	1400–2700
V	270–417	240–442	<40-42	<40-50

1.3.5 Biotoxicity

Leachates were prepared from the three test materials described earlier. One part of test material by volume was mixed with four parts of water on a volume basis. Because of the higher solid-to-liquid ratio used for the toxicity testing, concentrations of many trace elements were higher than concentrations obtained from the environmental leaching which uses a 1:20 solid-to-liquid ratio by weight.

Despite higher concentrations of several potentially toxic trace elements, the results of toxicity testing indicated little differences between the lime and fly ash–stabilized soils. Both showed limited increases in toxicity to all species except the earthworm, which was essentially unaffected by the fly ash–soil and lime–soil leachates. All aquatic toxicity tests demonstrated measurable responses from both lime–soil and fly ash–soil leachates. Soil leachates demonstrated no detrimental effects for any of the species tested.

1.4 Conclusions

Conclusions from laboratory analyses are presented in two ways. First, the laboratory leaching results are explained by site. Second, each element is examined, including the solids and leachings. Sites 1–11 and the simulated rainfall demonstration are considered separately.

It is important to note that batch leaching using SPLP, ASTM D3987, and LTL were used for generating data in this report. The decision to use these tests was made considering that either groundwater or, more likely, rainwater would be the leaching solution in real-world scenarios. TCLP leaching was deliberately left out because of the extreme unlikeliness of acetic acid

leaching solutions contacting stabilized soils. It is highly recommended that future studies use these batch leaching tests or tests that are similar.

1.4.1 Sites 1-11

The following describes the leaching results from Sites 1–11 in detail. Conclusions are based on Minnesota groundwater and national drinking water regulations. All concentrations are well below RCRA and UTS leaching limits.

1.4.1.1 Site 1

Site 1 was an arena floor subgrade Eagan Class C fly ash–soil stabilization prior to the placement of a sand base and concrete floor. The 30-day leachate was not tested for sulfate because of a lack of leachate sample. The only seven parameters with detectable values from the core composite leachings are Ba, B, Cr, Hg, Mo, Tl, and sulfate. All Tl results exceed the HRL and MCLG but are below the MCL, although only one Tl value is detected above the LLQ. All other concentrations are below regulatory levels.

Site 1 was included in the duplicate leaching sample set because very few elements yielded results above the LLQs. The duplicate results are not very different from the original leaching. Thallium is no longer seen above the LLQ and cannot accurately be evaluated based on the HRL and SDWR limits. All other concentrations are below regulatory limits.

Site 1 does not appear to pose a threat to the surrounding environment.

1.4.1.2 Site 2

Site 2 was a subdivision street subgrade Eagan Class C fly ash–soil stabilization prior to placement of a base course and wear surface. A lack of material resulted in the 30-day leaching experiment not being performed. Leaching of the parameters Ba, B, Cr, Hg, Mo, Se, Ag, Tl, V, and sulfate is seen above the LLQs. Exceedances are noted in B, Tl, and V. The boron SPLP and 60-day leachings are above the HRL limit of 600 μ g/L. The 18-hour thallium concentration of 1.11 μ g/L is above the HRL and MCLG but below the MCL. The 60-day vanadium concentration of 59 μ g/L is slightly above the HRL of 50 μ g/L. All other concentrations are below HRL, HBV, or MCL regulatory limits.

1.4.1.3 Site 3

Site 3 was the first one-half mile road subgrade of a 2-mile stretch. Riverside Unit 7 Class C fly ash was used for the soil stabilization. Twelve parameters leached detectable levels including As, Ba, B, Cr, Hg, Mo, Ni, Se, Ag, Tl, V, and sulfate. Exceedances above the HRL are found for B, Tl, and V. No MCL exceedances are noted. The boron values of 640° 940 μ g/L are higher than the HRL limit of 600μ g/L. The 18-hour and 30-day thallium concentrations of 1.14 and 1.27 μ g/L are above the HRL of 0.6 μ g/L and the MCLG of 0.5 μ g/L, but below the MCL of 2 μ g/L. The SPLP and 18-hour vanadium concentrations of 57 and 56 μ g/L, respectively, are

slightly above the HRL limit of 50 μ g/L, while the 30- and 60-day concentrations are higher at 95 and 97 μ g/L, respectively. All other concentrations are below regulatory limits.

Site 3 was chosen for the duplicate sample set because the original leachate values were generally in the midrange. Increases in all leachate concentrations are seen for B, Mo, Se, and sulfate. The boron values of 1200, 1500, and 1600 are all above the HRL. Arsenic and vanadium showed decreases in the 18-hour and 30-day values, but increases in the 60-day values. Barium, chromium, and nickel showed increases or no change initially, but decreases in the LTL results. Thallium no longer is seen as leaching above the LLQ, but values for cobalt and iron are noticed. The cobalt 60-day leaching concentration of 2.8 μ g/L is below the HBV of 30 μ g/L. The iron values are well below the SDWR of 300 μ g/L.

Boron and vanadium are the most problematic elements at Site 3, according to MPCA limits.

1.4.1.4 Site 4

Site 4 was the second one-half mile road subgrade of a 2-mile stretch. It was stabilized with a 14-part mixture consisting of 2/3 Sherco Unit 3 fly ash and 1/3 Riverside Unit 8 Class C fly ash. Thirteen parameters leached detectable concentrations. These are As, Ba, B, Cr, Mn, Hg, Mo, Ni, Se, Ag, Tl, V, and sulfate. Nickel is below the HRL limit. This is the only site where manganese, at a concentration of 8 μ g/L, leached above the LLQ of 5 μ g/L. The boron SPLP concentration of 910 μ g/L is above the HRL. The molybdenum concentrations ranged from 49.7 to 82.4 μ g/L, the highest of all leachates in Sites 1–11, and all above the HBV of 30 μ g/L. The vanadium concentrations are all much above the HRL limit of 50 μ g/L, ranging from 180 to 340 μ g/L. The Mo and V concentrations are indicative of the Riverside Unit 8 fly ash present in the mixture. The 18-hour Tl concentration is above the HRL and MCLG. The SPLP and 60-day sulfate concentrations are above the SDWR of 250,000 μ g/L.

Duplicate leachings of Site 4 were performed because many of the elemental leaching concentrations are high since Riverside Unit 8 fly ash was included in the mixture. Increases in all of the leachate concentrations are seen for Ba, B, Mo, Se, and sulfate. The boron concentrations of 970–1300 μ g/L are all above the HRL limit of 600 μ g/L, and the sulfate concentrations are above the SDWR of 250,000 μ g/L. Arsenic showed decreases in the 18-hour and 30-day values, but an increase in the 60-day values. The changes in the chromium values are mixed. A nickel value is noted for the 18-hour leaching, and the long-term values decreased from the original. The 18-hour and 30-day vanadium concentrations increased, but the 60-day concentration decreased. An iron concentration of 20 μ g/L for the 18-hour leaching is seen. The Mn and Tl values are no longer detected above the LLQs.

Boron, molybdenum, vanadium, and sulfate are of concern for Site 4.

1.4.1.5 Site 5

Site 5 was the third one-half mile stretch of road, which had a subgrade stabilized with Sherco Unit 3 fly ash. The eleven parameters that leached are As, Ba, B, Cr, Co, Hg, Mo, Ni, Se, V, and sulfate. The only cobalt concentrations above the LLQ are from Site 5; these are below all

regulatory limits. All leachates except the 18-hour had boron concentrations above the HRL. The 30- and 60-day V concentrations of 76 and 90 μ g/L, respectively, are above the HRL of 50 μ g/L. The SPLP and 60-day sulfate concentrations are above the SDWR of sulfate. All other concentrations are below regulatory limits.

Boron, molybdenum, vanadium, and sulfate may be problematic at Site 5.

1.4.1.6 Site 6

Site 6 was the fourth one-half mile of the 2-mile stretch of road and had a subgrade stabilized with a 14-part mixture consisting of 2/3 Sherco Unit 3 fly ash and 1/3 Riverside Unit 7 Class C fly ash. The parameters that leached detectable values are As, Ba, B, Cr, Hg, Mo, Ni, Se, Ag, V, and sulfate. The only exceedances are for B and V. The SPLP concentration of 1100 μ g/L for boron is above the HRL limit of 600 μ g/L and the 18-hour concentration is slightly above it. The vanadium 30- and 60-day concentrations of 90 and 99 μ g/L, respectively, are above the HRL limit of 50 μ g/L. All other concentrations are below regulatory levels.

1.4.1.7 Site 7

Site 7 was a street subgrade Eagan Class C fly ash–soil stabilization prior to the placement of a base course and wear surface. The ten parameters that leached are Ba, B, Cr, Fe, Hg, Mo, Se, Tl, V, and sulfate. Only B, Tl, and V concentrations are above the HRLs. The boron concentrations ranged from 440 to 810 μ g/L with the SPLP and 60-day values above the HRL of 600 μ g/L. Thallium has a detectable value of 1.01 μ g/L, which is above the HRL and MCLG. The 30- and 60-day V concentrations of 65 and 76 μ g/L, respectively, are above the HRL of 50 μ g/. All other elements are below major regulatory limits.

1.4.1.8 Site 8

Site 8 was a water main trench backfill project. Soil and Eagan Class C fly ash were mixed, backfilled into the trench, and compacted. Ten parameters, As, Ba, B, Cr, Fe, Hg, Mo, Ag, V, and sulfate, leached. Both detectable vanadium concentrations, from the 30- and 60-day leachings, are above the HRL limit. All other parameters are below regulatory limits. Site 8 does not appear to be problematic.

1.4.1.9 Site 9

Site 9 was a subgrade Eagan Class C fly ash–soil stabilization inside a building prior to the placement of a sand base and concrete floor. Ba, B, Cd, Cr, Fe, Hg, Mo, Se, V, and sulfate leached. Boron, Cr, Mo, and V concentrations are higher than Minnesota state limits. The boron concentrations ranged from 1010 to 1400 μ g/L, which is approximately two times higher than the HRL limit of 600 μ g/L. Site 9 is the only site, from Sites 1–11, that showed leaching of cadmium, 0.96 μ g/L, above the LLQ; this is below the MCL of 5 μ g/L. The chromium concentrations are 110, 84, 113, and 131 μ g/L for the SPLP, 18-hour, 30- and 60-day leachings,

respectively. Three of the values are above the HRL and MCL limits of 100 μ g/L. One Mo value is slightly above the HBV of 30 μ g/L. The vanadium concentrations ranged from 44 to 73 μ g/L with the 30- and 60-day leachates above the HRL limit of 50 μ g/L. All other concentrations are below regulatory levels.

Boron, chromium, and vanadium are problematic elements for Site 9.

1.4.1.10 Site 10

Site 10 was a subgrade Eagan Class C fly ash–soil stabilization beneath basketball arena parking lots prior to the placement of a base course and wear surface. The ten parameters that leached at detectable levels are As, Ba, B, Cr, Pb, Hg, Mo, Se, V, and sulfate. Only B and V leached above regulatory levels. All boron concentrations are above the HRL limit of 600 μ g/L. The only lead that leached in Sites 1°11 is in the SPLP leaching for Site 10. The concentration is 9.2 μ g/L, which is below the MCL action level of 15 μ g/L. The SPLP and 18-hour values for vanadium are below and the 30- and 60-day values are above the HRL limit of 50 μ g/L. All other parameters are below regulatory limits.

1.4.1.11 Site 11

Site 11 was a subgrade Eagan Class C fly ash–soil stabilization beneath parking lots prior to the placement of a base course and wear surface. The ten parameters that leached are Ba, B, Cr, Fe, Hg, Mo, Se, Ag, V, and sulfate. Only two elements leached above any regulatory limits: boron and vanadium. Three of the boron concentrations are above the HRL limit of 600 μ g/L. The detectable vanadium leachate concentrations are 48 and 51 μ g/L for the 30- and 60-day leachates, respectively; the HRL limit is 50 μ g/L. Site 11 would be considered a safe soil stabilization site.

1.4.2 Elements

The following is a summary of data for Sites 1° 11 and the duplicate results for Sites 1, 3, and 4 for each of the twenty parameters included in this study. Data are presented in terms of $\mu g/g$ for solids and $\mu g/L$ for leachates and other liquid samples. Additional comparative values are also included in this discussion. Some of the reference values and calculated values from reference oral doses (RfDs) are in mg/kg/day and mg/L, which are the standard terms. The values for RfD, lowest observed adverse effect level (LOAEL) and no observed adverse effect level (NOAEL) were taken from a U.S. EPA list of substances on IRIS (Integrated Risk Information System), an on-line service that is regularly updated. This information can be obtained on the Internet at http://www.epa.gov/iris/subst/index.html. Calculated values from RfD, LOAEL, and NOAEL are based on an adult human weighing 70 kg, drinking 2 liters of water per day. Intakes of the elements listed are not corrected for other dietary intakes associated with food.

Nearly all of the elements had higher bulk concentrations in the fly ash than the soil. This trend of higher values in fly ash compared to soil is consistent except for iron, manganese, and thallium. In the cases of these three elements, the soil mean is higher than the fly ash mean value

although the differences in thallium concentrations are likely within experimental error at near the LLQ. No detectable values are noted for antimony, beryllium, or zinc in the laboratory leachates.

1.4.2.1 Antimony

Antimony is found to be present in fly ash at concentrations between 2.3 and 3.8 μ g/g and in soil at between 0.3 and 2.5 μ g/g. Mean values for the fly ash and soil are 3.12 and 0.71 μ g/g, respectively.

The RfD for antimony is 0.0004 mg/kg/day. This gives a calculated reference dose of $14 \mu g/L$. The LOAEL is reported to be 0.35 mg/kg/day which at this value is 12.25 mg/L for a 70-kg person drinking 2 L of water per day.

Leaching concentrations are all below 3 μ g/L, placing antimony concentrations well below safe drinking water limits. The concentrations of antimony in leachates are below calculated values based on NOAEL of 14 μ g/L and are also below the HRL and MCL of 6 μ g/L. The concentrations are well below the UTS level of 1500 μ g/L. Antimony should not be a problem at the study sites.

1.4.2.2 Arsenic

Arsenic concentrations in bulk materials are 11.9-19.0 and $3.5-9.7 \mu g/g$ for fly ash and soil, respectively.

The RfD for arsenic is 0.0003 mg/kg/day with a LOAEL at 0.014 mg/kg/day and a NOAEL of 0.0008 mg/kg/day. This calculates to drinking water containing 10.5 μ g/L for the reference dose, 490 μ g/L for the LOAEL, and 28 μ g/L for the NOAEL, using the assumptions for drinking water shown above.

Leaching concentrations for arsenic are <4.0 to 14 μ g/L with a mean concentration of 8.1 μ g/L. Twenty-two of 43 leachates had arsenic concentrations below the required LLQ of 4 μ g/L. The leaching concentrations in the duplicates are <4.0 to 7.4 μ g/L. Arsenic concentrations in leachates are below the MCL of 50 μ g/L and the NOAEL of 30 μ g/L. Values of 11 μ g/L for the 18-hour leachates at Sites 3, 4, and 5 and 60-day leachate at Site 8, 12 μ g/L for the 30-day leachate at Site 5, and 14 μ g/L for the 30-day leachate at Site 4 are above the reference dose of 10.5 μ g/L. All values are well below the RCRA and UTS levels of 5000 μ g/L.

The percentage of arsenic that leached ranged from 1.01% to 3.17% and from 1.42% to 1.69% of the calculated maximums of leachability in the original and duplicate leachings, respectively. Arsenic should not be a problem in the study sites, with respect to the MCL.

1.4.2.3 Barium

Barium concentrations in bulk materials are 134–6870 and 263–679 μ g/g for fly ash and soil, respectively.

The RfD for barium is 0.07 mg/kg/day; the LOAEL is 115 mg/kg/day; and the NOAEL is 0.21 mg/kg/day. This translates to drinking water containing 2.45 mg/L for the reference dose, 4025 mg/L for the LOAEL, and 7.35 mg/L for the NOAEL, using the assumptions described above.

Barium leached at $42-296 \mu g/L$ and $59-227 \mu g/L$ in the duplicates, which is well below the HRL and MCL of $2000 \mu g/L$ and the reference dose, LOAEL, and NOAEL levels. These values are also below the RCRA level of $10,000 \mu g/L$ and the UTS level of $2100 \mu g/L$.

The barium that leached is 0.08%–1.00% of the potential leachable barium. The potential leachable barium that leached in the duplicate samples is 0.11%–0.77%. Barium should not be a problem at the study sites.

1.4.2.4 Beryllium

Beryllium concentrations in bulk materials are 1.5-5.3 and $0.3-1.2 \mu g/g$ for fly ash and soil, respectively.

The RfD for beryllium is 0.002 mg/kg/day. Using RfD and with the assumptions regarding water intake listed above, a safe drinking water limit would be 70 μ g/L. The leaching concentrations for beryllium are all <1 μ g/L, which is well below the safe limit as indicated by the current RfD and are all below the MCL of 4 μ g/L. It was not determined if beryllium concentrations are below the HRL of 0.08. This is not unexpected for ash from coals in the United States, as they typically contain very low concentrations of beryllium. The leachate concentrations are below the UTS level of 1220 μ g/L. Beryllium should not present a problem at the study sites.

1.4.2.5 Boron

Boron concentrations in bulk materials are 480–1392 and <4 to 39 μ g/g for fly ash and soil, respectively.

The RfD for boron is 0.09 mg/kg/day. Using this value, a calculated safe drinking water limit would be 3.15 mg/L. The NOAEL is 8.8 mg/kg/day, and the LOAEL is 29 mg/kg/day. This translates to 308 and 1015 mg/L for drinking water, respectively, to provide the referenced maximum dose. Although boron is not especially toxic to humans and other mammals, it can be relatively toxic to plants. For this reason, irrigation standards exist for boron. These irrigation standards are 0.75 mg/L for long-term irrigation and 2.0 mg/L for short-term irrigation.

Boron leachate concentrations are between 260 and 1400 μ g/L in the original leachings and between 250 and 1600 μ g/L in the duplicate leachings. All boron concentrations are well below

the short-term irrigation standard of 2.0 mg/L. Fifteen of 43 leachate concentrations are above the long-term irrigation standard of 0.75 mg/L, as are six of the nine duplicate concentrations. Twenty-five of the 43 original leachate concentrations and six of the duplicate leachate concentrations are above the HRL of 600 μ g/L. All leachate concentrations are well below the human thresholds of 308 and 1015 mg/L for NOAEL and LOAEL, respectively.

The leachate concentrations are 4.72%–33.67% and 6.19%–35.88% of the potential maximums for the original and duplicate leachings, respectively. Boron at these leachate concentrations could be problematic for plants if used continuously for irrigation in the form of undiluted leachate. It is viewed as a problem in Minnesota since the HRL is exceeded, but not on a national level.

Boron is one of the trace elements that can exist as an oxyanionic species in aqueous solution. Boron can, for this reason, be substituted into an ettringite structure during the hydration of alkaline fly ash. In Sites 4, 6, 7, and 10, boron concentrations decrease as leaching using distilled, deionized water approaches 60 days (see Appendix F, Figure F-6). This, because of the relatively high solubility of most boron compounds, provides indirect evidence for ettringite formation and likely accounts for the decreasing concentrations of this element over time as indicated by the LTL. It is likely that boron concentrations would continue to decrease with time for these sites and perhaps others as time went on.

1.4.2.6 Cadmium

Cadmium concentrations in bulk materials are 0.55-1.99 and $0.11-1.06 \mu g/g$ for fly ash and soil, respectively.

The RfD for cadmium is 0.0005 mg/kg/day for water, giving a safe drinking water limit of 17.5 μ g/L. The NOAEL for water is 0.005 mg/kg/day. This translates to 175 μ g/L for drinking water to provide the referenced maximum safe dose based on the NOAEL. Forty-two of 43 Cd leachings are less than 0.3 μ g/L, with one at 0.96 μ g/L. All duplicate leachings are less than 0.3 μ g/L. The measurable reading of 0.96 μ g/L is well below the HRL of 4 μ g/L, the MCL of 5 μ g/L, the reference dose of 17.5 μ g/L, and the allowed safe level of 175 μ g/L, as calculated from the NOAEL in water. It is 2.16% of what could have potentially leached. Cadmium should not present a problem at the study sites.

1.4.2.7 Chromium

Chromium concentrations in bulk materials are 35–95 and 11–46 μ g/g for fly ash and soil, respectively.

The RfD for chromium is 1.5 mg/kg/day for Cr(III) and 0.003 mg/kg/day for Cr(VI); however, it is not known what valence state of chromium was leached. It should likely be considered that both valence states are present in fly ash. Chromium(VI) is considered a carcinogen and has a Group A, known human carcinogen, rating by inhalation. Chromium(III) is rated as Class D, not a human carcinogen, by oral exposure.

The leaching results are $<1-131~\mu g/L$ in the originals and $3.5-46.5~\mu g/L$ in the duplicates. The HRL and MCL for chromium are $100~\mu g/L$; thus three leachates from Site 9, at 110, 113, and $131~\mu g/L$, are above regulatory limits. The 18-hour distilled water leachate for Site 9 is below this at $84.3~\mu g/L$. Site 9 had an addition of 14 parts Eagan Class C fly ash. Sites 1, 2, 7, 8, 10, and 11 with 12 parts Eagan Class C fly ash had leachate concentrations of chromium between <1 and $55.5~\mu g/L$. It would appear that some factor other than just the application of fly ash is occurring at Site 9, but what this might have been is unknown at this time. All other sites leached chromium at below the HRL and MCL. All values are below the RCRA of $5000~\mu g/L$ and the UTS of $600~\mu g/L$.

The leachate values ranged from 0.21%–5.63% of the calculated maximums of leachability. The duplicate samples leached 0.17%–2.48% of the potential. Other than one set of leachates from one of the sites, chromium should not present a problem at the study sites.

1.4.2.8 Cobalt

Cobalt concentrations in bulk materials are 13.0-29.9 and $9.0-18.0 \mu g/g$ for fly ash and soil, respectively.

The RfD for cobalt is not listed, and there are no reported NOAEL or LOAEL values in U.S. EPA IRIS tables. The only regulatory value for cobalt is an HBV of 30 μ g/L. Cobalt had two leachate concentrations (2.2 and 2.3 μ g/L) above the LLQ. The duplicate samples had leachate concentrations of 2.2 and 2.8 μ g/L that are above the LLQ.

These values are 0.42% and 0.44% of the calculated maximum; the duplicate values are 0.30% and 0.38% of the calculated maximum of leachability. Cobalt should not be problematic at the study sites.

1.4.2.9 Iron

Iron concentrations in bulk materials are 24.8–44.7 and 13.8–22.5 mg/g for fly ash and soil, respectively.

The RfD for iron is not listed, and there are no reported NOAEL and LOAEL values in the U.S. EPA IRIS tables. The leachate concentrations for all sites are between <10 and 24 μ g/L with 39 out of 43 values at <10 μ g/L. The duplicate leachates ranged from <10 to 42 μ g/L, with three values above 10 μ g/L. The concentrations of iron in leachates are well below the SDWR, which is 300 μ g/L.

The four values above the LLQ leached at 0.0013%–0.0025% of the calculated maximums of leachability. The duplicate values are 0.0019% and 0.0034% of the potential. Iron should not present a problem at the study sites.

1.4.2.10 Lead

Lead concentrations in bulk materials are $21.1-54.5 \mu g/g$ and $9.0-16.8 \mu g/g$ for fly ash and soil, respectively.

An RfD for lead is not available. The SPLP of Site 9 gave a leachate concentration of 9.2 μ g/L, which is 0.95% of what could have possibly leached. All other leachates are below 2 μ g/L, as well as all of the duplicate leachate concentrations. The concentrations of lead are well below the MCL, which is a treatment technique level of 15 μ g/L at the tap. The detected concentration is well below the RCRA level of 5000 μ g/L and the UTS level of 75 μ g/L. Lead should not present a problem at the study sites.

1.4.2.11 Manganese

Manganese concentrations in bulk materials are 129–558 and 212–1337 μ g/g for fly ash and soil, respectively.

The RfD for manganese is 0.14 mg/kg/day. There is no water LOAEL or NOAEL. The leachate values are $<5~\mu$ g/L with an exception of 8 μ g/L for Site 4. This is 0.013% of the calculated maximum of leachability. All duplicate leachate concentrations are $<5~\mu$ g/L, including Site 4. All leachate values are below the HRL of 100 μ g/L and the SDWR of 50 μ g/L. Manganese should not be problematic at the study sites.

1.4.2.12 Mercury

Mercury concentrations in bulk materials are 0.015– $0.600 \,\mu g/g$ and 0.011– $0.480 \,\mu g/g$ for fly ash and soil, respectively.

The RfD for mercury is 0.0003 mg/kg/day or a calculated reference dose of 10.5 μ g/L. Leachate values for mercury are between 0.0013 and 0.066 μ g/L with 29 out of 43 leachate values <0.01 μ g/L. No concentrations above the LLQ are detected in duplicate samples. The MCL for mercury is 2 μ g/L; thus all leachate concentrations are well below the MCL. All values are well below the RCRA level of 200 μ g/L and the UTS level of 25 μ g/L.

Mercury leaching values are at 0.01%–0.90% of the calculated maximums of leachability. Under current regulations, mercury should not be problematic at the study sites.

1.4.2.13 Molybdenum

Molybdenum concentrations in bulk materials are $7.6-25.0 \,\mu\text{g/g}$ and $0.2-3.2 \,\mu\text{g/g}$ for fly ash and soil, respectively.

The RfD for molybdenum is 0.005 mg/kg/day. The calculated safe maximum reference dose calculated from the RfD is $175 \mu g/L$. The reported LOAEL is 0.14 mg/kg/day. The LOAEL

gives a calculated drinking water value of 4.9 mg/L using the assumptions given above. There is no reported NOAEL.

The leaching concentrations for molybdenum ranged from less than 2 to 82.4 μ g/L, with only one value below 2 μ g/L. The duplicate leachate concentrations are 3–118 μ g/L. Leachates from Site 4 gave the highest leachate concentrations, ranging from 49.7 to 82.4 μ g/L in the original and 76.5 to 118 μ g/L in the duplicate leachates. Leachates from all other sites had leachate concentrations at or below 33.9 μ g/L in the originals and 46.5 μ g/L in the duplicates. An HBV of 30 μ g/L is the regulatory limit for the state of Minnesota. Seven of the 43 original leachates are above this limit; four of the values are from Site 4, which used Riverside Unit 8 fly ash in the mixture, and the other three values are slightly over the limit. Five of the nine duplicate leachings are above the HBV level, which included Site 4. Using the calculated limit from LOAEL, which is 4900 μ g/L, molybdenum concentrations should not be problematic. Molybdenum leachate concentrations are all below the calculated reference dose of 175 μ g/L. Molybdenum is potentially problematic at the study sites for Minnesota, but not nationally.

The leached molybdenum is 4.92%–40.83% of the calculated maximums for the original leachings and 6.05%–58.47% for the duplicate leachings.

This assessment of the potential for toxicity from molybdenum agrees well with that of Roffman in which it was concluded that both Allen S. King fly ash and Riverside Unit 8 fly ash with and without soil additions produced leachates using the SPLP test that indicated all calculated exposure pathways for molybdenum were below the hazard index of 1.0 and even 0.2 [19]. It was also stated in this report that the action limit set by the MPCA for the beneficial use of King and Riverside Unit 8 power plants should be raised to at least $500 \,\mu\text{g/L}$ in the SPLP leachate from applicable mixtures of fly ash and soil.

1.4.2.14 Nickel

Nickel concentrations in bulk materials are $16-165 \mu g/g$ and $8-108 \mu g/g$ for fly ash and soil, respectively.

The RfD for nickel is 0.02 mg/kg/day. This gives a calculated value of 0.7 mg/L using the assumptions for drinking water provided above. The leachate concentrations for nickel are <4 to $10 \,\mu\text{g/L}$, with 34 of 43 of these values <4. The duplicate leachate concentrations are <4 to 6.3 $\,\mu\text{g/L}$. The HRL for nickel is $100 \,\mu\text{g/L}$. The leachate concentrations are well below this standard, as well as the UTS level of $11,000 \,\mu\text{g/L}$.

The leachate concentrations are 0.17%–0.76% and 0.19%–0.27% of the potential leachable nickel for the original and duplicate leachings, respectively. Nickel should not be problematic at the study sites.

1.4.2.15 Selenium

Selenium concentrations in bulk materials are $15.1-25.2 \mu g/g$ and $1.3-11.6 \mu g/g$ for fly ash and soil, respectively.

The RfD for selenium is 0.005 mg/kg/day, which calculates to 175 μ g/L for drinking water. The NOAEL and LOAEL are reported to be 0.015 and 0.023 mg/kg/day, which translate to 525 and 805 μ g/L for drinking water limits.

Selenium leached between <2 and 7.1 μ g/L with 9 out of 43 values <2 μ g/L. The duplicate results are <2 to 6.4 μ g/L. All leachates are below the HRL of 30 μ g/L and the MCL of 50 μ g/L. Using the calculated values for NOAEL and LOAEL or the HRL and MCL, the leachates should be at safe levels for selenium. These values are below the RCRA level of 1000 μ g/L and the UTS level of 5700 μ g/L.

In a human study, the NOAEL was calculated at 0.85 and the LOAEL at 1.26 mg Se/day. The recommended dietary allowance for selenium is estimated to be 70 and 55 μ g/day for males and females, respectively. Using RDA values of 70 and 55 μ g/day, the highest intake of selenium for a leachate concentration of 7.1 μ g/L should be quite safe, providing only 14.2 μ g for a 2-liter water intake per day.

Selenium leached at 0.32%–3.02% of the calculated maximums of leachability. The duplicate samples leached at 2.51%–3.33% of the calculated maximums of leachability. Selenium should not be problematic at the study sites.

Selenium is another trace element that can exist as an oxyanionic species in aqueous solution. Thus selenium can be a substitute in an ettringite structure during the hydration of alkaline fly ash. Decreasing selenium concentrations are noticed as the leaching using distilled, deionized water approaches 60 days in Sites 4, 5, and 6 (see Appendix F, Figure F-26).

1.4.2.16 Silver

Silver concentrations in bulk materials are $1.18-1.94 \mu g/g$ and $0.10-1.14 \mu g/g$ for fly ash and soil, respectively.

The RfD for silver is 0.005 mg/kg/day. Leachate concentrations of silver ranged from <0.3 to 5.3 μ g/L with 34 out of 43 values reported at <0.3 μ g/L. All duplicate leachate concentrations are less than 0.3 μ g/L. The HRL for silver is 30 μ g/L, and the SDWR is 100 μ g/L; thus all leachates had concentrations below the reported HRL and SMCL. All values are below the RCRA level of 5000 μ g/L and the UTS level of 140 μ g/L. The silver values above the LLQ are 1.19%–15.10% of the calculated maximums of leachability. Silver should not be problematic at the study sites.

1.4.2.17 Sulfate

Sulfate was not determined in any of the solids. It was determined in leachates, however. Sulfate leached at concentrations between 16.4 and 295 mg/L. Two of the values for Site 4 are above the SDWR of 250 mg/L. The duplicate leachate concentrations are from 44.5 to 640 mg/L. The increase in concentration in the duplicate samples may be due to a change in temperature at the two separate concentration determination dates. No percentage of potential leachability could be determined without solid concentrations.

1.4.2.18 Thallium

Thallium concentrations in bulk materials are $0.37-0.68 \mu g/g$ and $0.20-0.67 \mu g/g$ for fly ash and soil, respectively.

The RfD for thallium is 0.00008 mg/kg/day, which translates to a reference dose of 2.8 μ g/L. The MCL is 2 μ g/L. Six of the leachates had thallium concentrations between 1.01 and 1.38 μ g/L, and the rest of the leachates, including the duplicates, had thallium concentrations of <1.0 μ g/L. The UTS level of 20 μ g/L is above any detected values. All leachate concentrations of thallium are below the MCL of 2 μ g/L.

Of the potential leachable thallium, 3.92%–5.13% leached. Thallium should not be problematic at the study sites.

1.4.2.19 Vanadium

Vanadium concentrations in bulk materials are $56-312~\mu\text{g/g}$ and $16-103~\mu\text{g/g}$ for fly ash and soil, respectively.

The RfD for vanadium is 0.009 mg/kg/day or 315 μ g/L. The NOAEL is reported at 0.89 mg/kg/day, which calculates a NOAEL-based reference dose at 31.15 mg/L. The NOAEL and other values in the IRIS list are for vanadium pentoxide, which assumes a V(V) species in solution.

The leachate concentrations for vanadium are <40 to 340 μ g/L. The highest leachate concentration, a single data point from Site 4, of 340 μ g/L would provide a 70-kg adult with 680 μ g of vanadium, assuming a consumption level of 2 liters of water per day. This is slightly above the calculated 630 μ g/day (from the RfD); however, all other concentrations are at or below 290 μ g/L, which would provide 580 μ g/day or less of vanadium. The highest vanadium concentrations are found in Site 4, which contained fly ash from the Riverside Unit 8 plant. That fly ash is from a cyclone boiler that burns 5%–10% petroleum coke, which is known to contain elevated vanadium concentrations. Slightly elevated vanadium would be expected in leachates from these ash samples. Other than leachate levels of 200, 180, 290, and 340 μ g/L from Site 4, the leachate concentrations are all below 100 μ g/L. One hundred μ g/L would provide a dose of 200 μ g from drinking water at this concentration. All concentrations are well below the UTS level of 1600 μ g/L.

Although twenty-two of the values are above the HRL of $50 \,\mu\text{g/L}$, the leachate values are 0.90%–5.89% of the calculated maximums of leachability. Except for one leachate with a vanadium concentration above the calculated vanadium maximum from the RfD, vanadium should not be problematic at the study sites.

The duplicate leachate results range from <40 to $320 \,\mu\text{g/L}$. The highest values of 190, 300, and $320 \,\mu\text{g/L}$ are from the duplicate for Site 4. All other values are $110 \,\mu\text{g/L}$ or less. The duplicate leachate concentrations are 0.79%–5.54% of the calculated maximums of leachability.

This assessment of the potential for toxicity from vanadium agrees well with that of Roffman in which it was concluded that both Allen S. King and Riverside Unit 8 fly ash with and without soil additions produced leachates using the SPLP test that indicated all calculated exposure pathways for vanadium were below the hazard index of 1.0 and even 0.2 [20]. It was also stated in this report that the action limit set by the MPCA should be raised to at least $1000 \, \mu g/L$ in the SPLP leachate.

1.4.2.20 Zinc

Zinc concentrations in bulk materials are $50-175 \mu g/g$ and $26-174 \mu g/g$ for fly ash and soil, respectively.

The RfD for zinc is 0.3 mg/kg/day. The LOAEL is reported at 1.0 mg/kg/day. These would translate to 10.5 and 35 mg/L, respectively, for drinking water limits. All zinc concentrations in leachates are below 30 μ g/L. This concentration of <30 μ g/L would provide <60 μ g in drinking water. The RDA for zinc has been currently set at 15 mg/day for males and 12 mg/day for females. All leachate concentrations of zinc are below the HRL of 2000 μ g/L, the SMCL of 5000 μ g/L, and the UTS level of 4300 μ g/L. Zinc should not be problematic at the study sites.

This summary indicates that extremely low concentrations of the trace elements studied are found in nearly all of the leaching solutions. Boron which would not be problematic to humans might in some cases (14 out of 43 leachates) be somewhat toxic to some plants if applied directly as concentrated leachate as a source of long-term irrigation. Boron, however, was above the HRL in some sites. Chromium appeared at above the MCL in three of 43 leachates. All three of these are from Site 9, as well as the highest concentrations of boron, and appear to be related to conditions that might not be directly related to the fly ash. High amounts of molybdenum and vanadium are seen in Site 4, which used fly ash incorporated with petroleum coke for the soil stabilization.

It would be useful to be able to determine the source of trace elements, especially in the case of an increase with ash addition. With the technology available for this project, this was not possible. It is likely that there are no techniques available at this time to assign sources to trace elements from relatively complex mixtures. The tendency would be to say that the source is the fly ash; however, with hydration reactions occurring, pH changing, and various other geochemical changes, this may not always be the case.

1.4.3 Simulated Rainfall Demonstration

A simulated rainfall event experiment was conducted by Paul Bloom and Hero Gollany, both with the Department of Soil, Water, and Climate at the University of Minnesota St Paul, Minnesota. The experiment was conducted at the University of Minnesota Rosemount Research and Outreach Center. The complete report of this research can be found in Chapter 2 of this report. Leaching results of samples from the sites treated with Allen S. King fly ash and agricultural lime are summarized below. Both samples were included in the duplicate sample set with distilled, deionized leachings performed.

1.4.3.1 Site 12a

Site 12a was the fly ash–soil plot composite. The eleven parameters that leached above the LLQs are As, Ba, B, Cd, Cr, Hg, Mo, Se, Ag, V, and sulfate. Boron, molybdenum, and vanadium leached HRL or HBV limits. The B values are twice as high as the HRL limit of 600 μ g/L. The detectable mercury value of 0.0236 μ g/L for the 18-hour leachate is well below regulatory limits. The molybdenum and vanadium values are high, as expected, because the fly ash was burned with 10% petroleum coke. The Mo values ranged from 216–285 μ g/L, which are well above the HBV limit of 30 μ g/L. The V values ranged from 270–417 μ g/L, which is above the HRL limit of 50 μ g/L, but still well below the UTS limit of 1600 μ g/L. The Mo and V values are also higher in the King fly ash than in any other of the fly ashes used in the project.

Site 12a was included in the duplicate sample set because of the use of King fly ash in the soil stabilization. Increases in all of the leachate concentrations are noted for As, Ba, and Mo. The B, Se, and V concentrations are lower for the 18-hour leachate and higher for both of the long-term leachates. The increases in the selenium values are well below regulatory limits. The chromium changes are mixed. The sulfate values decreased in the 18-hour and 30-day leachings and increased in the 60-day leachate. Values are no longer reported above the LLQs for cadmium and silver.

1.4.3.2 Site 12b

Site 12b was the lime–soil plot composite. The ten parameters that leached above the LLQs are As, Ba, Cr, Co, Hg, Mo, Ni, Se, V, and sulfate. No boron leached above the LLQ of 200 μ g/L, which is unlike the fly ash–soil composites in the project. All elements leached below major regulatory limits. The silver 60-day leachate value of 26 μ g/L is below the SDWR of 100 μ g/L, but is questionable because it is higher than the estimated calculated maximum of leachability. This is likely due to a source of contamination.

Site 12b was included in the duplicate sample set because many of the elemental leachate concentrations are low. Increases in all values are seen in As, Ba, and Se. Changes in cobalt and nickel concentrations are mixed. The concentrations of Mo and V decreased or did not change for the 18-hour leaching and increased in the LTLs. The vanadium concentrations are still below or at regulatory limits. Values above the LLQs are no longer reported for chromium and silver. The fact that no silver was detected in the duplicate leachings shows that the previous 60-day leaching value of $26 \,\mu\text{g/L}$ was likely due to a source of contamination.

1.4.4 Conclusion Summary

Several issues are associated with the lower levels of quantitation specified in this research project. The LLQs specified are more than adequate for determination of potential adverse environmental impact within the framework of understanding of toxicity of inorganic trace elements. Mercury is a special issue, however, because of the extremely low potential detection limit offered by modern atomic fluorescence instrumentation. Mercury can be detected down to 0.1 to 0.01 pg absolute mass of mercury using atomic fluorescence detection. The problem in detection of mercury at this concentration level lies in reducing blank mercury levels in reagents and laboratory air to below what is necessary for determination of sub-picogram levels. Mercury concentrations in rain can be as high as 10 ng/L, posing some interesting questions regarding attempting to determine leachate concentrations to 0.2 ng/L which may not be an attainable concentration level considering the concentration of mercury in the source rain water. Additionally, mercury in mercury amalgam fillings in laboratory personnel can be problematic during sample preparation and analysis unless special precautions are taken to divert or treat exhaled air. It may not be possible to perform accurate mercury analyses at these detection limits for routine monitoring of potential mercury release under environmental conditions. It is likely that environmental monitoring under field conditions could be extremely expensive and problematic. The LLQs specified for other trace elements, although low, are achievable using conventional techniques.

The values obtained from leaching the core composites could have been interpreted more thoroughly if the soils, fly ashes, and lime had been leached individually. This would have provided more information as to how the addition of fly ash or lime to the soils affected the mobility of elements.

Overall, this study confirms the outcomes of other similar studies that fly ash, if used properly, is not a hazard to the environment when used for soil stabilization at the addition concentrations used in the sites for this project.

MPCA Permit SW-532 contains specific application criteria. Setbacks representing separation distances to be maintained whenever fly ash is applied are summarized in Table 1-17.

From the results of the real-world leaching, the runoff experiments conducted by the University of Minnesota, biotoxicity testing, and the Roffman reports, it is apparent that the setbacks specified in Permit SW-532 are extremely strict. It is likely that many of the specified setbacks could be decreased with no potential for harm.

The MPCA has specified U.S. EPA Method 1312, the Synthetic Precipitation Leaching Test, as the test to be used for determining the water solubility of trace elements. This test is a suitable leaching test for many materials but is unsuitable for use in determining the mobility of trace elements from alkaline, reactive fly ash. It has been demonstrated in numerous research projects and is common knowledge that alkaline coal fly ash reacts with water and forms hydration products that are considerably different from the original constituents of the ash. Hydration products, often referred to as secondary hydrated phases, contain the mineral ettringite as a primary hydration phase. Observations in the lab have led us to believe that ettringite always

Table 1-17 Setback Requirements

	Encapsulated Use	Unencapsulated Use	Storage at Construction Site	
Existing Residences or Recreational Areas	25 feet	300 feet	200 feet	
Existing Private Drinking Water Supply Wells Minimum 50 feet or as designated by the local head protection requirements				
Existing Public Water Supply Wells	Minimum 50 feet or as designated by the local well-head protection requirements			
Existing Surface Water Bodies Including Lakes, Streams, Ponds, Rivers, and Wetlands	5 feet	25 feet	200 feet	
Potentiometric Groundwater Table as Identified Through Soil Borings for the Construction Project or as Certified by an Individual Knowledgeable in the Field of Hydrogeology	3 feet	8 feet	8 feet	

forms in alkaline ash hydration. During the formation of ettringite, several trace elements, including arsenic, boron, chromium, molybdenum, selenium, and vanadium, can be fixed into the crystalline structure of this mineral. Since the formation of ettringite and ash hydration in general can take from days to months, a leaching test with an 18-hour equilibration time such as that of the SPLP has too short a duration to accurately predict leaching. For this reason, the authors are recommending a leaching test with a minimum of 30 days' equilibration time. Although the use of synthetic acid precipitation in the manner specified in a batch-leaching test is minimally scientifically invalid, it is not likely to cause any major problems and can be used with the extended leaching time.

1.5 References

- [1] Baker, M. Coal Combustion By-Products Utilization Manual: Volume 1: Evaluating the Utilization Option; final report prepared for EPRI Research Project 1850-1, Feb 1984.
- [2] Helmuth, R. Fly Ash in Cement and Concrete; Portland Cement Association, 1987.
- [3] University of North Dakota Mining and Mineral Resources Research Institute. *Utilization of Ash Sourcebook;* Grand Forks, ND, 1988.
- [4] Erbe, M.W.; Keating, R.W.; Hodges, W.K. Evaluation of Water Quality Conditions Associated with the Use of Coal Combustion Products for Highway Embankments. In *Proceeding of the 14th International Symposium on Management and Use of Coal Combustion Products (CCPs): Volume 1*, EPRI, Palo Alto, CA: 2001. 1001158.

- [5] American Coal Ash Association, Inc. 1999: Coal Combustion By-Product Production and Consumption; Alexandria, VA, 2000.
- [6] American Coal Ash Association, Inc. 1997: Coal Combustion By-Product Production and Consumption; Alexandria, VA, 1998.
- [7] American Coal Ash Association, Inc. 1998: Coal Combustion By-Product Production and Consumption; Alexandria, VA, 1999.
- [8] Environmental Protection Agency. Federal Register 1986, 51 (g), 1750–1758.
- [9] Environmental Protection Agency. SW 846, Method 1312; Sept 1988.
- [10] American Society for Testing and Materials. Standard Test Method for Shake Extraction of Solid Waste with Water. In *Annual Book of ASTM Standards*; Section 11: Water and Environmental Technology, ASTM D 3987-85, 1989.
- [11] EPRI. Use of Coal Ash in Highway Construction: Michigan Demonstration Project Interim Report; EPRI GS-7175, Project 2422-7, Feb 1991.
- [12] Pflughoeft-Hassett, D.F.; Hassett, D.J.; Dockter, B.A. High-Volume Fly Ash Utilization and the Effects on Groundwater in North Dakota. In *High-Volume Uses/Concrete Applications;* Proceedings of the 10th International Ash Use Symposium, Orlando, FL, Jan 18–21, 1993; EPRI TR-101774, Project 3176, 1993; Vol. 1.
- [13] Hassett, D.J.; McCarthy, G.J.; Henke, K.R.; Korynta, E.D. Characterization of a Lignite Ash from the METC Gasifier III: Correlations with Leaching Behavior and Mineralogy. In *Fly Ash and Coal Conversion By-Products: Characterization, Utilization, and Disposal I*; McCarthy, G.J.; Lauf, R.J., Eds.; Materials Research Society, Pittsburgh, PA, 1985.
- [14] Hassett, D.J. Evaluation of Leaching Potential of Solid Coal Combustion Wastes; final report prepared for Indiana Coal Council, Inc., Dec 1991.
- [15] Hassett, D.J. Synthetic Groundwater Leaching Procedure. In *Encyclopedia of Environmental Analysis and Remediation*; Meyers, R.A., Ed.; John Wiley & Sons, Inc., 1998.
- [16] *Drinking Water Standards and Health Advisories*; EPA 822-B-00-001; Environmental Protection Agency, Office of Water: Washington, D.C. 2000; p 12.
- [17] Hassett, D.J.; Pflughoeft-Hassett, D.F.; McCarthy G.J. The Synthesis of Substituted Ettringites: Implications for Disposal of Hazardous Materials. Abstract Presented at the Joint Meeting of FACSS XVIII and Pacific Conference, Anaheim, CA, 1991.
- [18] Hassett, D.J.; Thompson, J. S. *Ettringite Formation as a Fixation Technology for Immobilizing Trace Elements*. final report to the Gas Research Institute, Feb 1997.

[19] Roffman, H. Report on Molybdenum Chemistry and Health Effects; prepared for Mineral Solutions, July 1999.

[20] Roffman, H. Report on Vanadium Chemistry and Health Effects; prepared for Mineral Solutions, July 1999.

1.6 List of Acronyms

ASTM American Society for Testing and Materials

CCB coal combustion by-product CVAA cold-vapor atomic absorption

EERC Energy & Environmental Research Center

EPA Environmental Protection Agency GFAA graphite furnace atomic absorption

HBV Health Based Values HRL Health Risk Limit IC ion chromatography

ICAP inductively coupled argon plasma ICP inductively coupled plasma

ICP/MS inductively coupled plasma/mass spectroscopy

IRIS Integrated Risk Information System

LLQ lower level of quantitation

LOAEL lowest observed adverse effect level

LTL long-term leaching

MCL Maximum Contaminant Level MCLG Maximum Contaminant Level Goal

MDL method detection limit

MPCA Minnesota Pollution Control Agency

MSI Mineral Solutions, Inc.

NOAEL no observed adverse effect level

RCRA Resource Conservation and Recovery Act

RDA Recommended Daily Allowance RfD Reference Dose (ingestion) rpm revolutions per minute

SGLP synthetic groundwater leaching procedure SDWR Secondary Drinking Water Regulations

SPLP synthetic acid precipitation leaching procedure TCLP toxicity characteristic leaching procedure

TDA/AAS thermal decomposition, amalgamation, and atomic absorption spectrophotometry

TT treatment technique

UTS Universal Treatment Standard

2 WATER QUALITY IN RUNOFF FROM FLY ASH-STABILIZED PADS

Under subcontract to the UND EERC, Paul R. Bloom and Hero T. Gollany of the University of Minnesota Department of Soil, Water, and Climate prepared Chapter 2.

2.1 Introduction

The use of fly ash in the stabilization of subgrade soils has become an increasingly common practice in the construction of building sites and roads. In many metropolitan areas, sites with the best soils on which to build are occupied, and developers are now taking a second look at remaining sites in good locations, but which may have lower-quality soils. In addition, construction of roads often requires dealing with lower-quality soils.

The lower-quality soils may be soft and compressible, or they may retain excessive moisture. If construction is to proceed in an expeditious manner, conventional methods dictate that the lower quality soils be removed and replaced with more competent soils at no small cost.

Stabilization with cementitious fly ash does away with the need to replace poor soils and results in a better subgrade than is possible with untreated soils. For example, it is not uncommon for California Bearing Ratio values to increase from 2 to 3 for the untreated soils to as high as 35–40 for the same soils treated with fly ash.

Fly ash is the fine, powdery residue that is entrained in boiler flue gases after the combustion of coal. In power plants, the fly ash is collected in air pollution control devices such as baghouses and electrostatic precipitators to prevent it from escaping to the atmosphere. Ultimately, it is either recycled or disposed in landfills.

Fly ash produced by the combustion of subbituminous coal ("Class C" fly ash) generally contains alkaline calcium aluminates and silicates which cause the fly ash to form cementitious compounds when combined with moisture. Chemically, it resembles soil, with its major constituents being the oxides of silicon, aluminum, and iron. Fly ash produced by the combustion of subbituminous coal ("Class C" fly ash) generally contains elevated levels of calcium oxide which causes the fly ash to form cementitious compounds when combined with moisture. The cementitious property, and a strong affinity for water, gives the material its value in soil-drying and stabilization applications.

As with soil, coal contains traces of many heavy metals. After combustion, those heavy metals remain in the coal ash. The primary metals of concern are arsenic, barium, chromium, selenium, and boron. Mercury, although not usually found in fly ash at concentrations much in excess of

that in soils, is also of interest, because of concern for the potential for mercury deposition into bodies of surface water.

In 1998, the Minnesota Pollution Control Agency (MPCA) issued a "Fly Ash Utilization Program" permit to Northern States Power Company (now known as Xcel Energy) and Mineral Solutions Inc. (MSI), a wholly owned subsidiary of Lafarge Corporation. The permit allows MSI to sell fly ash produced by Xcel Energy for use in certain construction applications, including soil drying and stabilization.

The permit requires that the companies conduct a "Surface Water Runoff Demonstration" to analyze surface water runoff from an area stabilized with fly ash. The purpose is to determine whether minimum setbacks (from bodies of surface water, wells, etc.) contained in the Permit were adequate for the protection of human health and the environment. Also of great interest to the MPCA is the question of whether mercury is released to the environment as a result of this construction practice.

The study that is described in this report is the result of the Permit condition imposed by the MPCA. It was conducted by Drs. Paul R. Bloom and Hero T. Gollany of the University of Minnesota Department of Soil, Water, and Climate, with the assistance of MSI and Xcel Energy.

In the study, Bloom and Gollany used a fly ash from a power plant that burns a mixture of 90% subbituminous coal and 10% petroleum coke. We chose this ash because inclusion of petroleum coke in the fuel results in a fly ash that is high in vanadium, nickel, and other elements of concern for the MPCA. Thus the results reported here should represent a worst case for runoff from soil treated with the various subbituminous fly ashes from the Xcel plants in Minnesota.

Because of the need to extend the results of the study to situations where ashes of different composition are used, we designed the study to yield data that allow for generalization of the results. In this effort, we applied the principles of geochemistry and soil science to formulate generalizations about runoff from fly ash-treated soil pads. To aid in interpretation, we included a lime (Ca(OH)₂) treatment. Lime is an alternative to fly ash for soil stabilization, but lime is extremely low in Hg and contains only very low concentrations of most of the other elements of concern to MPCA. We used a compacted soil control. Compacted soil is an alternative treatment when lime or ash is not used. We also report results for elements that are not on the MPCA list of elements of concern because these results can aid in the understanding of the behavior of other elements in ash–soil mixtures.

The mobilization and transport of mineral matter in runoff from soils are complex processes. Raindrops that strike a soil surface dislodge clay and silt-sized particles that are suspended in the runoff. Also, water running over the surface of a soil will dissolve soluble components from the soil. In this study, we separately analyzed total and soluble (filtered with 0.7-µm filter) concentrations.

Fly ash contains mostly silt-sized particles with an appropriate density to be mobilized in runoff, but the reaction with water and soil constituents results in cementation with soil particles [1]. The reactions of ash to form secondary products have been the subject of considerable research.

Mattigod et al. and Eary et al. reported the results of an EPRI-funded review of the geochemical factors controlling the mobilization of inorganic constituent from fossil fuel ashes when they come in contact with water [1,2]. This work provides a good general idea of the solubility behavior of many elements in equilibrium with ash. However, results reported in these reviews and subsequent studies of ash reaction products in situations where no soils are involved do not account for reaction of ash components with soil minerals. The behavior of ash materials in soils has been investigated in studies where ash has been used as a liming material. Wilson recently reviewed these studies. However, he was not able to find any studies of the composition of runoff from ash-treated soils [3].

The objectives of research reported here were 1) to document the effects of fly ash added as a stabilizing agent on the concentration of Hg and other elements of interest to MPCA in runoff under controlled but realistic conditions and 2) to determine whether the forms of these elements added in fly ash are more or are less easily mobilized in runoff than the native forms of these elements in soil.

2.2 Materials and Methods

2.2.1 Soil

A soil suitable for stabilization was identified by MSI at a construction site and transported to the test site. The topsoil was stripped before sampling. Analysis of particle size showed that the soil was a sandy clay loam containing 44% sand, 28.5% silt, and 27.5% clay. The pH was 7.8, and the soil contained 5.2% calcium carbonate.

2.2.2 Site Preparation and Excavation

This study was conducted at the University of Minnesota Rosemount Research and Outreach Center. Topsoil was removed from an area approximately 30 feet across the slope by 60 feet down the slope. The area was graded to approximately 5%. Test plots were prepared in 4.5 ft \times 4.5 ft and 8-in.-deep excavations that were filled with the test soil. The excavation and fill areas were larger than the 3.3 ft \times 3.3 ft (1 m \times 1 m) plot size to avoid border effects resulting from the contact of treated soils with the native soil at the site. The layout of the test plots is shown in Figure 2-1.

2.2.3 Pad Construction

The test soil was sieved through a rotating trommel screen with hammer mill in order to remove large rocks and other debris prior to weighing. Test pads were laid out in a 3×4 grid pattern. Soil pads were prepared as follows:

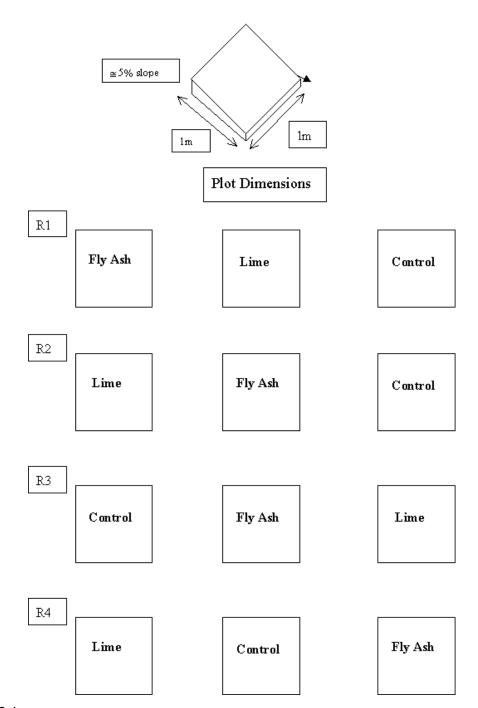


Figure 2-1 Plot Dimensions and Experiment Design for Runoff Study

- 1. **12% ash (dry weight)**, a typical application rate: The ash was from the Xcel Energy Allan S. King Plant, which burns a mixture of 90% subbituminous coal and 10% petroleum coke. This mixture produces a fly ash high in V, Ni, and other elements that are might be of environmental concern.
- 2. 5% lime (Ca(OH)₂), a typical application rate.

3. Compacted soil (control).

Fly ash and lime were mixed with soil in place using a rototiller. Soil was placed in 4-in. lifts, mixed, and compacted. Each row of test plots, containing one pad of each treatment, was prepared approximately 2 hours before the first rainfall event. Test plots were constructed in the following order: a) control (soil only), b) lime-stabilized, and c) fly ash-stabilized. Water was added to bring soil moisture content to about 10% above the optimum moisture content. All water used was ultrapure deionized water delivered from an Xcel power plant by tanker truck. The finished grade was sloped at 5%. The water content and bulk density were not greatly different among the treatments (Table 2-1). However, as expected, the water content in the control pads was somewhat less than the lime and ash pads.

Table 2-1
Moisture and Bulk Density of the Soil Pads

Sample	Moisture, %	Dry Bulk Density, g/cm³
Control Soils	19.6	1.66
Soil Plus 12% Ash	22.9	1.55
Soil Plus 5% Lime	21.9	1.59

Data supplied by GME Consultants.

2.2.4 Test Plot Frames

Prefabricated stainless steel test plot frames (3.3 ft \times 3.3 ft \times 6 in. high \times 1/8 in. thick) were placed on the compacted test plots shown in Figure 2-1. The downslope edge of the frame was cut at the corners and bent to form a spillway for the runoff from the plots. Runoff was collected from the spillways of the frames using Teflon[®] collectors fitted to the lower side of the frames. The edges of the frames were driven about 1 in. deep into the soil, or until the front lip of the frame was resting on the grade. The upslope edge was 1.97 in. higher than the downslope edge. One hundred percent of the runoff from the pads was directed through the spillways.

2.2.5 Decontamination and Protection of Treated Areas

Prior to the beginning of construction, all items that came into contact with soils, fly ash, lime, or water were decontaminated by washing with a detergent solution and rinsing with deionized

water. Tarps were placed over the test plots upon completion of construction and removed prior to starting the artificial rainfall events. Tarps were replaced over the test plots after the first rainfall event to prevent erosion until the second event was conducted 2 weeks later.

2.2.6 Rainfall Simulation

A rainfall simulator, a modification of a Purdue University design, was used [4]. The simulator has a 24-ft boom and can rain on one row of three plots simultaneously. This simulator has high-pressure nozzles that produce droplet sizes similar to rain droplets and propels the droplets to the soil surface at velocities similar to the terminal velocities of raindrops. This is important in a runoff study because the dislodging of soil particles from the surface and suspension in runoff water are very much dependent on the impact energy of the droplets. The suspended particles that are transported across the surface of a sloping soil pad are mostly the fine fraction of soil, generally silt and clay-sized particles.

Each rainfall event lasted for 2 hours. The rain intensity the first hour was about 5 cm/h to simulate a 25-year average storm event. The second hour rain was about 2.5 cm/h.

The water used was ultrapure deionized water from the Xcel Energy King power plant. High-purity water was necessary because tap water contains soluble Hg at concentrations similar to what we expected for soluble concentrations in the runoff. The Hg concentrations in the water after flowing through the rainfall simulator were $0.42 \text{ ng}^{-1} \pm 0.19 \text{ ng L}^{-1}$. The experiment included two rainfall events:

- A. Event 1: 2 to 3 hrs after preparing the ash plot in each row
- B. Event 2: 2 weeks later

Rainfall intensity was measured by collecting water in coffee cans placed next to each pad. The measured rainfall intensity during the first rainfall event was 4.10 cm/h in the first hour and 2.05 cm/h in the second hour. The measured rainfall during the second event was 3.08 cm/h in the first hour and 1.54 cm/h in the second hour.

2.2.7 Sample Collection

Erosional loss and runoff water quantity samples were collected manually over designated time intervals. The samples were collected in 500-mL borosilicate glass bottles that had been first washed with detergent solution then ultracleaned by treating for 12 h at 80°C in 30% HNO₃, followed by rinsing with ultrapure water and drying in a clean room, then double bagging in polyethylene bags. The samples were collected using a clean hands/dirty hands protocol. This required two-person sampling teams, both in lint-free suits, wearing surgical gloves. The clean hands person removed the bottle from the inner bag, collected the sample, and returned the sealed bottle to the inner bag and sealed it. The dirty hands person sealed the outer bag and placed the samples in an ice chest. The samples were returned to the laboratory at the end of the day and placed in a refrigerator. Samples were collected in 1.00-L volumetric cylinders to

determine runoff volume. During Event 1, five samples were collected for suspended sediment and chemical analyses: three in the first hour and two in the second hour. During Event 2, two samples were collected in the first hour and one in the second hour.

2.2.8 Chemical Analysis

Within 48 h of collection, the bottles were taken to a clean room for removal from the bags and processing. An ultraclean Teflon stir bar was placed in each bottle, and with rapid stirring to suspend the solids, two quantities of approximately 100 mL were transferred into ultraclean 250-mL borosilicate glass bottles using a Teflon vacuum liquid transfer apparatus. Transfer to one of the 250-mL bottles involved filtering through a 0.7- μ m glass fiber filter that had been fired at high temperature to remove volatiles. The filtered samples were used for determination of soluble concentrations. About 10 mL of filtered solution was transferred to acid-washed polyethylene tubes containing 100 μ L of ultrapure HNO3 and submitted for multielement inductively coupled plasma-optical emission (ICP) analysis. Twenty milliliters of nonfiltered sample were collected in 50-mL polyethylene tubes for HCl–HNO3 digestion at 95 °C for 2 h (USEPA Method 3005 A) and analysis with ICP.

Mercury was determined on the samples in the 250-mL glass bottles using the cold-vapor atomic fluorescence method. All the other elements were determined at the University of Minnesota Research Analytical Laboratory using a Perkin-Elmer Optima 3000DV ICP spectrometer. The concentrations of the elements of concern in the soil, ash, and lime were determined at Xcel Energy Environmental Laboratory (reported to the Energy & Environmental Research Center [EERC]).

2.2.9 Data Analysis

For some elements, the data included values less than the detection limit along with values greater than the detection limit. In order to report means and standard deviations and use the data for statistical analysis, we had to censor data for data sets with analytical values less than the detection limit. The general guidelines for censoring the data are as follows: 1) Each set of either soluble or total elemental analyses for each rainfall event was treated as a separate data set. 2) For data sets with more than 66% nondetects, the whole data set was reported as less than the detection limit. 3) For data sets with less than 50% nondetects, the data set was completed by reporting 0.5 times the detection limit for the nondetect samples. For selenium, all the data sets were reported as nondetects. However, examination of the data indicated detection of Se in the initial sampling time of both rainfall events of the ash-treated soil. This was observed for both the total and soluble analyses. These data were separated from the remainder of the data and were reported as detectable Se for the initial sampling time.

Most of the data sets containing both detects and nondetects were for the soluble concentrations. Some soluble elements were only detected in one of the runoff events. The mean and standard deviation from these single rainfall events are reported as representing the soluble data in these cases. Soluble manganese and nickel in the fly ash treatment were detected only in the first rainfall event. Soluble beryllium in the lime treatment and nickel in the control soil were only

detected in the second rainfall event. Soluble data sets with only a few detects (<66% of the data) included the Ag and Cd data for the control soil, Ag, Be, Cd, and Tl for the fly ash treatment, and Ag and Ni for the lime treatment. These data were reported as nondetectable. Soluble data sets where it was necessary to insert values of 0.5 times the detection limit for nondetects included Cr in the control soil treatment, Mn and Ni in the fly ash treatment, and Pb in the lime treatment.

The total elemental analysis data included only a few data sets that had both nondetect and detect values. Total analysis data sets with only a few detects (<66% of the data) included the B data for the control soil and Se for the fly ash treatment. These data were reported as nondetectable. The only total analysis data set where it was necessary to insert values of 0.5 times the detection limit for nondetects was Pb in the lime treatment.

2.2.10 Statistical Methods

The experimental design was randomized complete block design with three treatments and four replications. Time of sampling was nested in the replications. The general linear model (GLM) and procedure regression from the Statistical Analysis System (SAS) were used for testing possible significant differences due to rainfall event, soil treatment, or time of sampling within a rainfall event [5]. Least significant difference (LSD) test was used for pair comparison of the treatments.

2.3 Results and Discussion

2.3.1 Composition of Soil and Soil Mixtures

Like all mineral soils in temperate regions, the subsoil used in this study is mostly made up of aluminosilicate minerals and thus the major constituents are Si, Al, and O. The soil also contains many other elements that when found in high concentrations in water bodies might be a threat to the environment (Table 2-2). Like soil, fly ash contains aluminosilicate components. The difference in composition is mostly due to Ca, Na, and sulfate S. In addition, the ash contains significant concentrations of the minor elements in Table 2-2. These elements are found at concentrations in excess of the concentrations in soil, except for Ba, Mn, and Tl. The lime is mostly Ca(OH)₂ but also contains trace quantities of elements reported in Table 2-2. Only As, B, and Se are at concentrations in excess of that found in soil.

With the addition of 12% ash and 5% lime, the concentrations of Ca, Na, S, Sb, As, B, Cd, Cr, Fe, Pb, Hg, Mo, Ni, Se, Ag, V, and Zn were increased in the fly ash mixture relative to the control soil, and Ca and B were increased in the lime mixture. Elements found in the fly ash at 6-fold or less, than in the soil, will only increase the concentration in the mixture by 50% or less. Only Ca, Na, S, Sb, B, Mo, Ni, Se, and V were increased by more than 50% in the ash–soil mixture. We expected that these elements would be the most likely to be found in higher concentrations in the runoff from the ash treatment. However, we also were prepared to test the possibility that in the ash–soil mixture, some of the elements might be in forms either more or less available than in soils and thus would be either more or less easily mobilized in runoff.

Table 2-2
Materials Used in the Construction of Soil Pads, mg/kg

	Fly Ash	Lime	Soil
Antimony	6.59	0.10	0.65
Arsenic	26.3	6.2	5.4
Barium	432	5	514
Beryllium	3.64	0.12	1.16
Boron	2000	38	< 4
Cadmium	1.90	0.06	0.18
Chromium	78.2	4.3	37.9
Cobalt	32.4	12.8	11.9
Iron	43,900	1020	17,900
Lead	68.8	0.4	14.7
Manganese	321	106	468
Mercury	0.81	< 0.001	0.19
Molybdenum	105	0.2	1.2
Nickel	979	7.1	23.5
Selenium	29.4	24.6	1.8
Silver	1.87	0.06	0.38
Thallium	0.41	< 0.01	0.52
Vanadium	1540	3	80
Zinc	160	10	57

Data supplied by David Hassett, EERC University of North Dakota.

2.3.2 Sediment Yields, pH, and Runoff

The cementation of the soil due to the addition of ash or lime greatly reduced total solids (TS) in the runoff (Table 2-3 and Figure 2-2). The runoff from the lime and fly ash treatments contained only 26% and 29% as much TS as the control soil treatment, respectively. The data from the first runoff event were not significantly different from those in the second event; therefore, the linear regression lines in Figure 2-2 were drawn using the mean value of aggregated data for the two events. The data show that despite the decrease in rainfall intensity in the second hour of each event, we did not observe a significant decrease in TS in the second hour of each event. The data clearly show that the cementation due to lime and ash additions was effective in reducing the rate of detachment of soil particles from soil surface. The data also show that the reactions occurring in the fly ash- and lime-treated soil between the first runoff event at 2 hrs and the second runoff event at 2 weeks did not significantly change the TS in the runoff.

Table 2-3
Total Solids in Runoff

		Control		Fly Ash		Lime		P > F
Total Solid (g/L)	mean	6.73	а	1.94	b	1.71	b	0.0002
	sd	2.30		0.90		1.01		

Means followed by different letter(s) are significantly different at the 0.05 probability level. sd: Standard deviation.

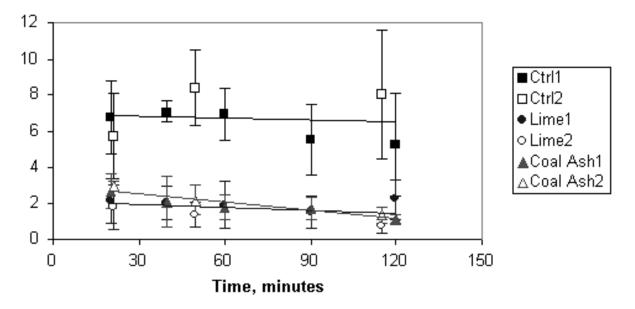


Figure 2-2
Total Solids in Runoff over the Time of Rainfall Event 1 at 2 h and Rainfall Event 2 at 2 Weeks

The runoff solutions contained dissolved salts as well as suspended solids. However, the salt concentrations were small, and the TS obtained by drying the samples closely approximated the concentration of total suspended solids (TSS). By far the greatest salt concentrations were in the runoff from the fly ash treatment, but even for this treatment, the dissolved salt concentrations were only sufficient to make a small a difference between TS and TSS. The major ions dissolved in the ash were Ca^{2+} , Na^+ , and SO_4^{2-} (Table 2-4). Calculations of cationic and anionic charge show that the solutions were essentially in charge balance with just these three ions at a concentration of 3.8 mmol (+ and -) L^{-1} . Drying at $105\,^{\circ}$ C would yield 0.22 g L^{-1} of gypsum ($CaSO_4\cdot 2H_2O$) and 0.10 g L^{-1} of Na_2SO_4 : a total of 0.32 g. This is only 15% of TS. The soluble salt content in the control and lime treatment are much less than for the fly ash treatment.

Table 2-4
Soluble Concentration, Mean, and Standard Deviation of Data for the Two Runoff Events

			Cor	ncentration, µg/L	-	
Elem	ent		Treatments			Detection Limit
		Control	Fly Ash	Lime	P > F	
Sb	mean	nd	nd	nd		3.70
As	mean	nd	nd	nd		11.36
Ba	mean	337 a	244 b	172 c	0.0004	0.34
	sd	126	57	86.3		
Be	mean	0.129 a	nd	0.066 b	0.0450	0.02
	sd	0.072		0.022		
В	mean	137 b	999 a	62.2 b	0.0002	3.82
	sd	43	763	27.7		
Cd	mean	nd	nd	nd		0.63
Ca	mean	7860 c	49,500 a	36,200 b	0.0030	2.00
	sd	2470	44,400	32,800		
Cr	mean	2.1 b	14.2 a	1.6 b	0.0001	0.82
	sd	1.2	11.5	1.9		
Co	mean	nd	nd	nd		0.46
Fe	mean	568 a	5.6 b	42.7 b	0.0006	0.47
	sd	467	6.3	31.9		
Pb	mean	nd	nd	nd		6.23
Mn	mean	3.85 a	0.58 b	0.37 b	0.0017	0.04
	sd	2.80	0.45	0.41		
Hg	mean	0.0040 b	0.0021 c	0.0099 a	0.0047	0.0006
	sd	0.0014	0.0014	0.0087		
Mo	mean	3.2 b	367 a	3.5 b	0.0002	1.45
	sd	3.2	425	2.1		
Ni	mean	3.16 a	1.71 a	nd	0.0205	1.28
	sd	4.45	0.98			
Ag	mean	nd	nd	nd		0.28
S	mean	2060 b	60,700 a	426 b	0.0002	12.70
	sd	4090	66,400	418		
Se	mean	nd	nd	nd		9.92
Na	mean	1700 b	31,300 a	1000 b	0.0002	34.60
	sd	916	30,800	1030		
Sr	mean	21.7 b	699 a	41.0 b	0.0001	0.01
	sd	9.8	562	30.7		
TI	mean	nd	nd	nd		2.36
V	mean	6.41 b	88.3 a	6.77 b	0.0001	0.26
	sd	7.35	21.2	3.84		
Zn	mean	50.3 a	24.0 b	10.6 b	0.0002	0.47
	sd	64.8	25.0	18.4		

sd: standard deviation; nd: not detected.

Treatment means within a row followed by different letter(s) are significantly different at the 0.05 probability level.

The pH is an important variable for defining the solubility of many compounds that form in ash and ash—soil mixtures, and it is important in defining the nature of the soluble ions [1,2,3]. The mean values of pH in the runoff were all greater than 8.0 (Table 2-5). For both runoff events on the control soil, the pH was 8.2, a value that is expected for a calcareous soil that has a pH of 7.8.

Addition of both the fly ash and lime raised the pH. In the first runoff event, the pH was 1 unit higher in the fly ash treatment and 2 units higher in the lime treatment. With time, much of the calcium in the fly ash reacts with aluminum and sulfate to form compounds like ettringite and with carbon dioxide to form carbonate. Thus the pH decreases in the second event. Similar reactions occur with lime additions. In the second event, the pH in the fly ash treatment is only slightly greater than the pH in the control.

Table 2-5 pH in Runoff Solutions

•	Contro	ol	Fly A	sh	Lime		
	mean	sd	mean	sd	mean	sd	
Event 1 (2 h)	8.2	0.47	9.2	0.22	10.1	0.53	
Event 2 (2 wk)	8.2	0.30	8.6	0.42	8.9	0.41	

2.3.3 Statistical Analysis of the Results of Chemical Analytical Data

Statistical analysis of the data showed that at a 95% probability (P < 0.05), the two rainfall events gave the same results for most elements (Table 2-6). Detailed description of the statistical procedure and an example of SAS output for one element (soluble boron) is illustrated in Appendix H. Since the two events were not statistically different, we aggregated the data from the two events to test for differences between the treatments and differences among the plots within treatments. Statistical procedures and an example of SAS output for comparing treatment (LSD) are shown in Appendix I. In testing significance of the treatment difference, we used the F test. In this test, F = treatment mean square/error mean square. A P-value (Probability > F) of 0.0001 indicates that there is less than 1 in 10,000 of obtaining an F value this large by chance alone. This means that there is a 99.99% probability that the data sets are indeed different. We denoted this level of significant difference by ***. Lower probabilities of significant difference were denoted by ** and *. For any calculated P > F greater than 0.05 (less than 95% probability that the difference is significant), the values were considered to be not significantly different (ns). An example of SAS output showing significant differences between the treatments and among the plots within treatments is illustrated in Appendix J.

The three treatments gave significantly different concentrations for both total and soluble analyses for all elements, except for soluble Ca and total As and Ca (Tables 2-4, 2-6, and 2-7). In Tables 2-4 and 2-7, we use the letters a, b, and c to designate similarity or differences in the mean treatment values for each element. Different letters adjacent to the mean values indicate that the values are statistically different at the 0.05 significant level. The statistical analysis also showed that the replication (four different square-meter plots of each treatment) tended to give different results for total concentrations of the immobile elements (defined below), Be, Cr, Co Fe, Mn, Hg, Ni, and Pb and the moderately mobile Ca ("replication" column in Table 2-6). Only the soluble Fe and Ca showed differences among the plots within treatments (Table 2-6). The

Table 2-6
Analysis of Variance Summary for Elemental Concentration for the Two Runoff Events

Element		Т	otal			Sol	uble	
	Treatment	Event	Time	Replication	Treatment	Event	Time	Replication
Antimony (Sb)	na				na			
Arsenic (As)	ns	ns	***	ns	na			
Barium (Ba)	**	ns	**	***	***	ns	***	ns
Beryllium (Be)	***	ns	ns	***	*	ns	***	ns
Boron (B)	***	ns	*	ns	***	ns	***	ns
Cadmium (Cd)	na				na			
Calcium (Ca)	ns	***	***	**	**	ns	***	**
Chromium (Cr)	***	ns	***	***	***	ns	***	ns
Cobalt (Co)	***	ns	ns	***	na			
Iron (Fe)	***	ns	*	***	***	ns	***	*
Lead (Pb)	**	ns	ns	***	na			
Manganese (Mn)	***	ns	ns	***	**	ns	**	ns
Mercury (Hg)	***	ns	ns	*	**	ns	***	ns
Molybdenum (Mo)	***	ns	***	ns	***	ns	***	ns
Nickel (Ni)	**	ns	***	*	*	ns	ns	ns
Sliver (Ag)	na				na			
Sulfur (S)	***	ns	***	ns	***	ns	***	ns
Selenium (Se)	na				na			
Sodium (Na)	***	ns	***	ns	***	*	***	ns
Strontium (Sr)	***	ns	***	ns	***	ns	***	ns
Thallium (TI)	na				na			
Vanadium (V)	**	ns	***	ns	***	ns	**	ns
Zinc (Zn) * ** *** Significant	***	ns	*	***	***	ns	ns	ns

^{*, **, ***:} Significant at the 0.05, 0.01, 0.001 probability levels, respectively. na: not applicable because of insufficient data; ns: not significant at P = 0.05.

Table 2-7
Total Concentration, Mean, and Standard Deviation of Data for the Two Runoff Events

			Concentration, μg/L		
	•		Treatments		=
Element	=	Control	Fly Ash	Lime	P > F
Antimony (Sb)	mean	nd	nd	nd	
Arsenic (As)	mean	61.4	50.4	nd	ns
	sd	21.7	22.0		
Barium (Ba)	mean	934 a	912 a	237 b	0.0091
	sd	245	517	139	
Beryllium (Be)	mean	22.00 a	6.53 b	5.17 b	0.0005
	sd	5.14	2.82	3.43	
Boron (B)	mean	nd	1030 a	20.1 b	0.0001
	sd		726	10.5	
Cadmium (Cd)	mean	nd	nd	nd	na
Calcium (Ca)	mean	76,900	77,700	65,800	ns
	sd	22,400	52,300	35,700	
Chromium (Cr)	mean	139.0 a	57.9 b	33.7 c	0.0007
	sd	32.1	27.1	21.6	
Cobalt (Co)	mean	49.6 a	11.5 b	10.6 b	0.0007
	sd	15.9	4.9	8.1	
Iron (Fe)	mean	144,000 a	39,900 b	32,400 b	0.0004
	sd	34,300	16,900	22,300	
Lead (Pb)	mean	121.0 a	43.5 b	24.7 c	0.0011
	sd	31.9	21.4	18.9	
Manganese (Mn)	mean	3040 a	748 b	680 b	0.0012
	sd	1060	320	504	
Mercury (Hg)	mean	0.446 a	0.124 b	0.159 b	0.0001
	sd	0.121	0.066	0.111	
Molybdenum (Mo)	mean	4.30 b	339.0 a	5.40 b	0.0001
	sd	1.64	399.0	1.65	
Nickel (Ni)	mean	177 a	152 b	41.6 c	0.0115
		45.3	95.3	28.4	
Silver (Ag)	mean	nd	nd	nd	na
Sulfur (S)	mean	1360 b	57,900 a	549 b	0.0001
	sd	1580	58,500	495	
Selenium (Se)	mean	nd	nd	nd	na
Sodium (Na)	mean	1790 b	32,100 a	1120 b	0.0001
	sd	824	32,000	1010	
Strontium (Sr)	mean	177 b	1090 a	80.6 b	0.0001
	sd	53.4	701	35.2	
Vanadium (V)	mean	277 b	368 a	77.4 c	0.0085
	sd	63.9	206	45.5	
Thallium(TI)	mean	nd	nd	nd	na
Zinc (Zn)	mean	463 a	131 b	101 c	0.0002
	sd	102	58.0	66.2	

sd: standard deviation; nd: not detected; na: not available; ns: not significant.

Treatment means within a row followed by different letter(s) are significantly different at the 0.05 probability level.

differences among the replicates for total concentrations of the immobile elements may, in part, be due to differences in erosional losses among plots caused by differences in contouring and slope of the surfaces of the plots. This is due to the use of real-world construction techniques for preparing the plots. It is important to remember that although there were differences among the replicate plots with respect to total immobile element concentrations, the differences are not sufficient to cover up the differences between the treatments.

We observed significant differences in concentration with time of sampling for many elements. The concentrations of Na, Ca, Ba, B, Cr, Cu, Fe, Mo, S, Sr, and V generally decreased with time for both soluble and total concentrations. For Hg, only the soluble form significantly decreased with time, not the total concentrations. In addition, only the total concentrations for As and Zn showed significant decreases with time. Silver (Ag), Tl, and Sb, were not detected in the runoff from any of the treatments. Figures 2-3 and 2-4 show the changes in total and soluble concentrations of Mo over time. The plots showed similar results for the first and second rainfall events. They also showed greater initial concentration followed by little change over the remainder of each rainfall event. This is typical of the more highly soluble elements. Figure 2-5 shows the total Hg for which there was no statistically significant decrease with time. Figure 2-6 shows the small but significant decrease with time for soluble Hg. This is typical of the low solubility (immobile) elements. The Hg results are atypical in one aspect. While the soluble concentrations were similar in the first and second events for the control and ash-treated soils, the results for the first and second event for soluble Hg in the lime treatment were different (Figure 2-6).

The standard deviations for the treatment means shown in Tables 2-4 and 2-7 are high because of the variation in the results among the replicate pads within many of the treatments and the significant decrease in concentration with time for most of the elements. The standard deviations are particularly high for the highly soluble elements B, Mo, S, and Na. For these elements, the standard deviations were at least 70% of the mean values. This is caused by the very high concentrations in the initial sample of runoff as shown for Mo in Figures 2-2 and 2-3. We were able to determine significant differences between the treatments' mean values even when the standard deviation of the overall means were very high by using the GLM to account for the errors due to replication and time of sampling. The sampling time, nested in the replications, was used as the error term in the F-test.

2.3.4 Elemental Concentrations in the Runoff

The total elemental concentrations in Table 2-7 represent the sum of soluble forms plus the concentration transported as structural components of, or adsorbed on, finely divided mineral particles. The concentration of dissolved components in solution is given in Table 2-4. It is important to separate the concentration associated with the particles from the dissolved concentrations. The soluble concentration of a particular element usually represents a fraction that is highly available for uptake by organisms and is the fraction that is more readily transported to surface water bodies. The fraction in the suspended solids represents a fraction that is generally much less bioavailable and a fraction that can settle out from water.

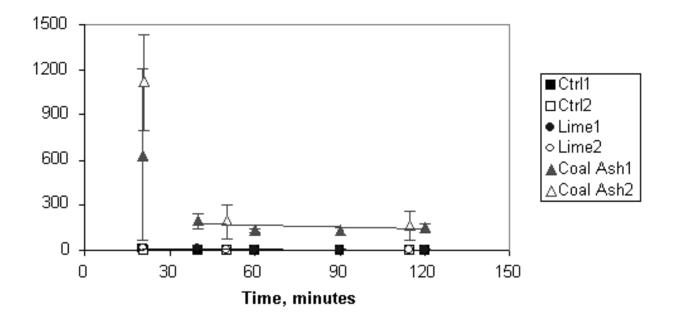


Figure 2-3
Total Mo in Runoff Over the Time of Rainfall Event 1 at 2 h and Rainfall Event 2 at 2 Weeks

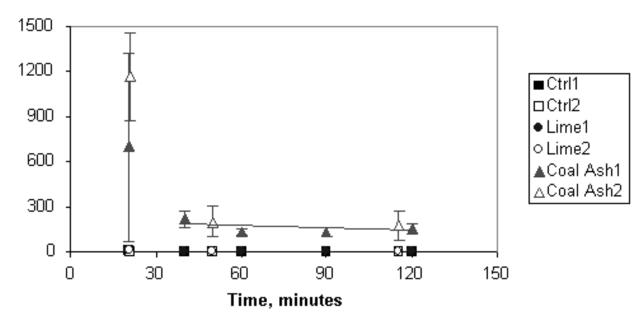


Figure 2-4 Soluble Mo in Runoff Over the Time of Rainfall Event 1 at 2 h and Rainfall Event 2 at 2 Weeks

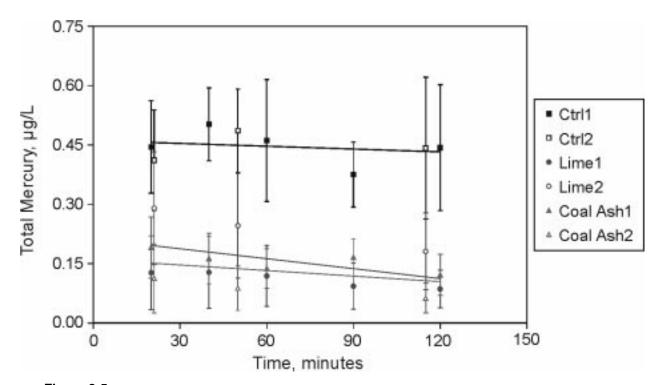


Figure 2-5
Total Hg in Runoff Over the Time of Rainfall Event 1 at 2 h and Rainfall Event 2 at 2 Weeks

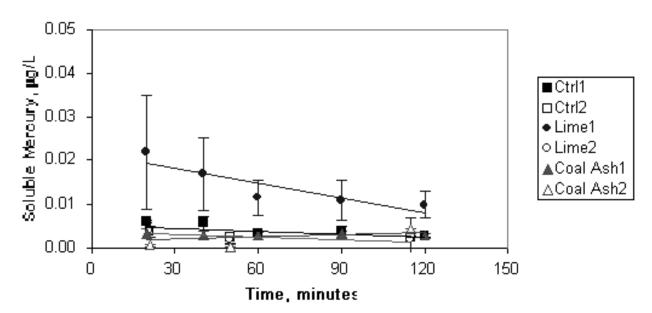


Figure 2-6 Soluble Hg in Runoff Over the Time of Rainfall Event 1 at 2 h and Rainfall Event 2 at 2 Weeks

In the discussion below, we separate immobile elements, which are primarily associated with the particulate fraction, from the mobile elements, which are primarily associated with the dissolved fraction. This separation is made based on the ratio of total to dissolved concentrations (Table 2-8). In our classification, we also defined a class of moderately mobile elements for which concentrations in runoff are partitioned more evenly between the soluble and particulate fractions. In general, elements that were not detected in either the soluble or total fractions were classified as immobile, except for Se and As. Based on literature discussion, Se and As are moderately mobile in high pH soils [6].

Table 2-8
Ratio of Total Concentrations (Table 2-7) to Soluble Concentrations (Table 2-4)

Element	Total	Soluble Concen	tration
	Control	Fly Ash	Lime
Antimony (Sb)	na	na	na
Arsenic (As)	na	na	1.2
Barium (Ba)	3	4	1
Beryllium (Be)	169	na	74
Boron (B)	na	1.0	0.3
Cadmium (Cd)	na	na	na
Calcium (Ca)	10	2	2
Chromium (Cr)	66	4	21
Cobalt (Co)	na	na	na
Iron (Fe)	254	6700	760
Lead (Pb)	na	na	na
Manganese (Mn)	790	1300	1800
Mercury (Hg)	114	59	16
Molybdenum (Mo)	1.3	0.9	1.5
Nickel (Ni)	56	89	na
Sulfur (S)	0.7	1.0	1.3
Selenium (Se)	na	na	na
Sodium (Na)	1.1	1.0	1.1
Strontium (Sr)	8	2	2
Thallium (TI)	na	na	na
Vanadium (V)	43	4	11
Zinc (Zn)	9	5	10

Although we do not intend to discuss the environmental impacts of the runoff, we include the tabulated MPCA discharge water quality standards for comparison only (Table 2-9). The regulatory restrictions on runoff from ash treated soil are yet to be determined. None of the mean elemental concentrations in Table 2-4 and 2-7 exceeds the values in Table 2-9.

Table 2-9
Discharge Water Quality Standards, Minnesota Pollution Control Agency

	Discharge Standards, μg/L											
Sb	180	Hg	4.9									
As	720	Ni	2836									
Cd	67	Se	40									
Cr	3469	Ag	4.1									
Co	872	TI	128									
Pb	164	Zn	234									

2.3.5 Immobile Elements

Silver (Ag), Be, Co, Fe, Hg, Mn, Pb, Ni, Sb, and Tl are elements that are very immobile in well-aerated high pH soils [6]. All of these elements were found in the runoff mostly associated with the suspended particulates or were not detected. All are generally present in well-aerated soils and ash as cations with 2+, 3+, or 4+ charge except for Ag which is a 1+ cation [1,2,6]. Also, antimony in soils can be either an anion (SbO₄²⁻) or cation 3+ [6]. For Be, Fe, Hg, Mn, and Ni, the measured total/soluble concentration ratios are generally >50 (Table 2-8). Cobalt and lead were detected only in the total analysis (Table 2-7). Antimony, thallium, and silver were not detected in either the total or soluble analyses of the runoff. The immobile cations are mostly contained in soil and ash as components of insoluble silicates and oxides or are strongly adsorbed on oxide and silicate soil particles. Lead can also be present as carbonates.

The data for Hg in Figures 2-5 and 2-6 illustrate the general behavior of the immobile elements during the rainfall events. The total concentrations in Figure 2-5 were much greater than the soluble concentrations in Figure 2-6. The total concentrations (Figure 2-5) did not show a significant change with time but the soluble concentrations did decrease slowly over the time of the experiment (Figure 2-6). For most of the other immobile elements, the total concentrations did decrease with time (Table 2-6).

We were interested in determining if changes in concentration in runoff due to the addition of fly ash or lime are in proportion to the change in concentration in the soil mixtures when lime and fly ash are added to soil. Or are the changes in runoff concentration more or less than the proportional change in the concentration in the soil mixtures? The goal was to evaluate whether or not the elemental forms added in ash are more easily mobilized than the native forms. To

investigate this question, we developed a mathematical model to predict the ratio of concentration of immobile elements in runoff from fly ash- or lime-treated soils to the concentration in runoff from the control soil treatment. The model (Eq. 1) assumes the contribution of added concentrations to total concentrations in the runoff is proportional to the concentration in the final mixture. The ratio of total concentration in the runoff from plots treated with 12% ash to the total concentration in runoff from the control soil is then given by:

$$\frac{C_{ash}}{C_{soil}} = \left[\frac{(Q_{ash})(0.12) + (Q_{soil})(0.88)}{Q_{soil}} \right] (0.29)$$
 [Eq. 1]

In Eq. 1, C_{ash} and C_{soil} are total concentrations in the runoff, Q_{ash} and Q_{soil} are concentrations in the soil and ash, and 0.29 is the ratio of suspended sediment in the ash runoff to the sediment content in the soil runoff (Table 2-2). A similar calculation was also applied to the 5% lime—soil mixture. Ratios calculated using Eq. 1 are compared to measured ratios in Table 2-10. If the concentration of an element in fly ash were the same as in the soil, the calculated ratio should be 0.29: the ratio of TS in the ash treatment to TS in the control soil. For Be, Co, Fe, Hg, Mn, Pb, and Ni, the calculated ratios in the ash runoff are all greater than the measured ratios. This demonstrates that the quantity added in the fly ash is less available for mobilization than the native forms of these elements in soil. The most dramatic example is Ni. The concentration of Ni in the ash is 42 times the concentration in the soil. If the Ni in the ash had the same relative potential for mobilization as the Ni in the soil, addition of 12% ash should have resulted in total Ni in the fly ash runoff that is 1.70 times the concentration in the soil runoff (Table 2-10). However, the data show total Ni in ash runoff was 0.86 times Ni concentration in the soil runoff. For Ag, Sb, and Tl, data were not available for calculation of the ratio.

Lower measured ratios than predicted by Eq. 1 were also generally seen for the lime treatments. For Hg, however, the measured ratio is greater than the predicted value. Also, the total/soluble ratio for the lime treatment was only 16 (Table 2-8). The total runoff concentration for the lime treatment was not significantly greater than for the fly ash treatment, but the soluble concentration was about 5 times greater than for the fly ash treatment. The increase in soluble Hg is likely related to the greater pH for runoff from lime treatment. The Hg²⁺ ion forms strong complexes with colloidal soil organic matter and with OH⁻. Soluble organic matter is mobilized at high pH values and the Hg²⁺ forms very strong organic complexes in soil [7].

The Hg concentration in the control runoff, per unit mass of suspended sediment, is $67 \mu g/kg$, which is similar to the concentration found in the fine fraction of soils in the region. Nater and Grigal reported a mean of $52 \mu g/kg$ for silt and clay soils from the North Central region [8].

We investigated several possible mechanisms that might control the relationship between the total concentration of immobile elements in Table 2-7 and the soluble concentrations given in Table 2-4. Contributions to the measured soluble concentrations include 1) Very fine colloidal particles that pass through the 0.7-µm filters can affect the soluble contribution. If this is a major contributor to the soluble fraction, the measured soluble concentration should decrease with reduction of suspended solids. 2) Equilibrium solubility for dissolution of very low solubility solids controls soluble concentrations. In this case, the soluble concentration should not change with change in concentration of suspended solids. However, the solubility of most silicates,

oxides, and hydroxides is pH dependent in the pH range measured for the runoff. At pH values less than 8, the solubility is expected to decrease with increase in pH. However, at pH values above 8, the solubility of some of these materials can increase with increasing pH because of the formation of soluble hydroxide complexes. For example at pH greater than 8.5, the solubility of Fe(OH)₃ increases with increase in pH [2]. As discussed above, the solubility of Hg²⁺ can also increase at high pH due to the formation of hydroxide complexes. For the very immobile

Table 2-10
Predicted (using Eq. 1) and Measured Ratio of Total Concentrations in Fly Ash or Lime Pad Runoff to Total Concentration in Runoff from the Control Soil Pads

	Fly	Ash	Li	me
Treatments	Predicted	Measured	Predicted	Measured
	Ash/Soil	Ash/Soil	Lime/Soil	Lime/Soil
Antimony	0.61	na	0.25	na
Arsenic	0.42	0.82	0.26	na
Barium	0.28	0.98	0.25	0.25
Beryllium	0.36	0.30	0.25	0.24
Cadmium	0.62	na	0.25	na
Chromium	0.33	0.42	0.25	0.24
Cobalt	0.35	0.23	0.26	0.21
Iron	0.34	0.28	0.25	0.23
Lead	0.42	0.36	0.25	0.20
Manganese	0.28	0.25	0.25	0.22
Mercury	0.40	0.28	0.25	0.36
Nickel	1.70	0.86	0.25	0.24
Selenium	0.82	na	0.42	na
Silver	0.43	na	0.25	na
Thallium	0.28	na	0.25	na
Vanadium	0.93	1.33	0.25	0.28
Zinc	0.35	0.28	0.25	0.22

elements discussed above, except for Fe, pure solids are not found in soil or ash and estimation of equilibrium solubility is not possible. 3) The minerals may be in the process of dissolving but have not yet come to equilibrium. 4) Adsorbed ions on mineral surfaces are partitioned between the solid particles and the solution. For surface adsorption, the effect of a quantity of element added in ash on solution concentrations depends on how much of the element in the ash dissolves and is adsorbed by soil particles. For a given fraction of adsorbed ions on mineral particle surfaces, changes in suspended solid concentrations should have little effect on the solution concentration, if pH is constant. Adsorption of cations increases with increasing pH, so with pH increases, soluble concentrations should decrease.

The soluble concentrations of Fe, Mn, Be, and Hg decreased with addition of fly ash or lime. The addition of the ash did increase pH, but for Fe, the pH increase in this range should result in an increase in solubility of Fe(OH)₃ [2]. Thus the solubility of Fe(OH)₃ is not likely controlling the measured soluble fraction. Surface adsorption may control the measured solubility, but it is not possible to rule out contributions from colloidal particles and incomplete dissolution.

For Ni, the total and soluble concentrations in runoff from the soil were not greatly different from the concentrations measured for the fly ash treatment. In this case, however, increase in concentration in the fly ash—soil mixture compared to the control soil was much greater than for Fe, Mn, Be, and Hg, and the suspended particles have relatively higher Ni concentrations. For Ni, it is not possible to distinguish among the mechanisms proposed above.

Although we were not able to measure Ag, Co, Pb, Sb, and Tl in solution, we expect that, like the other highly immobile elements, the addition of ash will not increase the soluble concentration.

If we had used an acidic soil, the increase in pH due to the liming effect of the fly ash would have reduced the solubility for most of the immobile cations. Thus with an acidic soil, the expected decrease in soluble concentration would be even greater than observed in the present study.

2.3.6 Highly Mobile Elements

Sulfur, molybdenum, boron, and sodium are highly soluble and weakly bound to soil particles. The first three are all present as the oxyanions sulfate, molybdate, and borate, while sodium is a singly charged cation. The suspended sediment does not contribute significantly to the total transport of these elements, and the ratios of total/soluble concentrations for these ions are 1.5 or less (Table 2-8). These mobile ions are present in ash at much higher concentrations than in the soil (Table 2-2, Na and S results not given). Thus the runoff from the ash treatment contained much higher concentrations of these ions than the runoff from the other two treatments. The lime and control plots did not differ greatly from each other (Tables 2-4 and 2-7).

We were interested in testing whether the added concentrations of these soluble elements behave in proportion to the quantity added to the soil mixtures. We developed a mathematical model, Eq. 2, to predict the ratio of the concentration of soluble elements in runoff from the fly ash treatment to the soluble concentration in the runoff from the control plots. This is similar to Eq. 1

for immobile elements. Unlike Eq. 1, Eq. 2 does not include the 0.29 term for decrease in TS with addition of fly ash. For the runoff from plots treated with 12% ash, the ratio of the soluble concentration in the runoff from the fly ash treatment to the soluble concentration in the control soil is given by:

$$\frac{C_{ash}}{C_{soil}} = \left[\frac{(Q_{ash})(0.12) + (Q_{soil})(0.88)}{Q_{soil}} \right]$$
 [Eq. 2]

where C_{ash} and C_{soil} are soluble concentrations in the runoff, Q_{ash} and Q_{soil} are concentrations in the soil and ash. This equation assumes equal transport rates into the runoff for all soluble components. We only had data to do this calculation for Mo. The calculated ratio is 11, and the measured ratio is 79. Thus Mo added in the ash dissolves more readily than the native Mo in the soil. In soils, Mo is most mobile at high pH [6].

Analysis of the behavior of B was complicated by contamination of the soluble fraction due to filtration with glass fiber filters. The soluble concentrations from the control and lime treatments were greater than the total concentrations because of the B dissolved from the oven-fired glass fiber filters used to remove the suspended solids. Glass filters were required by the protocol for Hg analysis. The results for total elemental content in Table 2-7 better represent soluble B in the soil and lime treatments than do the soluble results presented in Table 2-4.

Boron is somewhat more strongly retained than Mo in the ash-treated soil. The concentration of B in the ash-soil mixture was 19 times the Mo concentration, but the B concentration in runoff from the ash treatment was only 3 times as great as Mo. After being released to solution during weathering, borate can substitute for carbonate in calcium carbonate and can be incorporated into secondary hydrated phases, such as ettringite, that form from ash components. This reduces B mobility in the ash and lime treatments. Also, at high pH, borate can be adsorbed on soil mineral particles with a maximum adsorption at pH 8–9 [3].

The upper limit of the concentration of sulfate in runoff from the ash treatments is the solubility limit of gypsum ($CaSO_4 \cdot 2H_2O$) [2]. Gypsum is formed from the reaction of the ash with water [1]. The measured concentrations of sulfate in the fly ash runoff, however, were about an order of magnitude less than expected for gypsum solubility. The limit on the concentration of S in the runoff from the ash treatment may be controlled by the rate of dissolution of sulfate from the soil surface.

2.3.7 Moderately Mobile Elements

We classified As, Ca, Ba, Cr, Se, Sr, V, and Zn as moderately mobile elements. Zinc and cadmium are minor element 2+ cations and are heavy metals. They behave in many ways like the immobile cations. Calcium, strontium, and barium are alkaline-earth 2+ metallic cations and are exchangeable cations that readily adsorb on the permanent charge sites of silicate clays in soils. Arsenic, selenium, and vanadium have complex chemistries but in well-aerated soils and ash are oxyanions. Chromium is found in ash and soils both as a 3+ cation and the chromate oxyanion.

Zinc is a relatively immobile cation with total/soluble concentration ratios in the range of 5 to 10 (Table 2-10). Thus about 80% to 90% of the Zn in runoff is as particulates. Like the other metallic cations discussed above, the measured ratio of total Zn in fly ash runoff to that in the control runoff was less than predicted by Eq. 1 for both fly ash and lime (Table 2-10). Also, the soluble Zn in the fly ash and lime runoff was less than that for the control runoff (Table 2-7). Zinc adsorbs on aluminosilicate clay edges and oxides and substitutes in calcium carbonate in high pH soils [6].

Cadmium, a metal ion with many properties similar to Zn, was not detected in the runoff. The concentration of Cd in the soil was only 0.06 mg kg⁻¹ and in the ash was only 1.9 mg kg⁻¹. We assume that soil responds to additions of Cd in fly ash like the response to Zn.

Barium, calcium, and strontium adsorb on soil ion exchange sites, precipitate as sulfates, and in high pH soils precipitate as carbonates [6]. In weathered fly ash, these elements form carbonates and sulfates. In high sulfate environments, Ba forms BaSO₄, a mineral that is much less soluble than gypsum. In soil, the total/soluble ratio for Ba ranged from 1 to 4 (Table 2-8). Thus more than 20% of the Ba in the runoff is in the soluble form. The ratio of total concentration Ba in the runoff from the ash treatment to the total concentration in the runoff from the control soil is much greater than predicted by Eq. 1 (Table 2-10). Thus the Ba added in the fly ash is more mobile than the native Ba in the soil. The total Ba in the runoff from the fly ash-treated plots was the same as from the control soil despite the fact that the concentration in the added fly ash was slightly lower than the concentration in the soil and the runoff from the fly ash contained much less suspended sediment. The soluble Ba was less for the fly ash treatment than for the control treatment. The decrease in solubility in the fly ash treatment is probably due to the sulfate in the fly ash.

The ratio of total to soluble concentration for Ca in the control soil was 10 compared to 2 in the fly ash and lime treatments (Table 2-8). In the control treatment, much of the Ca is bound to clay ion exchange sites. The ratios of 2 for the fly ash and lime treatments mean that half of the Ca is in the soluble fraction. The total concentration was similar for both the lime and fly ash treatments, and the soluble concentration for the lime treatment was slightly less than for the fly ash treatment.

Strontium had total to soluble ratios similar to Ca (Table 2-8). However, the total concentration of Sr was much greater in the fly ash treatment (Tables 2-4 and 2-7).

Chromium is an element that can be present in soils and fly ash as both the very immobile Cr³⁺ cation and more the mobile chromate anion, CrO₄²⁻ [2,6]. The concentration of Cr in the fly ash is only about twice the concentration in the soil, and the addition of fly ash did not greatly increase the quantity of Cr in the soil. The ratio of total to soluble concentrations in the runoff from the soil was 66, suggesting the Cr in the soil is quite immobile, but when ash was added, the ratio decreased to 4 (Table 2-8). Also, the soluble Cr increased by a factor of 7, and the ratio of total concentration in the runoff from the ash treatment to the concentration in runoff from the control soil is slightly greater than predicted by Eq. 1 (Table 2-10). Thus the small additional concentration of Cr added in the ash is more mobile than the native Cr in the soil.

Vanadium is present in soils as the vanadyl cation (VO^{2+}) and as the vanadate (VO_4^{3-}) anion [6]. The ratio of total/soluble concentrations was much greater for the control, 43, than for the fly ash treatments, 4 (Table 2-10). The ratio of total V in the fly ash treatment to the total concentration in the control treatment was greater than predicted by Eq. 1 (Table 2-10). Also, the addition of fly ash increased the soluble concentration even more than it increased the total concentration. This suggests that V added by the ash is more mobile than the native V in the soil.

Arsenic is present in well-aerated soils as the arsenate (AsO_4^{3-}) anion, which has many similarities with phosphate [6]. Arsenate is expected to be relatively immobile. Arsenic was only detected in the total analysis of the control and ash runoff. The ratio of these two concentrations is somewhat greater than the ratio predicted by Eq. 1 (Table 2-10). This suggests that the As added may be somewhat more mobile than the native As in the soil.

The stable forms of Se in high pH soils is selenate (SeO₄²⁺), an oxyanion [3]. The ash adds excess Se to the ash–soil mixture, but this Se was only detected in the first sampling of the fly ash treatment, in both rainfall events. The total concentration was $22.2 \pm 14.9 \,\mu gL^{-1}$, and the soluble concentration was $25 \pm 17.3 \,\mu gL^{-1}$. Thus the Se detected in the initial runoff from the ash-treated pads is all dissolved in solution. The Se was not detected during the remainder of the sampling periods.

2.4 Conclusions

In this conclusion section, we will focus on the effects of the addition of fly ash from the Allen S. King plant on the elements of concern. These are the elements listed Table 2-2.

Elemental concentrations in runoff from the soil, ash-treated soil pads, and lime-treated pads are similar whether the rainfall event occurs within 2 hours of the construction of pads or 2 weeks later. The reactions that occurred during interim resulted in lower pH in the runoff from the fly ash- and lime-treated pads, but otherwise there was little consequence for runoff composition.

The cementation caused by the addition of fly ash and lime decreased suspended solids in the runoff. Addition of 12% King power plant fly ash decreased the TS to 29% of the TS in the runoff from the control soil plots. The addition of 5% lime yielded similar results.

The immobile elements are mostly associated with suspended particles, and the total and soluble concentrations in runoff from the ash-treated pads did not increase with the addition of ash. In fact, for most elements, the concentrations decreased. The immobile elements include Ag, Be, Co, Fe, Hg, Mn, Pb, Ni, Sb, and Tl. For these elements, the concentrations added in fly ash have lower mobility than the forms of these elements in soil. The calculated ratio of concentration in runoff from fly ash-treated soils to the total concentration in the runoff from the control soil (Table 2-10) was generally greater than the measured values. For Be, Fe, Hg, and Mn, we measured decreases in soluble concentrations, but for Ni, there was no significant change. We were not able to detect soluble concentrations of Ag, Co, Pb, Sb, and Tl.

We classified B and Mo as mobile elements. When borate and molybdate are added to soil as soluble salts, these ions are very mobile. A significant fraction of these ions in fly ash exists in

highly soluble forms. In the runoff, total concentrations in runoff are similar to the dissolved concentrations. Both B and Mo added in the fly ash are more mobile than the native forms in the soil. However, the added B is more strongly retained in soil than the added Mo. The high Mo was due to the 10% petroleum coke in the King fuel mixture.

The behavior of the moderately mobile elements was more complex. For As, Ba, Cd, Cr, Se, V, and Zn, both the dissolved fraction and suspended solid fraction in runoff contributes to the total concentration. Zinc is like the immobile elements with lower total concentration in the runoff than predicted by Eq. 1 and decreases in both total and soluble Zn with addition of fly ash. Thus Zn in ash is less mobile than the native Zn in the soil. We did not detect Cd, but we expect it to behave somewhat like Zn.

Arsenic, Ba, Cr, and V are all transported in runoff mostly as suspended solids, but the effect of the addition of these elements in fly ash on total concentrations in the runoff is somewhat greater than predicted by Eq. 1. Barium is normally considered to be more mobile than the other metallic cations listed in Table 2-2. In the ash, however, high sulfate limits the solubility of BaSO₄. Addition of fly ash did not increase either the soluble or total concentrations of Ba in runoff compared to the control soil. The Cr added in the fly ash was more mobile than the native Cr in soil. The addition of fly ash did increase the soluble concentration, but the total concentration actually decreased. The concentration of V in the fly ash is much greater than Cr, and additions of the ash increased both the total and soluble concentrations in runoff, but the soluble concentration increased to a much greater degree. The increase in total concentrations of these elements was greater than predicted by Eq. 1. Thus the forms of these elements added in fly ash are more mobile than the native forms in the soil.

Because of the relatively low content of As in the ash, the addition of King fly ash did not increase total As in runoff from fly ash pads relative to runoff from soil pads. The soluble concentrations in runoff were not detectable.

Selenium was only detected in the initial sampling of each rainfall event for the ash-treated plots. In later samples, the concentration was too low to detect. The initial sampling data suggest Se in runoff is all in the soluble form.

2.5 References

- [1] Mattigod S.V., D. Rai, L.E. Eary, and C.C. Ainsworth. 1990. Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements. J. Environ. Qual. 19:202–214.
- [2] Eary, L.E., D. Rai, S.V. Mattigod, and C.C. Ainsworth. 1990. Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements. J. Environ. Qual. 19:202–214.
- [3] Wilson, N.E. 1999. Soil processes affecting the mobility and fate of constituents of concern in land applied coal ash. Unpublished MS professional paper. Department of Soil, Water, and Climate, University of Minnesota.

- [4] Meyer, L.D. and W.C. Harmon. 1979. Multiple-intensity rainfall simulator for erosion research on row sideslopes. Trans. Amer. Soc. Agric. Eng. 22:100–103.
- [5] SAS Institute, 1996.
- [6] Kabata-Pendias, A. 2000. Trace elements in soils and plants. 3rd edition. CRC Press. Boco Raton, Florida.
- [7] Skyllberg, U.L., K. Xia, P.R. Bloom, E.A. Nater, and W.F. Bleam. 2000. Binding of mercury(II) to reduced sulfur in soil organic matter along upland-peat soil transects. J. Environ. Qual. 29:855–865.
- [8] Nater, E.A. and D.F. Grigal. 1992. Regional trends in mercury distribution across the Great Lakes states, north central USA. Nature 358:139–141.

A APPENDIX A – EERC: COMPLETE BULK COMPOSITION RESULTS

Table A-1 Bulk Composition of Fly Ash and Lime Samples, $\mu g/g$

Site/Element	1	2	3	4	5	6	7	8	9	10	11	12a	12b
Sb	2.4	2.7	2.5	3.7	3.8	3.7	2.6	2.4	2.5	2.3	2.6	6.6	0.10
As	11.9	15.4	15.4	14.7	13.9	14.6	15.5	17.0	15.6	19.0	17.4	26.3	6.2
Ва	4747	5973	4241	134	139	246	5395	6589	6719	6606	6870	432	5
Ве	1.5	3.8	3.6	2.4	2.2	2.7	3.9	4.7	4.6	5.3	5.2	3.6	0.12
В	596	1084	669	1392	1329	1296	806	602	480	550	569	2005	38
Cd	1.21	1.17	1.22	0.78	0.55	0.78	1.22	1.70	1.84	1.99	1.65	1.90	0.06
Cr	37	89	81	47	35	58	95	72	91	75	74	78	4.3
Со	13.0	24.6	26.2	16.9	13.4	18.3	26.1	28.2	26.2	27.7	29.9	32.4	12.8
Fe	30,989	41,183	41,319	28,290	24,825	30,073	44,666	36,885	37,132	36,018	37,403	43,885	1022
Pb	50.0	50.6	46.7	23.3	21.1	27.7	46.1	49.1	54.5	50.0	51.6	68.8	0.4
Mn	153	133	136	487	558	412	162	139	135	138	129	321	106
Hg	0.60	0.25	0.48	0.19	0.015ª	0.20	0.30	0.267	0.288	0.236	0.162	0.810	< 0.001 ^a
Мо	7.6	8.6	8.7	25.0	13.2	10.0	8.8	9.6	8.2	8.9	10.2	105.1	0.2
Ni	16	41	46	165	27	33	52	66	98	66	68	979	7.1
Se	15.1	20.2	20.8	17.7	18.2	21.0	21.3	21.5	23.9	20.8	25.2	29.4	24.6
Ag	1.90	1.44	1.45	1.26	1.18	1.36	1.47	1.70	1.75	1.72	1.94	1.87	0.06
TI	0.40	0.50	0.45	0.38	0.47	0.37	0.51	0.49	0.51	0.48	0.68	0.41	< 0.01
V	196	181	190	312	56	109	202	167	182	160	165	1537	3
Zn	54	72	89	59	50	61	103	173	160	175	157	160	10
^a EPA Method	7473												

Table A-2 Bulk Composition of Soil Samples, $\mu g/g$

Site/ Element	1	2	3	4	5	6	7	8	9	10	11	12c
Sb	0.3	0.6	0.8	0.8	0.6	0.8	0.3	0.7	2.5	1.0	0.4	0.7
As	4.5	6.0	7.8	8.0	7.6	7.3	4.4	9.7	8.5	3.5	5.8	5.4
Ва	263	495	630	655	628	640	498	547	528	679	374	514
Be	0.3	1.0	1.2	1.2	1.2	1.1	0.8	1.1	1.0	1.2	0.6	1.2
В	19	6	8	4	6	< 4	8	15	28	39	12	< 4
Cd	0.11	0.17	0.31	0.48	0.22	0.29	0.14	0.87	0.76	0.70	1.06	0.18
Cr	11	35	46	39	37	38	21	38	40	45	24	38
Со	9.0	12.5	13.3	11.5	10.1	10.1	17.8	14.4	18.0	12.0	8.7	11.9
Fe	13,830	19,080	22,502	20,624	21,081	18,387	14,237	17,442	16,927	18,007	13,913	17,925
Pb	9.0	13.1	15.3	13.6	15.9	13.1	12.3	14.1	15.2	15.7	16.8	14.7
Mn	656	597	887	1337	873	648	607	785	514	212	618	468
Hg	0.10	0.26	0.20	0.14	0.14	0.14	0.48	0.024ª	0.026	0.030	0.011ª	0.190
Мо	0.2	1.5	1.9	1.1	0.9	1.2	1.9	3.1	3.2	0.7	1.1	1.2
Ni	8	22	34	36	22	25	14	37	69	108	77	24
Se	5.1	1.8	1.9	1.9	1.3	3.0	2.4	11.6	8.5	7.9	11.6	1.8
Ag	0.10	0.33	0.38	0.33	0.34	0.34	0.31	0.58	0.66	1.14	0.48	0.38
TI	0.20	0.46	0.58	0.61	0.53	0.46	0.38	0.67	0.59	0.67	0.41	0.52
V	31	76	103	88	81	83	39	63	69	88	16	80
Zn	26	57	69	64	66	69	41	78	115	174	88	57
^a EPA Met	hod 747	3										

A-2

B

APPENDIX B – EERC: COMPLETE LEACHING RESULTS

Table B-1 SPLP Leachates of Composites, $\mu g/L$

Site / Element	1	2	3	4	5	6	7	8	9	10	11	12a	12b
Sb	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
As	< 4	< 4	6.3	4.5	5.4	4.9	< 4	6.6	< 4	< 4	< 4	4.5	6.7
Ва	144	66	59	95	80	80	121	57	170	142	85	97	13
Be	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
В	260	950	940	910	1300	1100	810	410	1200	710	730	1200	< 200
Cd	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Cr	9.1	53	21.1	4.2	< 1	< 1	< 1	< 1	110	64	35.5	2.4	< 1
Со	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Fe	< 10	< 10	< 10	< 10	< 10	< 10	11	< 10	14	< 10	< 10	< 10	< 10
Pb	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	9.2	< 2	< 2	2.6
Mn	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Hg	< 0.01	0.066	< 0.01	0.03	0.044	0.034	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Мо	2.5	14	22.7	82.4	30.2	20.7	13	16	33	22.3	10	285	< 2
Ni	< 4	< 4	< 4	4.3	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	11
Se	< 2	4.4	4.4	5.8	4.0	5.8	3.5	< 2	5.9	4.3	2.2	5.2	< 2
Ag	< 0.3	2.7	0.49	0.34	< 0.3	0.57	< 0.3	0.80	< 0.3	< 0.3	0.48	3.25	0.99
SO ₄	52,700	72,400	64,800	261,000	295,000	246,000	86,100	24,000	61,900	56,700	33,600	190,000	2900
TI	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
V	< 40	< 40	57	200	< 40	< 40	< 40	< 40	44	47	< 40	280	< 40
Zn	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30

Table B-2 18-hour Leachates of Composites, $\mu g/L$

Site / Element	1	2	3	4	5	6	7	8	9	10	11	12a	12b
Sb	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
As	< 4	< 4	11	11	11	9.6	< 4	5.3	< 4	4.5	< 4	4.6	6.0
Ва	80	66	42	59	50	46	70	105	106	96.2	60	91.0	< 10
Ве	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
В	260	570	640	560	540	620	500	430	1010	1040	548	1300	< 200
Cd	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Cr	13.1	40.3	14.7	5.4	6.9	10.4	17.9	25.2	84.3	41.3	26.9	3.6	< 1
Со	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Fe	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Pb	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Mn	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Hg	0.0187	0.0188	0.0409	0.0655	0.0439	0.0158	0.0176	0.0123	0.0019	0.0188	0.0060	0.0236	0.0306
Мо	< 2	9.1	10	49.7	18	13.0	6.5	13	22.0	14	8.8	218	4.7
Ni	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	9.4
Se	< 2	2.5	2.2	5.6	3.1	5.3	2.3	< 2	5.1	4.1	< 2	5.2	< 2
Ag	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
SO₄	26,900	34,300	35,900	182,000	145,000	156,000	16,400	22,400	65,100	82,200	33,300	227,000	3700
ΤI	< 1	1.11	1.14	1.14	< 1	< 1	1.01	< 1	< 1	< 1	< 1	< 1	< 1
V	< 40	< 40	56	180	44	43	< 40	< 40	45	43	< 40	270	< 40
Zn	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30

Table B-3 30-day Leachates of Composites, μg/L

Site /													
Element	1	2	3	4	5	6	7	8	9	10	11	12a	12b
Sb	< 3	NT	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
As	< 4	NT	10	14	12	10	< 4	9.1	< 4	< 4	< 4	7.4	11
Ва	93	NT	147	105	122	134	223	85	135	142	76	92	< 10
Be	< 1	NT	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
В	260	NT	920	570	640	460	440	530	1400	950	650	1250	< 200
Cd	< 0.3	NT	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Cr	19.6	NT	59	6.6	11.7	20.6	36.1	31.8	113	55.5	40.1	2.6	1.3
Со	< 2	NT	< 2	< 2	2.2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	2.4
Fe	< 10	NT	< 10	< 10	< 10	< 10	< 10	24	< 10	< 10	12	< 10	< 10
Pb	< 2	NT	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Mn	< 5	NT	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Hg	0.0030	NT	0.0125	0.0080	0.0035	0.0013	0.0019	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Мо	5.0	NT	21.5	64.1	25.2	22.0	14.0	17	25.6	17	12	225	2.2
Ni	< 4	NT	6.7	8.2	7.1	4.5	< 4	< 4	< 4	< 4	< 4	< 4	11
Se	< 2	NT	4.8	4.7	2.2	2.4	2.4	< 2	7.1	4.6	2.1	5.0	< 2
Ag	< 0.3	NT	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	5.3	< 0.3	< 0.3	0.38	< 0.3	5.20
SO ₄	NT	NT	63,600	218,000	204,000	169,000	40,200	25,100	83,100	77,100	81,300	206,000	5300
TI	< 1	NT	1.27	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
V	< 40	NT	95	290	76	90	65	58	70	83	48	340	42
Zn	< 30	NT	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30

Table B-4 60-day Leachates of Composites, μg/L

Site / Element	1	2	3	4	5	6	7	8	9	10	11	12a	12b
Sb	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
As	< 4	< 4	< 4	5.9	8.1	4.8	< 4	11	< 4	4.5	< 4	< 4	12
Ва	68	163	234	222	162	296	232	57	141	148	98	86	11
Ве	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
В	360	800	920	420	710	380	630	470	1200	710	700	1270	< 200
Cd	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.96	< 0.3	< 0.3	0.45	< 0.3
Cr	20.3	83	67	11.4	13.2	27.2	45	31	131	53.8	53.1	3.5	1.4
Со	< 2	< 2	< 2	< 2	2.3	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Fe	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Pb	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Mn	< 5	< 5	< 5	8	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Hg	0.0080	0.0034	0.0028	0.0027	0.0028	0.0121	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Мо	5.7	17	22.0	72.0	33.9	26.6	13	14	28.7	15	14	216	2.4
Ni	< 4	< 4	8.3	10.0	8.5	6.3	< 4	< 4	< 4	< 4	< 4	< 4	8.4
Se	< 2	3.6	4.7	3.2	2.4	2.4	2.5	< 2	6.8	4.9	2.4	< 2	< 2
Ag	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	1.4	< 0.3	< 0.3	< 0.3	5.2	26
SO₄	32,900	57,400	63,600	284,000	254,000	240,000	49,000	26,200	85,500	72,000	43,800	194,000	17,800
TI	1.38	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
V	< 40	59	97	340	90	99	76	75	73	72	51	417	< 40
Zn	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30

C APPENDIX C – EERC: LEACHING CHARTS BY SITE

The leachate results are plotted for each fly ash—soil stabilized site. Only the elements that yielded results above the LLQs are displayed. When no bars are evident on the graph, the results are too small to be seen because of the scale of the graph. The vertical dotted line inside the graph indicates a separation between two y-axes, each of which is the concentration of the element in μ g/L. The leachate results for sulfate are not included in the graphs because the high values make extending the y-axis difficult.

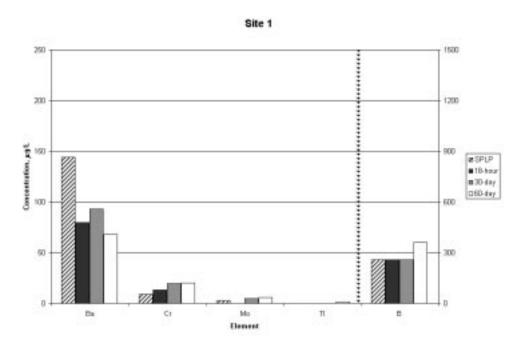


Figure C-1 Site 1

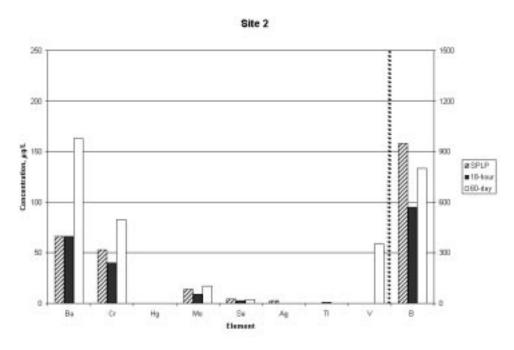


Figure C-2 Site 2

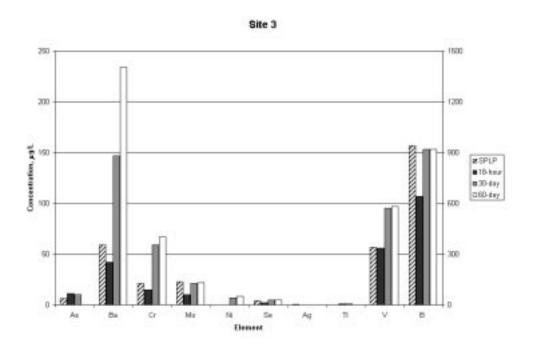


Figure C-3 Site 3

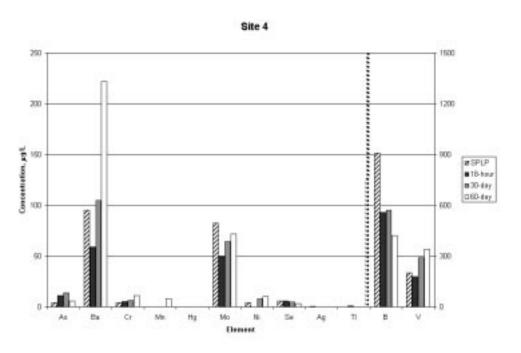


Figure C-4 Site 4

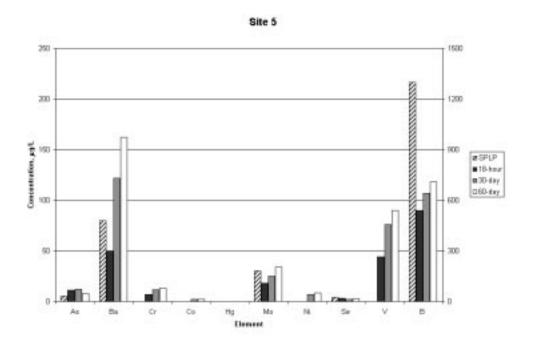


Figure C-5 Site 5

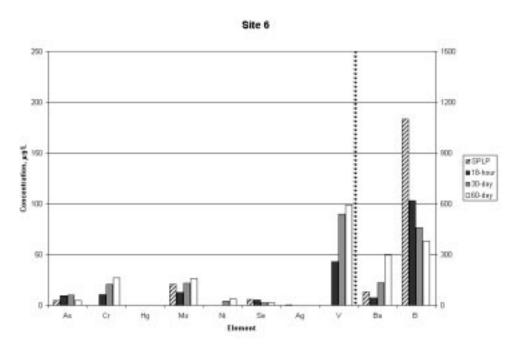


Figure C-6 Site 6

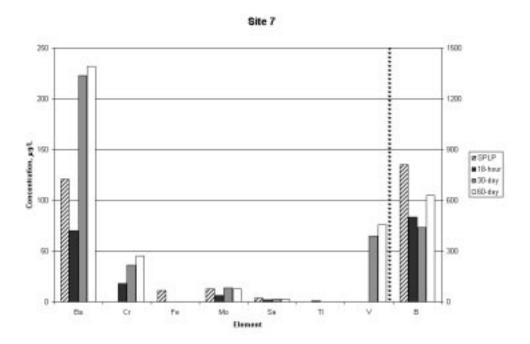


Figure C-7 Site 7

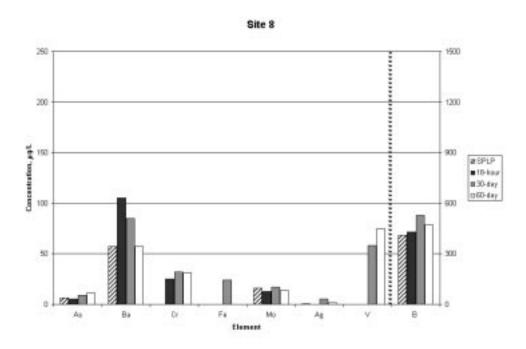


Figure C-8 Site 8

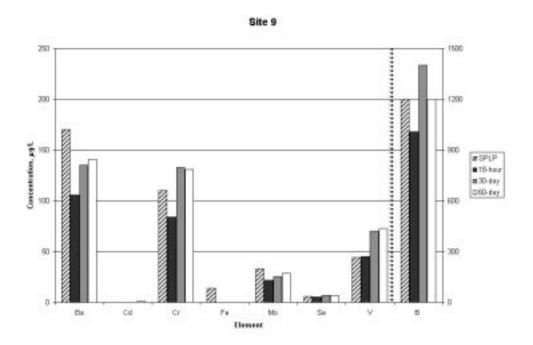


Figure C-9 Site 9

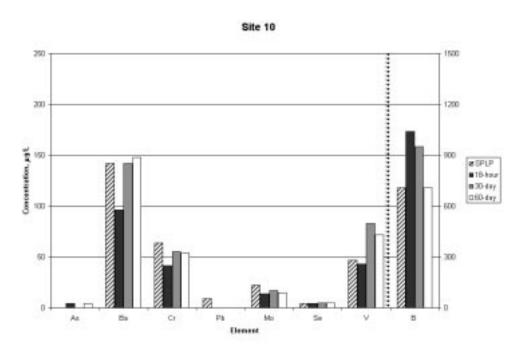


Figure C-10 Site 10

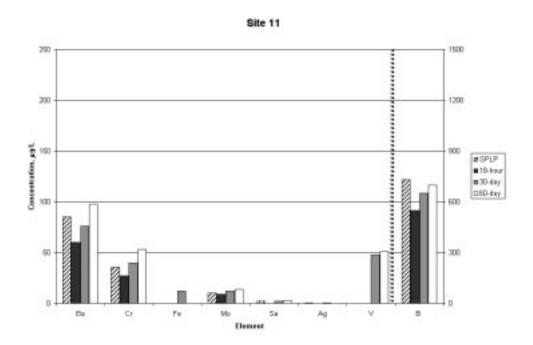


Figure C-11 Site 11

DAPPENDIX D – EERC: LEACHING CHARTS BY ELEMENT

Leachate results are sorted according to element. Since no results are seen above the LLQs for antimony, beryllium, and zinc, no graphs are plotted. The horizontal dashed line indicates the LLQ for that element.

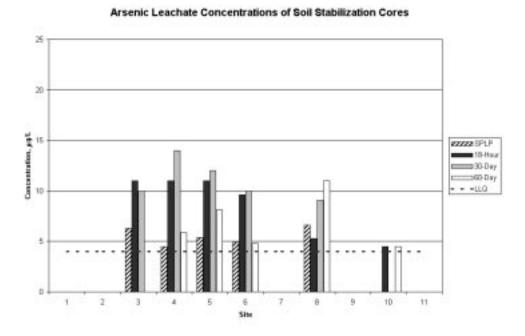


Figure D-1
Arsenic Leachate Concentrations of Soil Stabilization Cores

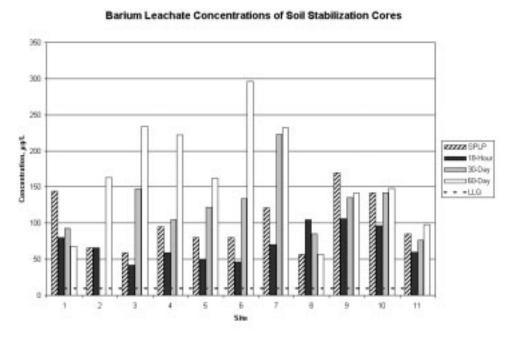
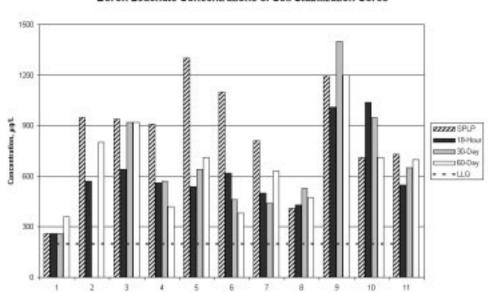


Figure D-2
Barium Leachate Concentrations of Soil Stabilization Cores



Site

Boron Leachate Concentrations of Soil Stabilization Cores

Figure D-3
Boron Leachate Concentrations of Soil Stabilization Cores

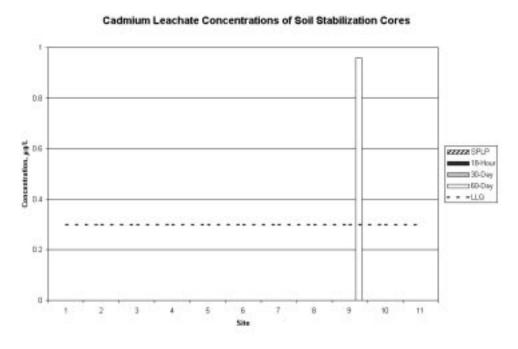


Figure D-4
Cadmium Leachate Concentrations of Soil Stabilization Cores

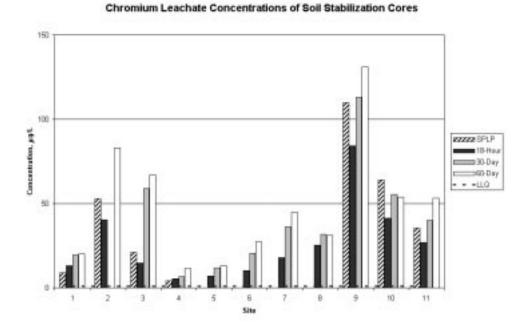


Figure D-5
Chromium Leachate Concentrations of Soil Stabilization Cores

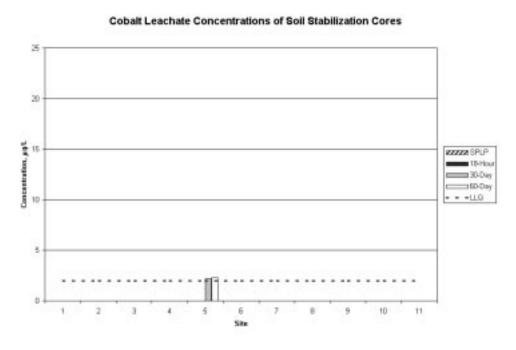
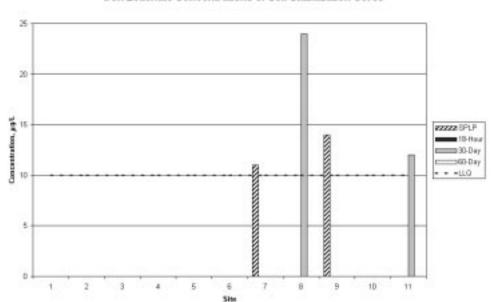


Figure D-6
Cobalt Leachate Concentrations of Soil Stabilization Cores



Iron Leachate Concentrations of Soil Stabilization Cores

Figure D-7 Iron Leachate Concentrations of Soil Stabilization Cores

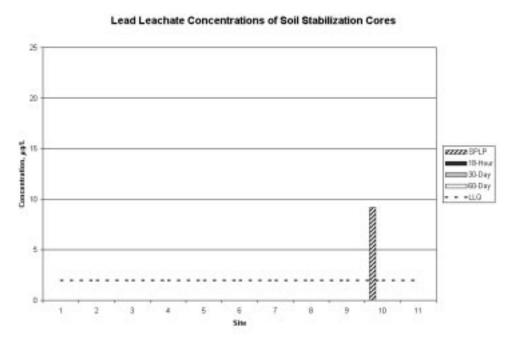


Figure D-8
Lead Leachate Concentrations of Soil Stabilization Cores

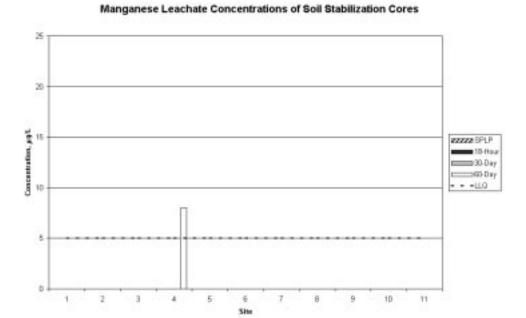


Figure D-9
Manganese Leachate Concentrations of Soil Stabilization Cores

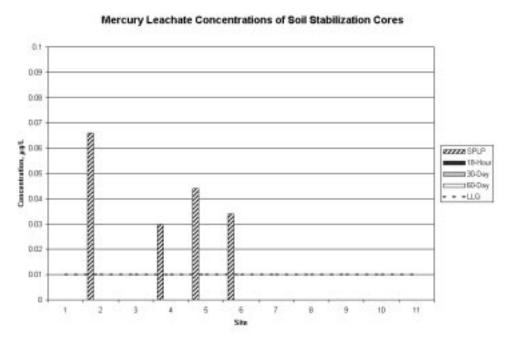


Figure D-10
Mercury Leachate Concentrations of Soil Stabilization Cores

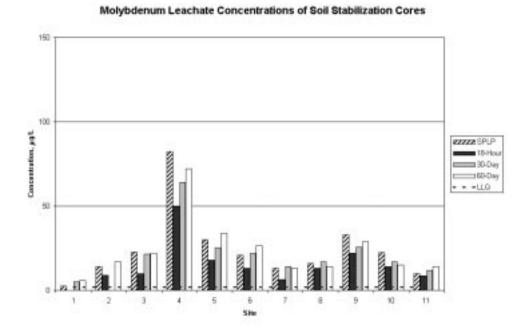


Figure D-11 Molybdenum Leachate Concentrations of Soil Stabilization Cores

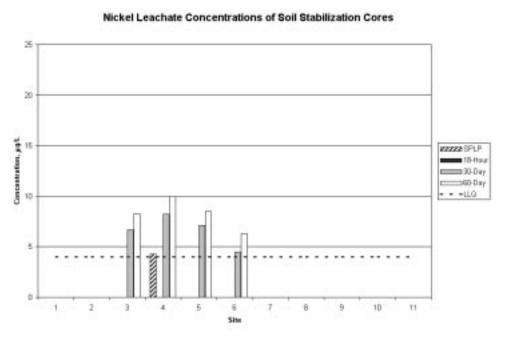


Figure D-12 Nickel Leachate Concentrations of Soil Stabilization Cores

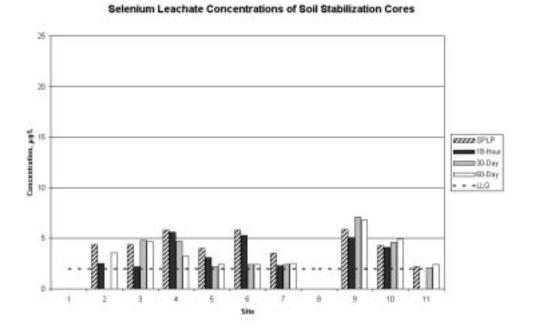


Figure D-13
Selenium Leachate Concentrations of Soil Stabilization Cores

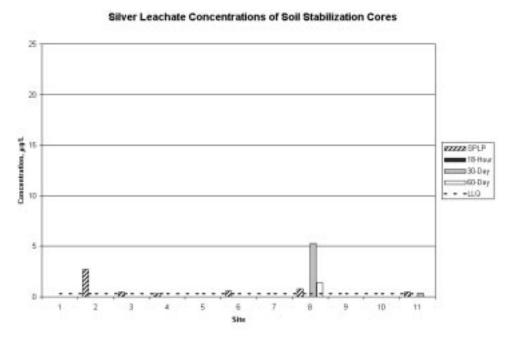
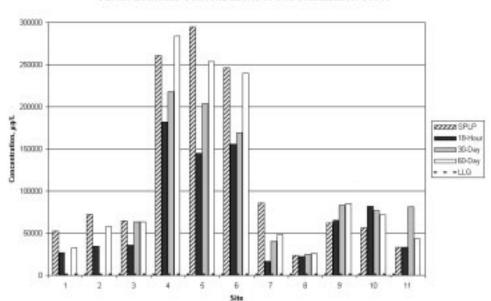


Figure D-14
Silver Leachate Concentrations of Soil Stabilization Cores



Sulfate Leachate Concentrations in Soil Stabilization Cores

Figure D-15
Sulfate Leachate Concentrations of Soil Stabilization Cores

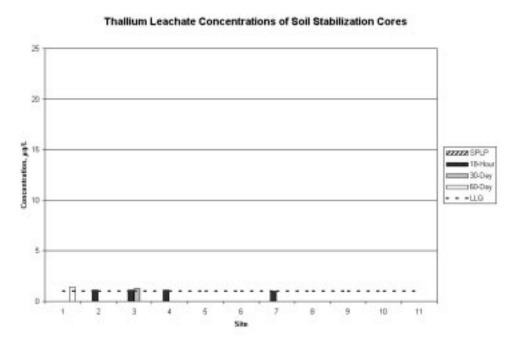


Figure D-16
Thallium Leachate Concentrations of Soil Stabilization Cores

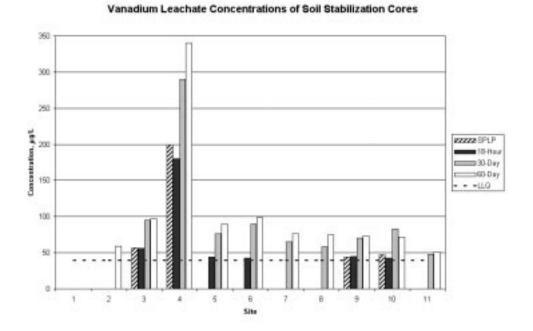


Figure D-17 Vanadium Leachate Concentrations of Soil Stabilization Cores

E

APPENDIX E - EERC: CALCULATED MAXIMUM OF LEACHABILITY BY SITE

A table for each site (1–11) is presented. The bulk compositions of the fly ash and soil as well as the respective calculated maximum of leachability are displayed. The calculated maximum of the fly ash—soil stabilized core is represented with the leachate results. No value for the boron in soil was detected above the LLQ, so half of the LLQ was listed, and the subsequent calculations are highlighted. Also listed are the actual percentages of possible leachability as figured from the calculated maximum of leachability.

Table E-1 Site 1

Site 1	Fly Ash	Calc. Max.	Soil	Calc. Max.
Element	μg/g	μg/L	μg/g	μg/L
Sb	2.4	120	0.3	15
As	11.9	595	4.5	225
Ва	4747	237,350	263	13,150
Be	1.5	75	0.3	15
В	596	29,800	19	950
Cd	1.21	60.5	0.11	5.5
Cr	37	1850	11	550
Co	13.0	650	9.0	450
Fe	30,989	1,549,450	13,830	691,500
Pb	50.0	2500	9.0	450
Mn	153	7650	656	32800
Hg	0.60	30	0.10	5
Мо	7.6	380	0.2	10
Ni	16	780	8	390
Se	15.1	755	5.1	255
Ag	1.90	95	0.10	5
TI	0.40	20	0.20	10
V	196	9800	31	1550
Zn	54	2700	26	1300
SO ₄ 2-				

Core Calc.								
Max.	SPLP	SPLP	18 hour	18 hour	30-Day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
26.25								
264.6								
37,171	144	0.39	80	0.22	93	0.25	68	0.18
21.4								
4041	260	6.43	260	6.43	260	6.43	360	8.91
11.39								
689	9.1	1.32	13.1	1.90	19.6	2.84	20.3	2.95
471								
783,423								
670								
30105								
7.7								
49.6	2.5	5.04			5	10.07	5.7	11.48
431.8								
308.6								
14.6								
11.1							1.38	12.46
2434								
1450								
	52,700		26,900		not tested		32,900	

Table E-2 Site 2

Site 2	Fly Ash	Calc. Max.
Element	μg/g	μg/L
Sb	2.7	133
As Ba	15.4	770
Ва	5973	298,650
Be	3.8	188
В	1084	54,200
Cd	1.17	58.5
Cr	89	4445
Be B Cd Cr Co Fe Pb	24.6	1230
Fe	41,183	2,059,150
Pb	50.6	2530
Mn	133	6650
Hg Mo	0.25	12.5
Мо	8.6	430
Ni	41	2060
Se	20.2	1010
Ag	1.44	72
Ag TI V Zn	0.50	25
V	181	9050
Zn	72	3600
SO ₄ ²⁻		

	Calc.
Soil	Max.
μg/g	μg/L
0.6	28.5
6.0	300
495	24,750
1.0	48.5
6	300
0.17	8.5
35	1760
12.5	625
19,080	954,000
13.1	655
597	29,850
0.26	13
1.5	75
22	1075
1.8	90
0.33	16.5
0.46	23
76	3800
57	2850

Core Calc. Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
39.70					NT			
350.4					NT			
54,096	66	0.12%	66	0.12%	NT		163	0.30%
63.45					NT			
6075	950	15.64%	570	9.38%	NT		800	13.17%
13.9					NT			
2047.7	53	2.59%	40.3	1.97%	NT		83	4.05%
689.8					NT			
1,072,409					NT			
855.9					NT			
27,364					NT			
12.95	0.066	0.51%	,		NT			
113.0	14	12.39%	9.4	8.32%	NT		17	15.04%
1180.5					NT			
188.6	4.4	2.33%	2.5	1.33%	NT		3.6	1.91%
22.45	2.7	12.03%	,		NT			
23.21			1.11	4.78%	NT			
4363					NT		59	1.35%
2930					NT			
	72,400		34,300	,	NT	1	57,400	

Table E-3 Site 3

Site 3	Fly Ash	Calc. Max.	Soil	Calc. Max.
Element	μg/g	μg/L	μg/g	μg/L
Sb	2.5	123.5	0.8	42
As	15.4	770	7.8	390
Ва	4241	212,050	630	31,500
Be	3.6	177.5	1.2	61.5
В	669	33,450	8	400
Cd Cr	1.22	61	0.31	15.5
Cr	81	4035	46	2285
Со	26.2	1310	13.3	665
Fe	41,319	2,065,950	22,502	1,125,100
Pb	46.7	2335	15.3	765
Mn	136	6800	887	44,350
Hg	0.48	24	0.20	10
Мо	8.7	435	1.9	95
Ni	46	2280	34	1680
Se	20.8	1040	1.9	95
Ag	1.45	72.5	0.38	19
TI	0.45	22.5	0.58	29
Ag TI V	190	9500	103	5150
Zn	89	4450	69	3450
SO ₄ ²⁻				

Core Calc. Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
52.01								
436.7	6.3	1.44%	11	2.52%	10	2.29%		
53,673	59	0.11%	42	0.08%	147	0.27%	234	0.44%
75.75								
4459	940	21.08%	640	14.35%	920	20.63%	920	20.63%
21.09								
2499.9	21.1	0.84%	14.7	0.59%	59	2.36%	67	2.68%
744.2								
1,240,643								
957.8								
39,739								
11.72								
136.8	22.7	16.60%	10	7.31%	21.5	15.72%	22	16.09%
1753.7					6.7	0.38%	8.3	0.47%
211.1	4.4	2.08%	2.2	1.04%	4.8	2.27%	4.7	2.23%
25.57	0.49	1.92%						
28.20		·	1.14	4.04%	1.27	4.50%		
5684	57	1.00%	56	0.99%	95	1.67%	97	1.71%
3573								
	64,800		35,900		63,600		63,600	

Table E-4 Site 4

Site 4	Fly Ash	Calc. Max.	Soil	Calc. Max.
Element	μg/g	μg/L	μg/g	μg/L
Sb	3.7	186	0.8	40
As	14.7	735	8.0	400
Ва	134	6700	655	32,750
Be	2.4	118.5	1.2	58
В	1392	69,600	4	200
Cd	0.78	39	0.48	24
Cr	47	2365	39	1950
Cd Cr Co Fe	16.9	845	11.5	575
Fe	28,290	1,414,500	20,624	1,031,200
Pb	23.3	1165	13.6	680
Mn	487	24,350	1337	66,850
Hg	0.19	9.5	0.14	7
Мо	25.0	1250	1.1	55
Ni	165	8250	36	1800
Se	17.7	885	1.9	95
Ag	1.26	63	0.33	16.5
Ag TI	0.38	19	0.61	30.5
V	312	15,600	88	4400
Zn	59	2950	64	3200
SO ₄ ²				

Core Calc.								
Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
57.93								
441.1	4.5	1.02%	11	2.49%	14	3.17%	5.9	1.34%
29,551	95	0.32%	59	0.20%	105	0.36%	222	0.75%
65.43								
8723	910	10.43%	560	6.42%	570	6.53%	420	4.81%
25.84								
2001.0	4.2	0.21%	5.4	0.27%	6.6	0.33%	11.4	0.57%
608.2								
1,078,272								
739.6								
61,631							8	0.01%
7.31	0.03	0.41%						
201.8	82.4	40.84%	49.7	24.63%	64.1	31.77%	72	35.69%
2592.1	4.3	0.17%			8.2	0.32%	10	0.39%
192.0	5.8	3.02%	5.6	2.92%	4.7	2.45%	3.2	1.67%
22.21	0.34	1.53%						
29.09			1.14	3.92%				
5775	200	3.46%	180	3.12%	290	5.02%	340	5.89%
3169								
	261,000		182,000		218,000		284,000	

Table E-5 Site 5

Site 5	Fly Ash	Calc. Max.	Soil	Calc. Max.
Element	μg/g	μg/L	μg/g	μg/L
Sb	3.8	190.5	0.6	30.5
As	13.9	695	7.6	380
Ва	139	6950	628	31,400
Be	2.2	112	1.2	59.5
В	1329	66,450	6	300
Cd Cr Co	0.55	27.5	0.22	11
Cr	35	1760	37	1835
Co	13.4	670	10.1	505
Fe	24,825	1,241,250	21,081	1,054,050
Pb	21.1	1055	15.9	795
Mn	558	27,900	873	43,650
Hg	0.015	0.75	0.14	7
Мо	13.2	660	0.9	45
Ni	27	1350	22	1080
Se	18.2	910	1.3	65
Ag	1.18	59	0.34	17
Ag TI	0.47	23.5	0.53	26.5
V	56	2800	81	4050
Zn	50	2500	66	3300
SO ₄ 2-				

Core Calc.								
Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
50.15								
418.7	5.4	1.29%	11	2.63%	12	2.87%	8.1	1.93%
28,397	80	0.28%	50	0.18%	122	0.43%	162	0.57%
65.95								
8424	1300	15.43%	540	6.41%	640	7.60%	710	8.43%
13.03								
1825.8			6.9	0.38%	11.7	0.64%	13.2	0.72%
525.3					2.2	0.42%	2.3	0.44%
1,077,039								
826.9								
41716								
6.232	0.044	0.71%						
120.5	30.2	25.06%	18	14.93%	25.2	20.91%	33.9	28.13%
1113.2					7.1	0.64%	8.5	0.76%
168.8	4	2.37%	3.1	1.84%	2.2	1.30%	2.4	1.42%
22.16								
26.13								
3896			44	1.13%	76	1.95%	90	2.31%
3202								
	295,000		145,000		204,000		254,000	

Table E-6 Site 6

Site 6	Fly Ash	Calc. Max.	Soil	Calc. Max.
Element	μg/g	μg/L	μg/g	μg/L
Sb	3.7	183.5	0.8	38
As	14.6	730	7.3	365
Ва	246	12,300	640	32,000
Be	2.7	132.5	1.1	55.5
Be B	1296	64,800	2	100
Cd Cr Co Fe	0.78	39	0.29	14.5
Cr	58	2885	38	1900
Co	18.3	915	10.1	505
Fe	30,073	1,503,650	18,387	919,350
Pb	27.7	1385	13.1	655
Mn	412	20,600	648	32,400
Hg	0.20	10	0.14	7
Мо	10.0	500	1.2	60
Ni	33	1635	25	1265
Se	21.0	1050	3.0	150
Ag	1.36	68	0.34	17
Ag TI	0.37	18.5	0.46	23
V	109	5450	83	4150
Zn	61	3050	69	3450
SO ₄ ²⁻				

Core Calc.								
Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
55.87								
409.8	4.9	1.20%	9.6	2.34%	10	2.44%	4.8	1.17%
29,581	80	0.27%	46	0.16%	134	0.45%	296	1.00%
64.96								
8046	1100	13.67%	620	7.71%	460	5.72%	380	4.72%
17.51								
2021.0			10.4	0.51%	20.6	1.02%	27.2	1.35%
555.4								
991,106								
744.6								
30,951								
7.37	0.034	0.46%						
114.04	20.7	18.15%			22	19.29%	26.6	23.33%
1310.4			13	0.99%	4.5	0.34%	6.3	0.48%
260.5	5.8	2.23%			2.4	0.92%	2.4	0.92%
23.26	0.57	2.45%	5.3	22.78%				
22.45								
4310			43	1.00%	90	2.09%	99	2.30%
3401								
	246,000		156,000		169,000		240,000	

Table E-7 Site 7

Site 7	Fly Ash	Calc. Max.		Soil	Calc. Max.
Element	μg/g	μg/L		μg/g	μg/L
Sb	2.6	127.5	•	0.3	15
As	15.5	775		4.4	220
Ва	5395	269,750		498	24,900
Be	3.9	195		0.8	40
В	806	40,300		8	400
Cd	1.22	61		0.14	7
Cr	95	4745		21	1030
Cr Co	26.1	1305		17.8	890
Fe	44,666	2,233,300		14,237	711,850
Pb	46.1	2305		12.3	615
Mn	162	8100		607	30,350
Hg	0.30	15		0.48	24
Мо	8.8	440		1.9	95
Ni	52	2605		14	705
Se	21.3	1065		2.4	120
Ag	1.47	73.5		0.31	15.5
TI	0.51	25.5		0.38	19
Ag TI V	202	10,100		39	1950
Zn	103	5150		41	2050
SO ₄ ²⁻					

Core Calc.	2010		40.1					
Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
27.05								
279.5								
51,134	121	0.24%	70	0.14%	223	0.44%	232	0.45%
56.61								
4675	810	17.33%	500	10.70%	440	9.41%	630	13.48%
12.79								
1428.0			17.9	1.25%	36.1	2.53%	45	3.15%
934.5								
874,863			11	0.00%				
796.1								
27,966								
23.0								
132.0	13	9.85%	6.5	4.93%	14	10.61%	13	9.85%
908.6								
221.3	3.5	1.58%	2.3	1.04%	2.4	1.08%	2.5	1.13%
21.71								
19.70			1.01	5.13%				
2823		·			65	2.30%	76	2.69%
2382								
	86,100		16,400		40,200		49,000	

Table E-8 Site 8

Site 8	Fly Ash	Calc. Max.
Element	μg/g	μg/L
Sb	2.4	121
As	17.0	850
As Ba Be B Cd Cr Co Fe Pb	6589	329,454
Be	4.7	235
В	602	30,086
Cd	1.70	85
Cr	72	3617
Co	28.2	1410
Fe	36,885	1,844,226
Pb	49.1	2453
Mn	139	6938
Hg	0.267	13
Мо	9.6	479
Ni	66	3312
Se	21.5	1074
Hg Mo Ni Se Ag TI	1.70	85
TI	0.49	25
V	167	8371
Zn	173	8639
SO ₄ 2-		

Soil	Calc. Max.				
μg/g	μg/L				
0.7	34				
9.7	484				
547	27,326				
1.1	53				
15	773				
0.87	44				
38	1899				
14.4	722				
17,442	872,093				
14.1	703				
785	39,244				
0.024	1				
3.1	155				
37	1841				
11.6	581				
0.58	29				
0.67	33				
63	3149				
78	3924				

Core Calc. Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
43.2								
523.7	6.6	1.26%	5.3	1.01%	9.1	1.74%	11	2.10%
59,696	57	0.10%	105	0.18%	85	0.14%	57	0.10%
72.8								
3914	410	10.48%	460	11.75%	630	16.10%	470	12.01%
48.05								
2083			25.2	1.21%	31.8	1.53%	31	1.49%
796								
976,250					24	0.00%		
890								
35,783								
2.50								
190	16	8.43%	13	6.85%	17	8.96%	14	7.38%
1998.7								
634.2								
35.1	0.8	2.28%			5.3	15.11%	1.4	3.99%
32.5								
3709					58	1.56%	75	2.02%
4430								
	24,000		22,400		25,100		26,200	

Table E-9 Site 9

Site 9	Fly Ash	Calc. Max.		Soil	Calc. Max.
Element	μg/g	μg/L		μg/g	μg/L
Sb	2.5	124		2.5	123
As	15.6	781		8.5	425
Ва	6719	335,938		528	26,422
Be	4.6	230		1.0	49
В	480	24,023		28	1377
Cd Cr Co	1.84	92		0.76	38
Cr	91	4559		40	2016
Co	26.2	1310		18.0	902
Fe	37,132	1,856,618		16,927	846,330
Pb	54.5	2725		15.2	760
Mn	135	6756		514	25,685
Hg	0.288	14		0.026	1
Мо	8.2	409		3.2	161
Ni	98	4917		69	3447
Se	23.9	1195		8.5	425
Ag	1.75	87		0.66	33
Ag TI	0.51	25		0.59	29
V	182	9099		69	3440
V Zn	160			115	5760
SO ₄ 2-					

Core Calc. Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
122.92								
468.7								
64,433	170	0.26%	106	0.16%	135	0.21%	141	0.22%
71.35								
4158	1200	28.86%	1010	24.29%	1400	33.67%	1200	28.86%
44.42							0.96	2.16%
2328.3	110	4.72%	84.3	3.62%	113	4.85%	131	5.63%
951.9								
970,401	14	0.00%						
1001.5								
23,360								
2.909								
191.0	33	17.27%	22	11.52%	25.6	13.40%	28.7	15.02%
3627.3								
519.5	5.9	1.14%	5.1	0.98%	7.1	1.37%	6.8	1.31%
39.71								
28.78								
4135	44	1.06%	45	1.09%	70	1.69%	73	1.77%
6035								
	61,900		65,100		83,100		85,500	

Table E-10 Site 10

Site 10	Fly Ash	Calc. Max.		Soil	Calc. Max.
Element	μg/g	μg/L		μg/g	μg/L
Sb	2.3	113		1.0	48
As	19.0	950		3.5	175
Ва	6606	330,317		679	33,960
Be	5.3	263		1.2	60
В	550	27,486		39	1940
Cd	1.99	100		0.70	35
Cr	75	3760		45	2242
Co	27.7	1385		12.0	599
Fe	36,018	1,800,905		18,007	900,350
Pb	50.0	2502		15.7	787
Mn	138	6878		212	10577
Hg	0.236	12		0.030	2
Мо	8.9	443		0.7	35
Ni	66	3303		108	5376
Se	20.8	1041		7.9	393
Ag	1.72	86		1.14	57
TI	0.48	24		0.67	34
V	160	8009		88	4414
Zn	175	8733		174	8698
SO ₄ ²⁻					

Core Calc. Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
55.05								
257.9			4.5	1.74%			4.5	1.74%
65,712	142	0.22%	96.2	0.15%	142	0.22%	148	0.23%
81.68								
4677	710	15.18%	1040	22.24%	950	20.31%	710	15.18%
41.88								
2404.8	64	2.66%	41.3	1.72%	55.5	2.31%	53.8	2.24%
683.0								
996,838								
970.5	9.2	0.95%						
10,181								
2.604								
78.7	22.3	28.32%	14	17.78%	17	21.59%	15	19.05%
5153.8								
462.7	4.3	0.93%	4.1	0.89%	4.6	0.99%	4.9	1.06%
59.94								
32.62								
4799	47	0.98%	43	0.90%	83	1.73%	72	1.50%
8701								
	56,700		82,200		77,100		72,000	

Table E-11 Site 11

Site 11	Fly Ash	Calc. Max.	Soil	Calc. Max.
Element	μg/g	μg/L	μg/g	μg/L
Sb	2.6	131	0.4	19
As	17.4	872	5.8	290
Ва	6870	343,508	374	18,696
Be	5.2	258	0.6	30
В	569	28,463	12	623
B Cd Cr Co	1.65	82	1.06	53
Cr	74	3721	24	1198
Co	29.9	1497	8.7	435
Fe	37,403	1,870,155	13,913	695,652
Pb	51.6	2582	16.8	841
Mn	129	6444	618	30,918
Hg	0.162	8	0.011	1
Мо	10.2	509	1.1	53
Ni	68	3391	77	3865
Se Ag	25.2	1260	11.6	580
Ag	1.94	97	0.48	24
TI V	0.68	34	0.41	20
٧	165	8236	16	821
Zn	157	7849	88	4396
SO ₄ ²⁻				

Core Calc. Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
31.27								
352.2								
53,497	85	0.16%	60	0.11%	76	0.14%	98	0.18%
54.41								
3606	730	20.24%	548	15.20%	650	18.02%	700	19.41%
56.27								
1468.4	35.5	2.42%	26.9	1.83%	40.1	2.73%	53.1	3.62%
548.6								
821,492					12	0.00%		
1027.2								
28,296								
1.359								
102.0	10	9.81%	8.8	8.63%	12	11.77%	14	13.73%
3814.0								
652.6	2.2	0.34%			2.1	0.32%	2.4	0.37%
31.95	0.48	1.50%			0.38	1.19%		
21.75								
1616					48	2.97%	51	3.16%
4766								
	33,600		33,300		81,300		43,800	

APPENDIX F – EERC: CALCULATED MAXIMUM OF LEACHABILITY BY ELEMENT

Three presentations of the calculated maximum of leachability by element are portrayed in Appendix F. First, tables including the leachate results, calculated maximums, and percentage of calculated maximums are presented. No value for the boron in soil was detected above the LLQ, so half of the LLQ was listed, and the subsequent calculations are highlighted. Second, the leachate values are displayed graphically as a percentage of the fly ash—soil stabilized core calculated maximum of leachability. Third, the actual leachate values are plotted against the fly ash—soil stabilized core calculated maximums of leachability. Again, no graphs are plotted for antimony, beryllium, or zinc.

Table F-1 Antimony

Antimony	1	2	3	4	5	6	7	8	9	10	11
SPLP %											
18-hour %											
30-day %		NT									
60-day %											
FA Calc. Max.	120.0	133.0	123.5	186.0	190.5	183.5	127.5	121.0	124.0	113.0	131.0
Soil Calc. Max.	15.0	28.5	42.0	40.0	30.5	38.0	15.0	34.0	123.0	48.0	19.0
Core Calc. Max.	26.3	39.7	52.0	57.9	50.2	55.9	27.1	43.2	122.9	55.1	31.3
SPLP	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
18-hour	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
30-day	< 3	NT	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
60-day	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3

Table F-2 Arsenic

Arsenic	1	2	3	4	5	6	7	8	9	10	11
SPLP %			1.44	1.02	1.29	1.20		1.26			
18-hour %			2.52	2.49	2.63	2.34		1.01		1.74	
30-day %		NT	2.29	3.17	2.87	2.44		1.74			
60-day %				1.34	1.93	1.17		2.10		1.74	
FA Calc. Max.	595	770	770	735	695	730	775	850	781	950	872
Soil Calc. Max.	225	300	390	400	380	365	220	484	425	175	290
Core Calc. Max.	265	350	437	441	419	410	280	524	469	258	352
SPLP	< 4	< 4	6.3	4.5	5.4	4.9	< 4	6.6	< 4	< 4	< 4
18-hour	< 4	< 4	11	11	11	9.6	< 4	5.3	< 4	4.5	< 4
30-day	< 4	NT	10	14	12	10	< 4	9.1	< 4	< 4	< 4
60-day	< 4	< 4	< 4	5.9	8.1	4.8	< 4	11	< 4	4.5	< 4

Table F-3 Barium

Barium	1	2	3	4	5	6	7	8	9	10	11
SPLP %	0.39	0.12	0.11	0.32	0.28	0.27	0.24	0.10	0.26	0.22	0.16
18-hour %	0.22	0.12	0.08	0.20	0.18	0.16	0.14	0.18	0.16	0.15	0.11
30-day %	0.25	NT	0.27	0.36	0.43	0.45	0.44	0.14	0.21	0.22	0.14
60-day %	0.18	0.30	0.44	0.75	0.57	1.00	0.45	0.10	0.22	0.23	0.18
FA Calc. Max.	237,350	398,650	212,050	6700	6950	12,300	269,750	329,454	335,938	330,317	343,508
Soil Calc. Max.	13,150	24,750	31,500	32,750	31,400	32,000	24,900	27,326	26,422	33,960	18,696
Core Calc. Max.	37,171	54,096	53,673	29,551	28,397	29,581	51,134	59,696	64,433	65,712	53,497
SPLP	144	66	59	95	80	80	121	57	170	142	85
18-hour	80	66	42	59	50	46	70	105	106	96.2	60
30-day	93	NT	147	105	122	134	223	85	135	142	76
60-day	68	163	234	222	162	296	232	57	141	148	98

Table F-4 Beryllium

Beryllium	1	2	3	4	5	6	7	8	9	10	11
SPLP %											
18-hour %											
30-day %		NT									
60-day %											
FA Calc. Max.	75.0	188.0	177.5	118.5	112.0	132.5	195.0	235.0	230.0	263.0	258.0
Soil Calc. Max.	15.0	48.5	61.5	58.0	59.5	55.5	40.0	53.0	49.0	60.0	30.0
Core Calc. Max.	21.4	63.5	75.8	65.4	66.0	66.0	56.6	72.8	71.4	81.7	54.4
SPLP	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
18-hour	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
30-day	< 1	NT	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
60-day	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

Table F-5 Boron

Boron	1	2	3	4	5	6	7	8	9	10	11
SPLP %	6.43	15.64	21.08	10.43	15.43	13.67	17.33	10.48	28.86	15.18	20.24
18-hour %	6.43	9.38	14.35	6.42	6.41	7.71	10.70	10.99	24.29	22.24	15.20
30-day %	6.43	NT	20.63	6.53	7.60	5.72	9.41	13.54	33.67	20.31	18.03
60-day %	8.91	13.17	20.63	4.81	8.43	4.72	13.48	12.01	28.86	15.18	19.41
FA Calc. Max.	29,800	54,200	33,450	69,600	66,450	64,800	40,300	30,086	24,023	27,486	28,463
Soil Calc. Max.	950	300	400	200	300	100	400	773	1377	1940	623
Core Calc. Max.	4041	6075	4459	8723	8424	8046	4675	3914	4158	4677	3606
SPLP	260	950	940	910	1300	1100	810	410	1200	710	730
18-hour	260	570	640	560	540	620	500	430	1010	1040	548
30-day	260	NT	920	570	640	460	440	530	1400	950	650
60-day	360	800	920	420	710	380	630	470	1200	710	700

Table F-6 Cadmium

Cadmium	1	2	3	4	5	6	7	8	9	10	11
SPLP %											
18-hour %											
30-day %		NT									
60-day %									2.16		
FA Calc. Max.	60.5	58.5	61.0	39.0	27.5	39.0	61.0	85.0	92.0	100.0	82.0
Soil Calc. Max.	5.5	8.5	15.5	24.0	11.0	14.5	7.0	44.0	38.0	35.0	53.0
Core Calc. Max.	11.4	13.9	21.1	25.8	13.0	17.5	12.8	48.1	44.4	41.9	56.3
SPLP	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
18-hour	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
30-day	< 0.3	NT	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
60-day	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.96	< 0.3	< 0.3

Table F-7 Chromium

Chromium	1	2	3	4	5	6	7	8	9	10	11
SPLP %	1.32	2.59	0.84	0.21					4.72	2.66	2.42
18-hour %	1.90	1.97	0.59	0.27	0.38	0.51	1.25	1.21	3.62	1.72	1.83
30-day %	2.84	NT	2.36	0.33	0.64	1.02	2.53	1.53	4.85	2.31	2.73
60-day %	2.95	4.05	2.68	0.57	0.72	1.35	3.15	1.49	5.63	2.24	3.62
FA Calc. Max.	1850	4445	4035	2365	1760	2885	4745	3617	4559	3760	3721
Soil Calc. Max.	550	1760	2285	1950	1835	1900	1030	1899	2016	2242	1198
Core Calc. Max.	689	2048	2500	2001	1826	2021	1428	2083	2328	2405	1468
SPLP	9.1	53	21.1	4.2	<1	<1	<1	<1	110	64	35.5
18-hour	13.1	40.3	14.7	5.4	6.9	10.4	17.9	25.2	84.3	41.3	26.9
30-day	19.6	NT	59	6.6	11.7	20.6	36.1	31.8	113	55.5	40.1
60-day	20.3	83	67	11.4	13.2	27.2	45	31	131	53.8	53.1

Table F-8 Cobalt

Cobalt	1	2	3	4	5	6	7	8	9	10	11
SPLP %											
18-hour %											
30-day %		NT			0.42						
60-day %					0.44						
FA Calc. Max.	650	1230	1310	845	670	915	1305	1410	1310	1385	1497
Soil Calc. Max.	450	625	665	575	505	505	859	722	902	599	435
Core Calc. Max.	471	690	744	608	525	555	935	796	952	683	549
SPLP	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
18-hour	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
30-day	< 2	NT	< 2	< 2	2.2	< 2	< 2	< 2	< 2	< 2	< 2
60-day	< 2	< 2	< 2	< 2	2.3	< 2	< 2	< 2	< 2	< 2	< 2

Table F-9 Iron

Iron	1	2	3	4	5	6	7	8	9	10	11
SPLP %							0.0013		0.0014		
18-hour %											
30-day %		NT						0.0025			0.0015
60-day %											
FA Calc. Max.	1,549,450	2,059,150	2,065,950	1,414,500	1,241,250	1,503,650	2,233,300	1,844,226	1,856,618	1,800,905	1,870,155
Soil Calc. Max.	691,500	954,000	1,125,100	1,031,200	1,054,050	919,350	711,850	872,093	846,330	900,350	695,652
Core Calc. Max.	783,423	1,072,409	1,240,643	1,078,272	1,077,039	991,106	874,863	976,250	970,401	996,838	821,492
SPLP	< 10	< 10	< 10	< 10	< 10	< 10	11	< 10	14	< 10	< 10
18-hour	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
30-day	< 10	NT	< 10	< 10	< 10	< 10	< 10	24	< 10	< 10	12
60-day	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

Table F-10 Lead

Lead	1	2	3	4	5	6	7	8	9	10	11
SPLP %										0.95	
18-hour %											
30-day %		NT									
60-day %											
FA Calc. Max.	2500	2530	2335	1165	1055	1385	2305	2453	2725	2502	2582
Soil Calc. Max.	450	655	765	680	795	655	615	703	760	787	841
Core Calc. Max.	670	856	958	740	827	478	796	890	1002	971	1027
SPLP	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	9.2	< 2
18-hour	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
30-day	< 2	NT	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
60-day	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2

Table F-11 Manganese

Manganese	1	2	3	4	5	6	7	8	9	10	11
SPLP %											
18-hour %											
30-day %		NT									
60-day %				0.013							
FA Calc. Max.	7650	6650	6800	24,350	27,900	20,600	8100	6938	6756	6878	6444
Soil Calc. Max.	32,800	29,850	44,350	66,850	43,650	32,400	30,350	39,244	25,685	10,577	30,918
Core Calc. Max.	30,105	27,364	39,739	61,631	41,716	30,951	27,966	35,783	23,360	10,181	28,296
SPLP	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
18-hour	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
30-day	< 5	NT	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
60-day	< 5	< 5	< 5	8	< 5	< 5	< 5	< 5	< 5	< 5	< 5

Table F-12 Mercury

Mercury	1	2	3	4	5	6	7	8	9	10	11
SPLP %		0.51		0.41	0.71	0.46					
18-hour %	0.24	0.15	0.35		0.70	0.21	0.08	0.49	0.07	0.72	0.49
30-day %	0.04	NT	0.11	0.11	0.06	0.02	0.01				
60-day %	0.10	0.03	0.02	0.04	0.04	0.16					
FA Calc. Max.	30	12.5	24	9.5	0.75	10	15	13	14	12	8
Soil Calc. Max.	5	13	10	7	7	7	24	1	1	2	1
Core Calc. Max.	8	13	12	7	6	7	23	3	3	3	1
SPLP	< 0.01	0.066	< 0.01	0.03	0.044	0.034	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
18-hour	0.0187	0.0188	0.0409	< 0.01	0.0439	0.0158	0.0176	0.0123	0.0019	0.0188	0.0066
30-day	0.0030	NT	0.0125	0.0080	0.0035	0.0013	0.0019	< 0.01	< 0.01	< 0.01	< 0.01
60-day	0.0080	0.0034	0.0028	0.0027	0.0028	0.0121	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Table F-13 Molybdenum

Molybdenum	1	2	3	4	5	6	7	8	9	10	11
SPLP %	5.04	12.39	16.59	40.83	25.06	18.15	9.85	8.42	17.28	28.34	9.80
18-hour %		8.05	7.31	24.63	14.94	11.40	4.92	6.84	11.52	17.79	8.63
30-day %	10.08	NT	15.72	31.76	20.91	19.29	10.61	8.95	13.40	21.60	11.76
60-day %	11.49	15.04	16.08	35.68	28.13	23.33	9.85	7.37	15.03	19.06	13.73
FA Calc. Max.	380.0	430	435	1250.0	660.0	500	440.0	479	409	443	509
Soil Calc. Max.	10.0	75	95	55.0	45.0	60	95.0	155	161	35	53
Core Calc. Max.	50	113	137	202	121	114	132	190	191	79	102
SPLP	2.5	14	22.7	82.4	30.2	20.7	13	16	33	22.3	10
18-hour	< 2	9.1	10	49.7	18	13.00	6.5	13	22.0	14	8.8
30-day	5.0	NT	21.5	64.1	25.2	22.0	14.0	17	25.6	17	12
60-day	5.7	17	22.0	72.0	33.9	26.6	13	14	28.7	15	14

Table F-14 Nickel

Nickel	1	2	3	4	5	6	7	8	9	10	11
SPLP %				0.17							
18-hour %											
30-day %		NT	0.38	0.32	0.64	0.34					
60-day %			0.47	0.39	0.76	0.48					
FA Calc. Max.	780	2060	2280	8250	1350.0	1635.0	2605	3312	4917	3303	3391
Soil Calc. Max.	390	1075	1680	1800	1080.0	1365.0	705	1841	3447	5376	3865
Core Calc. Max.	432	1181	1754	2592	1113	1310	909	1999	3627	5154	3814
SPLP	< 4	< 4	< 4	4.3	< 4	< 4	< 4	< 4	< 4	< 4	< 4
18-hour	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4	< 4
30-day	< 4	NT	6.7	8.2	7.1	4.5	< 4	< 4	< 4	< 4	< 4
60-day	< 4	< 4	8.3	10.0	8.5	6.3	< 4	< 4	< 4	< 4	< 4

Table F-15 Selenium

Selenium	1	2	3	4	5	6	7	8	9	10	11
SPLP %		2.33	2.08	3.02	2.37	2.23	1.58		1.14	0.93	0.34
18-hour %		1.33	1.04	2.92	1.84	2.03	1.04		0.98	0.89	
30-day %		NT	2.27	2.45	1.30	0.92	1.08		1.37	0.99	0.32
60-day %		1.91	2.23	1.67	1.42	0.92	1.13		1.31	1.06	0.37
FA Calc. Max.	755	1010	1040	885	910	1050	1065.0	1074	1195	1041	1260
Soil Calc. Max.	255	90	95	95	65	150	120.0	581	425	393	580
Core Calc. Max.	309	189	211	192	169	261	221	634	520	463	653
SPLP	< 2	4.4	4.4	5.8	4.0	5.8	3.5	< 2	5.9	4.3	2.2
18-hour	< 2	2.5	2.2	5.6	3.1	5.3	2.3	< 2	5.1	4.1	< 2
30-day	< 2	NT	4.8	4.7	2.2	2.4	2.4	< 2	7.1	4.6	2.1
60-day	< 2	3.6	4.7	3.2	2.4	2.4	2.5	< 2	6.8	4.9	2.4

Table F-16 Silver

Silver	1	2	3	4	5	6	7	8	9	10	11
SPLP %		12.03	1.92	1.53		2.45		2.28			1.50
18-hour %											
30-day %		NT						15.10			1.19
60-day %								3.99			
FA Calc. Max.	95	72	72.5	63	59	68	73.5	85	87	86	97
Soil Calc. Max.	5	16.5	19	16.5	17	17	15.5	29	33	57	24
Core Calc. Max.	15	22	26	22	22	23	22	35	40	60	32
SPLP	< 0.3	2.7	0.49	0.34	< 0.3	0.57	< 0.3	0.80	< 0.3	< 0.3	0.48
18-hour	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
30-day	< 0.3	NT	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	5.3	< 0.3	< 0.3	0.38
60-day	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	1.4	< 0.3	< 0.3	< 0.3

Table F-17 Thallium

Thallium	1	2	3	4	5	6	7	8	9	10	11
SPLP %											
18-hour %		4.78	4.04	3.92			5.13				
30-day %		NT	4.50								
60-day %	12.43										
FA Calc. Max.	20	25	22.5	19	23.5	18.5	25.5	25	25	24	34
Soil Calc. Max.	10	23	29	30.5	26.5	23	19	33	29	34	20
Core Calc. Max.	11	23	28	29	26	22	20	33	29	33	22
SPLP	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
18-hour	< 1	1.11	1.14	1.14	< 1	< 1	1.01	< 1	< 1	< 1	< 1
30-day	< 1	NT	1.27	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
60-day	1.38	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

Table F-18 Vanadium

Vanadium	1	2	3	4	5	6	7	8	9	10	11
SPLP %			1.00	3.46					1.06	0.98	
18-hour %			0.99	3.12	1.13	1.00			1.09	0.90	
30-day %		NT	1.67	5.02	1.95	2.09	2.30	1.56	1.69	1.73	2.97
60-day %		1.35	1.71	5.89	2.31	2.30	2.69	2.02	1.77	1.50	3.16
FA Calc. Max.	9800	9050	9500	15600	2800	5450	10100	8371	9099	8009	8236
Soil Calc. Max.	1550	3800	5150	4400	4050	4150	1950	3149	3440	4414	821
Core Calc. Max.	2434	4363	5684	5775	3896	4310	2823	3709	4135	4799	1616
SPLP	< 40	< 40	57	200	< 40	< 40	< 40	< 40	44	47	< 40
18-hour	< 40	< 40	56	180	44	43	< 40	< 40	45	43	< 40
30-day	< 40	NT	95	290	76	90	65	58	70	83	48
60-day	< 40	59	97	340	90	99	76	75	73	72	51

Table F-19 Zinc

Zinc	1	2	3	4	5	6	7	8	9	10	11
SPLP %											
18-hour %											
30-day %		NT									
60-day %											
FA Calc. Max.	2700	3600	4450	2950	2500	3050	5150	8639	7996	8733	7849
Soil Calc. Max.	1300	2850	3450	3200	3300	3450	2050	3924	5760	8696	4396
Core Calc. Max.	1450	2930	3573	3169	3202	3401	2382	4430	6035	8701	4766
SPLP	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
18-hour	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
30-day	< 30	NT	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
60-day	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30

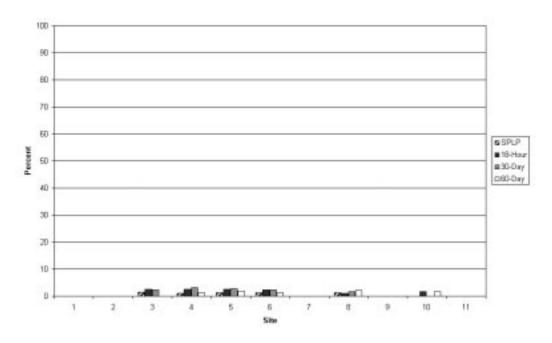


Figure F-1 Arsenic Percentage of Possible Leachability

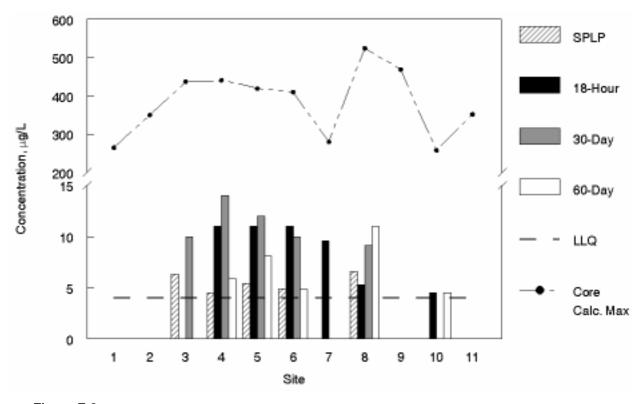


Figure F-2 Arsenic Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

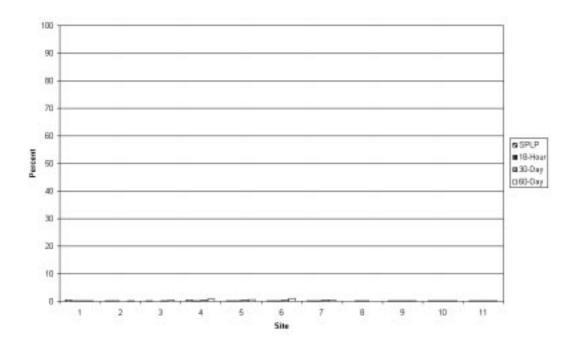


Figure F-3
Barium Percentage of Possible Leachability

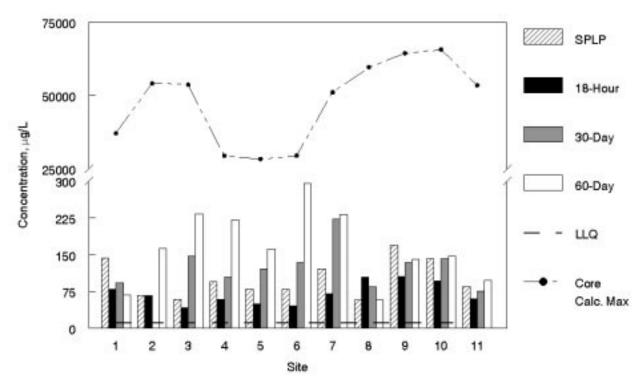


Figure F-4
Barium Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

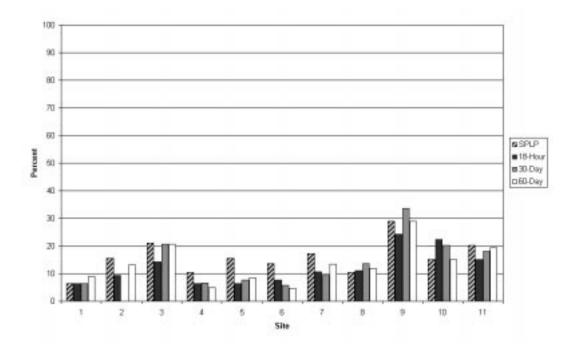


Figure F-5
Boron Percentage of Possible Leachability

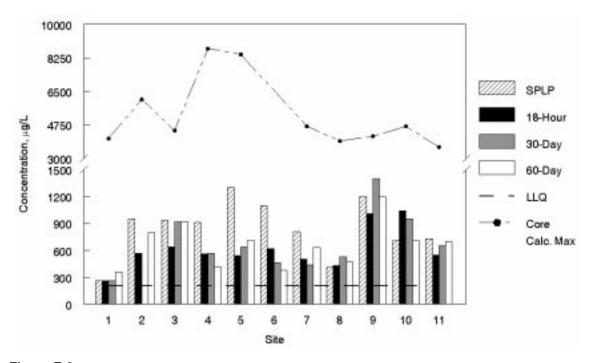


Figure F-6
Boron Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

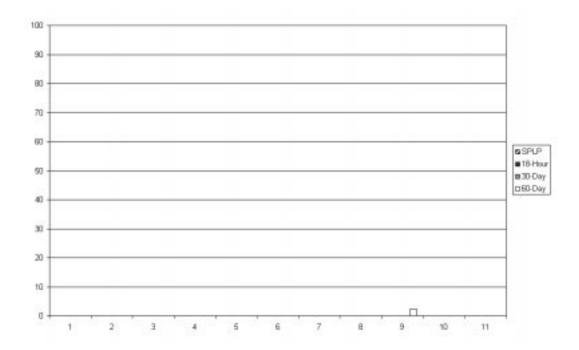


Figure F-7
Cadmium Percentage of Possible Leachability

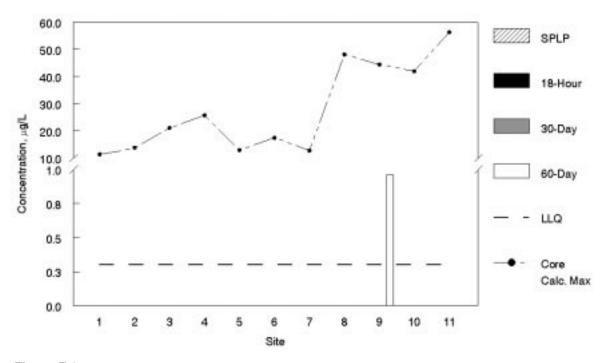


Figure F-8 Cadmium Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

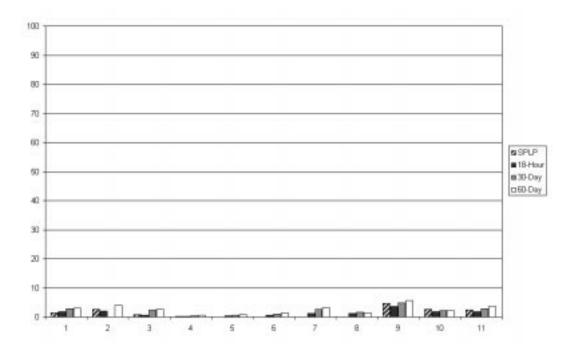


Figure F-9 Chromium Percentage of Possible Leachability

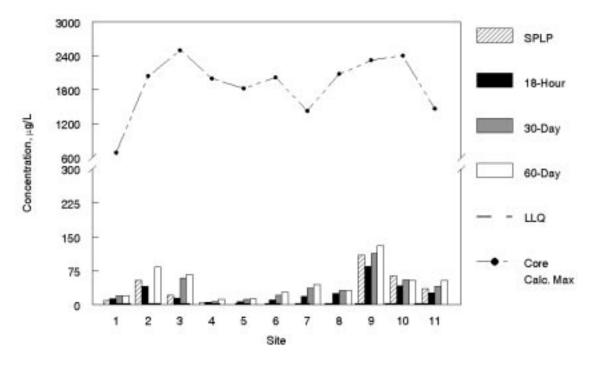


Figure F-10 Chromium Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

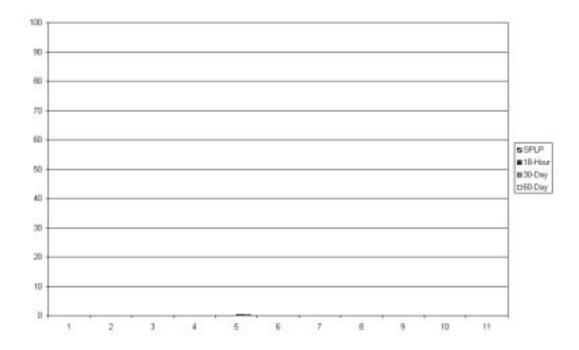


Figure F-11 Cobalt Percentage of Possible Leachability

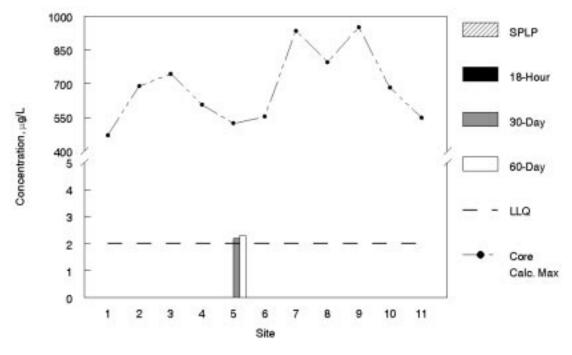


Figure F-12 Cobalt Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

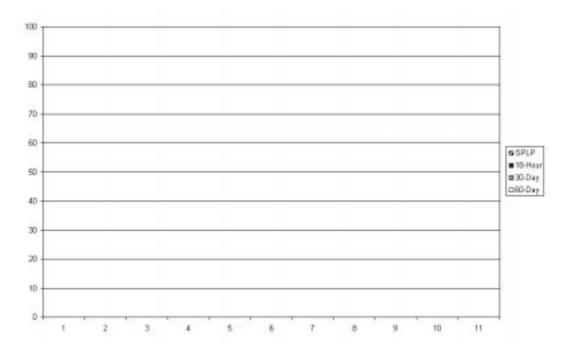


Figure F-13 Iron Percentage of Possible Leachability

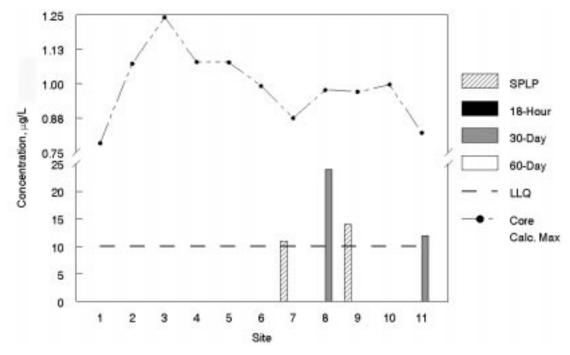


Figure F-14 Iron Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

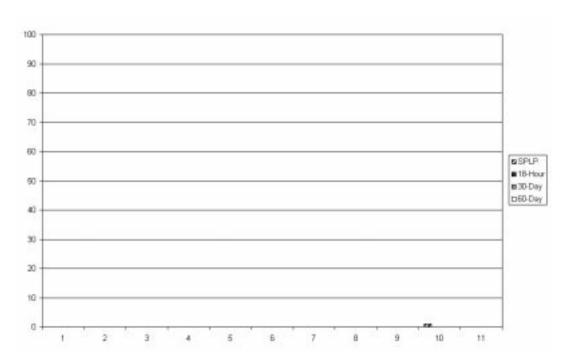


Figure F-15 Lead Percentage of Possible Leachability

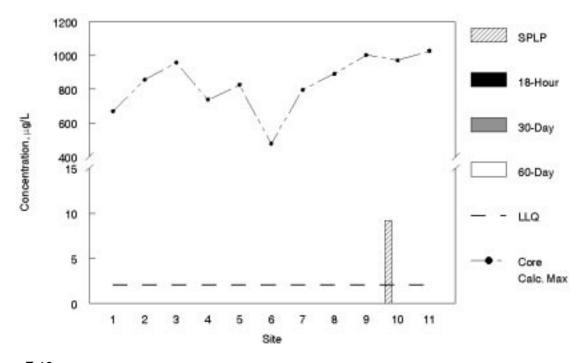


Figure F-16 Lead Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

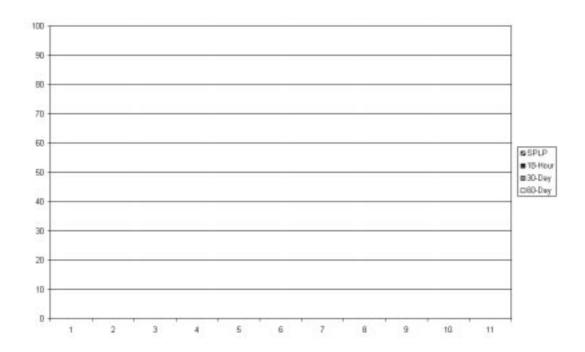


Figure F-17
Manganese Percentage of Possible Leachability

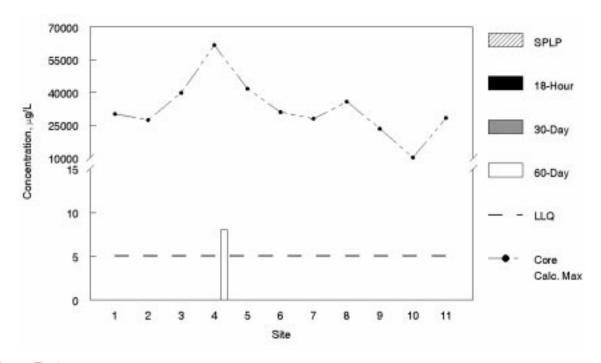


Figure F-18
Manganese Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

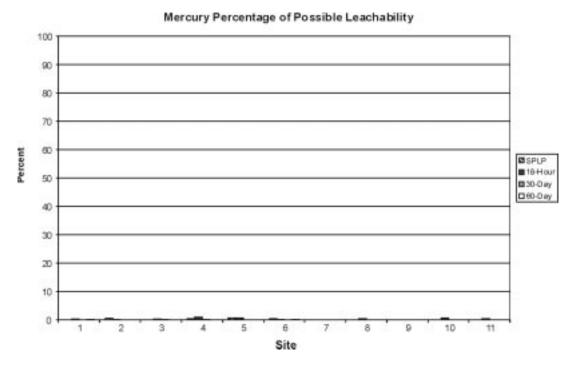


Figure F-19 Mercury Percentage of Possible Leachability

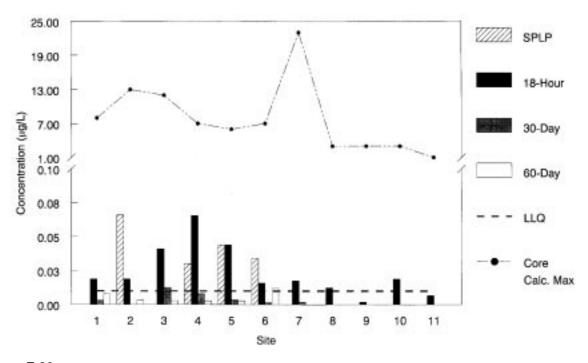


Figure F-20
Mercury Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

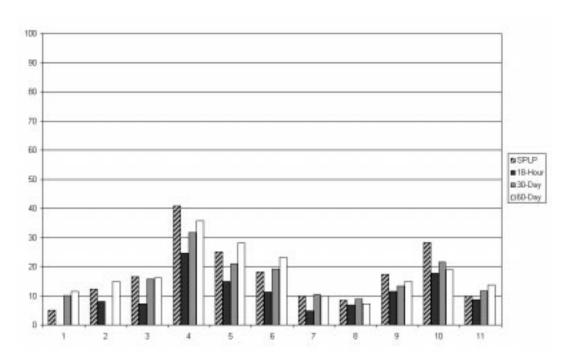


Figure F-21 Molybdenum Percentage of Possible Leachability

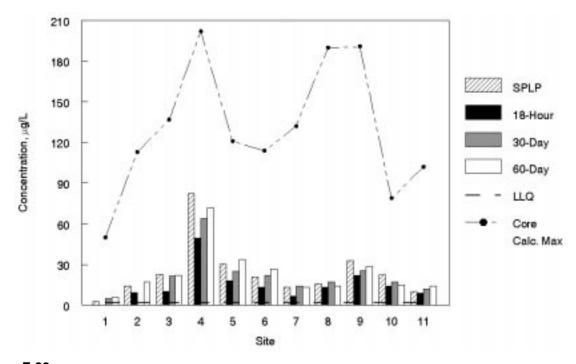


Figure F-22 Molybdenum Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

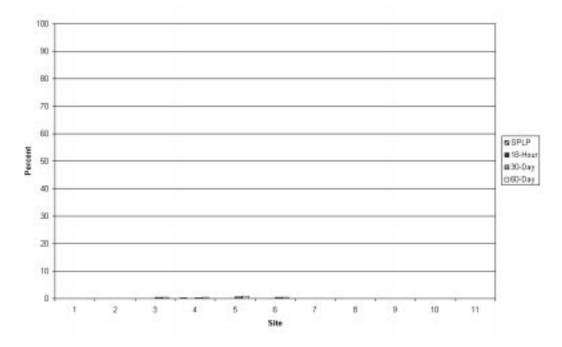


Figure F-23 Nickel Percentage of Possible Leachability

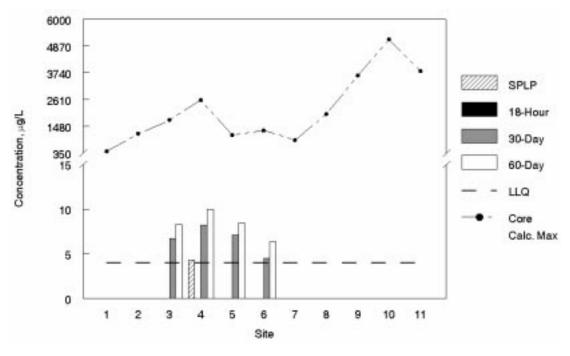


Figure F-24 Nickel Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

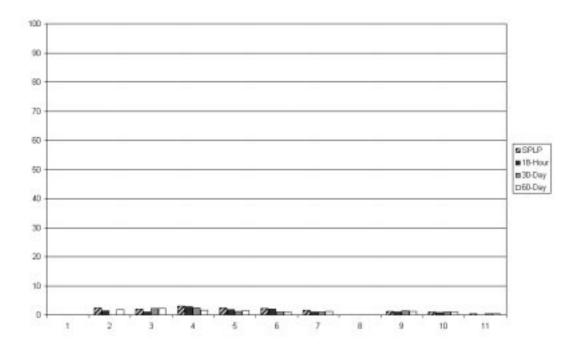


Figure F-25
Selenium Percentage of Possible Leachability

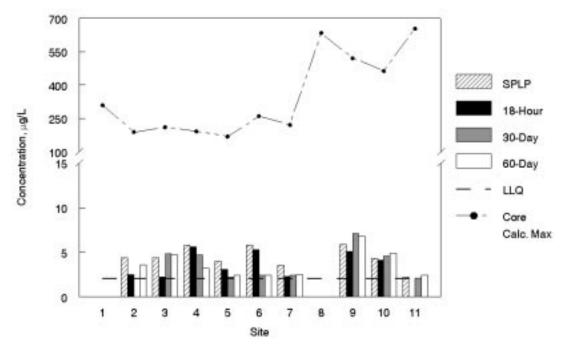


Figure F-26 Selenium Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

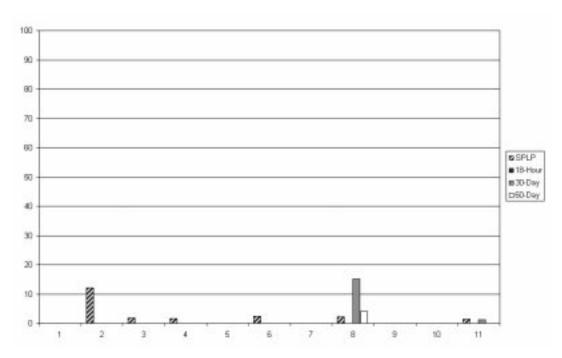


Figure F-27 Silver Percentage of Possible Leachability

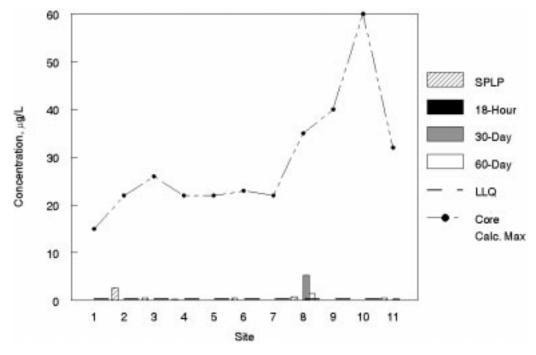


Figure F-28 Silver Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

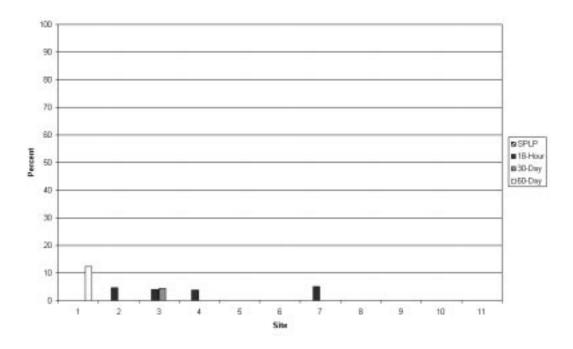


Figure F-29
Thallium Percentage of Possible Leachability

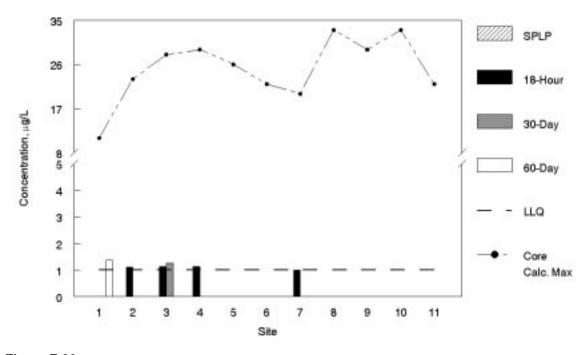


Figure F-30
Thallium Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

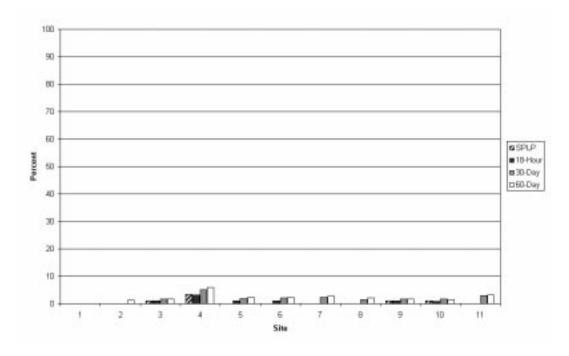


Figure F-31 Vanadium Percentage of Possible Leachability

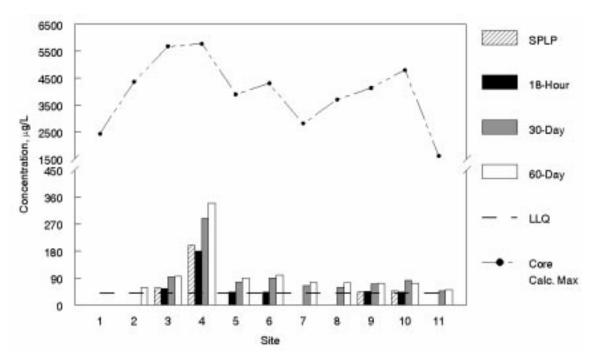


Figure F-32 Vanadium Leachate Concentrations in Soil-Stabilized Cores Plotted Against the Calculated Maximum

GAPPENDIX G – EERC: SIMULATED RAINFALL DEMONSTRATION LEACHING RESULTS

Appendix G contains tables and graphs for the simulated rainfall demonstration leaching results. The graphs are similar to those in previous appendices. Highlighted values in Tables G-1–G-3 are estimated since real concentrations are not detected in the indicated solid samples.

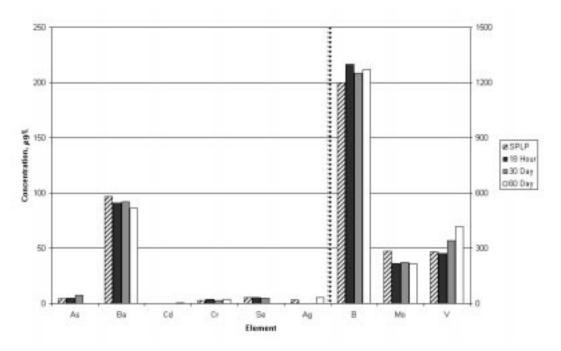


Figure G-1 Site 12a

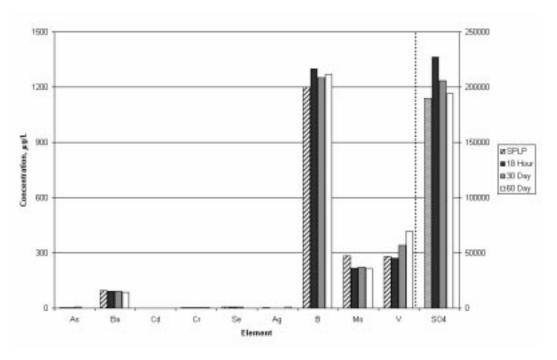


Figure G-2 Site 12a

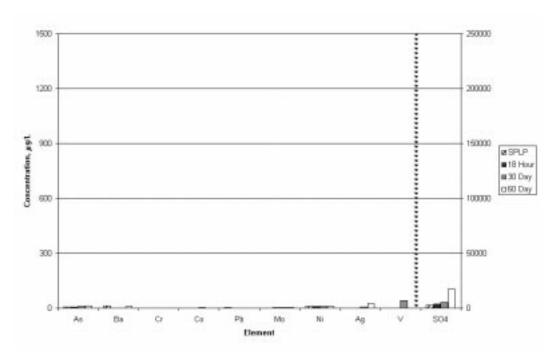


Figure G-3 Site 12b

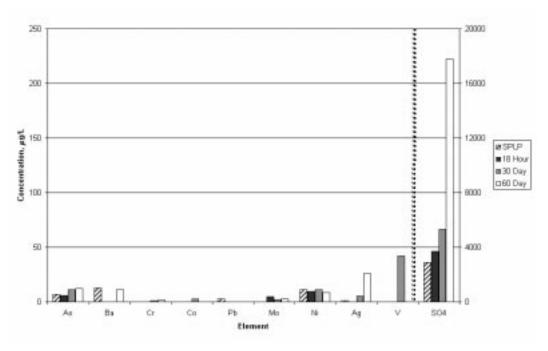


Figure G-4 Site 12b

Table G-1 Simulated Rainfall Demonstration Leaching Results

	Anti	mony	Ars	enic	Bar	ium	Bery	llium	Boro	n	Cadn	nium	Chror	nium
	12a	12b	12a	12b	12a	12b	12a	12b	12a	12b	12a	12b	12a	12b
SPLP %			1.18	2.46	0.38	0.05			11.08				0.11	
18-hour %			1.20	2.21	0.36				12.00				0.17	
30-day %			1.94	4.05	0.36				11.54				0.12	0.07
60-day %				4.41	0.34	0.04			11.73		2.47		0.17	0.08
FA or Lime Calc. Max.	330	5	1315	310	21,600	250	180	6	100,250	1900	95	3	3900	215
Soil Calc. Max.	35	35	270	270	25,700	25,700	60	60	100	100	9	9	1900	1900
Composite Calc. Max.	66.61	33.57	382	271.9	25,261	24,488	72.86	57.43	10,830.36	185.71	18.21	8.71	2114.3	1819.8
SPLP			4.5	6.7	97	13			1200				2.4	
18-hour			4.6	6.0	91				1300				3.6	
30-day			7.4	11	92		·	·	1250			·	2.6	1.3
60-day				12	86	11			1270		0.45		3.5	1.4

	Col	balt	Iro	n	Lead	k	Mang	anese	Mer	cury	Molyb	denum	Nic	kel
	12a	12b	12a	12b	12a	12b	12a	12b	12a	12b	12a	12b	12a	12b
SPLP %											46.22			0.95
18-hour %											35.36	8.16		0.81
30-day %		0.40									36.49	3.82		0.95
60-day %											35.03	4.17		0.72
FA or Lime Calc. Max.	1620	640	2,194,250	51,100	3440	20	16,050	5300	40.5	0.025	5255	10	48,950	355
Soil Calc. Max.	595	595	896,250	896,250	735	735	23,400	23,400	9.5	9.5	60	60	1200	1200
Composite Calc. Max.	704.8	597.1	1,035,321	856,005	1024.8	701	22,613	22,538	12.82	9.05	616.6	57.6	6316.1	1159.8
SPLP											285			11
18-hour											218	4.7		9.4
30-day		2.4									225	2.2		11
60-day									·		216	2.4		8.4

Table G-1 (continued)

	Sele	enium	Si	lver	Tha	llium	Vanac	lium	Z	inc	Sulf	ate
	12a	12b	12a	12b	12a	12b	12a	12b	12a	12b	12a	12b
SPLP %	2.19		12.05	4.93			2.37					
18-hour %	2.19						2.29					
30-day %	2.10			28.51			2.88	1.10				
60-day %			19.27	142.54			3.53					
FA or Lime Calc. Max.	1470	1230	93.5	3	20.5	0.25	76,850	150	8000	500		
Soil Calc. Max.	90	90	19	19	26	26	4000	4000	2850	2850		
Composite Calc. Max.	237.9	144.3	26.98	18.24	25.41	24.77	11,805	3817	3402	2738		
SPLP	5.2		3.25	0.9			280				190,000	2900
18-hour	5.2						270				227,000	3700
30-day	5			5.2			340	42			206,000	5300
60-day			5.2	26			417				194,000	17,800

Table G-2 Simulated Rainfall Demonstration Leaching Results

Site 12a	Fly Ash	Calc. Max.	Soil	Calc. Max.	Total Calc. Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
Element	μg/g	μg/L	μg/g	μg/L	μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
Sb	6.6	330	0.7	35	66.61								
As	26.3	1315	5.4	270	382.0	4.5	1.18	4.6	1.20	7.4	1.94		
Ва	432	21,600	514	25,700	25,261	97	0.38	91	0.36	92	0.36	86	0.34
Ве	3.6	180	1.2	60	72.86								
В	2005	100,250	2	100	10,830.36	1200	11.08	1300	12.00	1250	11.54	1270	11.73
Cd	1.90	95	0.18	9	18.21							0.45	2.47
Cr	78	3900	38	1900	2114.3	2.4	0.11	3.6	0.17	2.6	0.12	3.5	0.17
Co	32.4	1620	11.9	595	704.8								
Fe	43,885	2,194,250	17,925	896,250	1,035,321								
Pb	68.8	3440	14.7	735	1024.8								
Mn	321	16,050	468	23,400	22,613								
Hg	0.81	40.5	0.19	9.5	12.82								
Мо	105.1	5255	1.2	60	616.6	285	46.22	218	35.35	225	36.49	216	35.03
Ni	979	48,950	24	1200	6316.1								
Se	29.4	1470	1.8	90	237.9	5.2	2.19	5.2	2.19	5	2.10		
Ag	1.87	93.5	0.38	19	26.98	3.25	12.05					5.2	19.27
TI	0.41	20.5	0.52	26	25.41				-			-	
V	1537	76,850	80	4000	11,805	280	2.37	270	2.29	340	2.88	417	3.53
Zn	160	8000	57	2850	3402								
SO ₄ ²						190,000		227,000		206,000		194,000	

TableG-3 Simulated Rainfall Demonstration Leaching Results

Site 12b	Lime	Calc. Max.	Soil	Calc. Max.
Element	μg/g	μg/L	μg/g	μg/L
Sb	0.10	5	0.7	35
As	6.2	310	5.4	270
Ва	5	250	514	25,700
Be	0.12	6	1.2	60
В	38	1900	2	100
Cd Cr Co	0.06	3	0.18	9
Cr	4.3	215	38	1900
Co	12.8	640	11.9	595
Fe	1022	51,100	17925	896,250
Pb	0.4	20	14.7	735
Mn	106	5300	468	23,400
Hg	0.0005	0.025	0.19	9.5
Мо	0.2	10	1.2	60
Ni	7.1	355	24	1200
Se	24.6	1230	1.8	90
Ag TI	0.06	3	0.38	19
TI	0.005	0.25	0.52	26
V	3	150	80	4000
Zn	10	500	57	2850
SO ₄ ²⁻				

Total Calc. Max.	SPLP	SPLP	18 hour	18 hour	30 day	30 day	60 day	60 day
μg/L	μg/L	%	μg/L	%	μg/L	%	μg/L	%
33.57								
271.9	6.7	2.46	6	2.21	11	4.05	12	4.41
24,488	13	0.05					11	0.04
57.43								
185.71								
8.71								
1819.8					1.3	0.07	1.4	0.08
597.1					2.4	0.40		
856,005								
701.0								
22,538								
9.05								
57.6			4.7	8.16	2.2	3.82	2.4	4.17
1159.8	11	0.95	9.4	0.81	11	0.95	8.4	0.72
144.3								
18.24	0.9	4.93			5.2	28.51	26	142.56
24.77								
3817					42	1.10		
2738								
	2900		3700		5300		17,800	

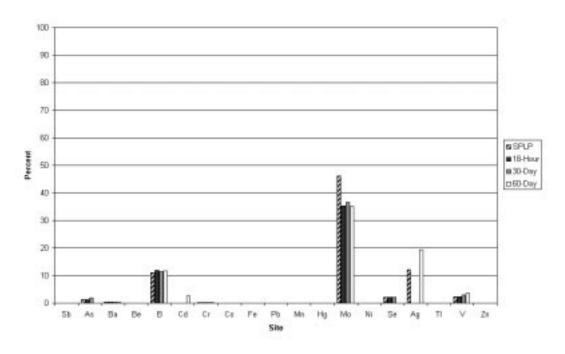


Figure G-5 Percent Leachability from Site 12a

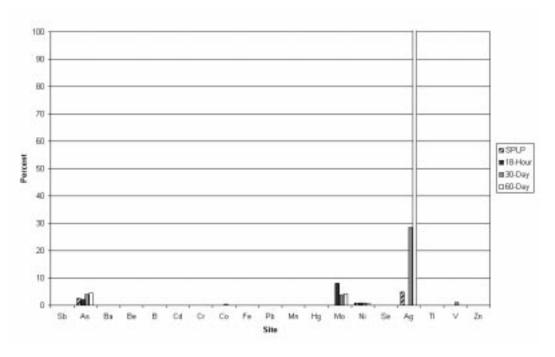


Figure G-6 Percent Leachability from Site 12b

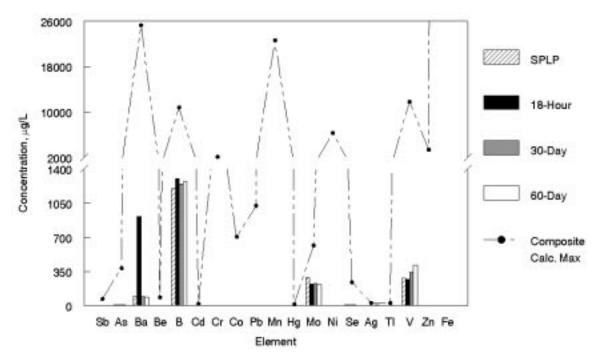


Figure G-7 Site 12a Leachate Concentrations in Fly Ash-Stabilized Soil Plotted Against the Calculated Maximum

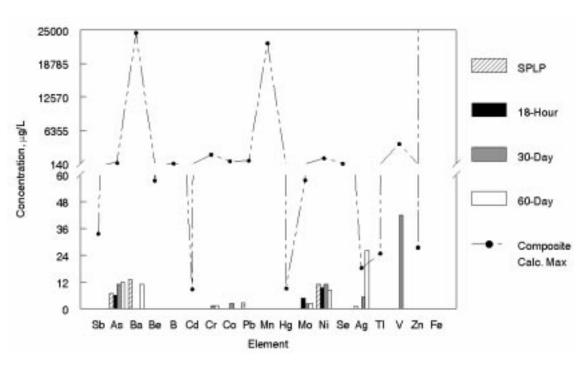


Figure G-8
Site 12b Leachate Concentrations in Lime-Stabilized Soil Plotted Against the Calculated Maximum

H APPENDIX H – UMN: SAS COMPUTER PROGRAM OUTPUT FOR SOLUBLE BORON

Title 1 'Fly Ash Runoff Comparison of the Soluble' Title 2 'Time Effect with Linear & Quadratic Regression for Run 2';

```
The PROCEDURE REG used 3 minutes 0.42 seconds.
data Soluble;
input Event mtrt $ Time rep Ec Hg Al As B Ba Be Ca Cr Cu Fe Mg Mn Mo Na Ni P S
Sb Se Si Zn;
cards;
SAS went to a new line when INPUT statement reached past the end of a line.
The data set WORK. SOLUBLE has 96 observations and 28 variables. The DATA
statement used 0.27 seconds.
data Soluble; set soluble;
if Event = 1; Timesq = Time*Time;
The data set WORK. SOLUBLE has 60 observations and 29 variables. The DATA
statement used 0.17 seconds.
proc reg data = Soluble;
     model B = Time /ssl;
      model B = Time timesq /ssl;
run;
60 observations read.
3 observations have missing values. 57 observations used in computations.
```

Output

Time Effect with Linear Quadratic Regression for Run 2

15:20 Friday, August 4, 19

Model: MODEL1

Dependent Variable: B

Analysis of Variance

Source		DF	Sum of Squares		ean are	F Value	Prob>F
Model Error C Total		1 34 35	0.65782 8.46939 9.12721	0.65 0.24		2.641	0.1134
		Root MSE Dep Mean C.V.	0.499 0.377 133.129	490 905	R-square Adj R-sq		0721 0448
Variable	DF	Paramete Estimate	er Standa:	rd T	for HO:	Prob > T	Type I SS
INTERCEP Time	1	0.585130			3.804 -1.625	0.0006 0.1134	5.059763 0.657823

Time Effect with Linear & Quadratic Regression for Run 2

15:20 Friday, August 4, 20

Model: MODEL2

Dependent Variable: B

Analysis of Variance

Source		DF	Sum of Squares	Me Squa	ean are	F Valu	e	Prob >F
Model Error C Total		2 33 35	1.14850 7.97871 9.12721	0.57		2.37	5	0.1087
		Root MSE Dep Mean C.V.	0.3	9171 7490 5825 .meter Es	R-square Adj R-sq timates		0.1258 0.0729	
Variable	DF	Parameten Estimate	Standa Error		for HO: eter = 0	Prob :	> T T	ype I SS
INTERCEP Time TimeSQ	1 1 1	1.006796 -0.021565 0.000130	0.33252 0.01293 0.00003	1088 -	3.028 1.670 1.425	0.0 0.1 0.1	043	5.059763 0.657823 0.490679

APPENDIX I – UMN: RESULTS FOR SAS COMPARISON OF TREATMENTS FOR SOLUBLE MECURY (LSD)

Title I 'Fly Ash Runoff Treatment Comparison for the Soluble'

```
data Soluble;
input event $ mtrt $ time rep Be Cr Cu Fe Hg Mn Mo Ni Se Zn;
;
cards;

NOTE: SAS went to a new line when INPUT statement reached past the end of a line.

Proc GLM data= Soluble;
Class mtrt time rep;
model Be Cr Cu Fe Hg Mn Mo Ni Se Zn= mtrt rep mtrt*rep time time*mtrt /ss3;
test h= mtrt e= mtrt*rep;

means mtrt /Isd;
run;
```

Output

Fly Ash Runoff Comparison of the Effect of Treatments on Soluble for both Runs (General Linear Models Procedure)

		Class Level Information
		Class Levels Values
MTRT	3	C Ca FA (C=control, Ca=lime, FA = flyash)
	-	00 40 50 60 00 445 400
Time	/	20 40 50 60 90 115 120
DED	4	1 0 2 4
REP	4	1 2 3 4

Number of observations in data set = 96

Group Obs Dependent Variables

1	45	Ве					
2	95	CR	CU	FE	Нg	MO	ZN
3	76	MN					
4	32	NI					
5	8	SE					

 ${\tt NOTE:}$ Variables in each group are consistent with respect to the presence or absence of missing values.

General Linear Models Procedure

T tests (LSD) for variable: HG

NOTE: This test controls the type I comparisonwise error rate not the experimentwise error rate.

Alpha= 0.05 df= 18 MSE= 0.200163 Critical Value of T= 2.10 Least Significant Difference= 0.3837

Means with the same letter are not significantly different.

T Grouping	Mean	N	MTRT
A	3.4592	12	С
В	2.8383	12	Ca
С	0.8942	12	FA

J

APPENDIX J: SAS OUTPUT SHOWING SIGNIFICANT DIFFERENCES BETWEEN THE TREATMENTS FOR SOLUBLE MERCURY

```
Data Soluble 2;
input event $ mtrt $ time rep Hg;
cards;
Proc GLM data= Soluble2;
Class mtrt time rep;
model Hg = mtrt rep mtrt*rep time time*mtrt /ss3;
test h= mtrt e= mtrt*rep;
means mtrt ;
run;
                      General Linear Models Procedure
Dependent Variable: HG
Source
              DF
                       Sum of Squares
                                       Mean Square
                                                    F Value
                                                           Pr > F
Model
              17
                        65.90938889
                                         3.87702288
                                                    19.37
                                                            0.0001
Error
               18
                        3.60293333
                                        0.20016296
Corrected Total
                          69.51232222
       R-Square
                         C.V.
                                     Root MSE
                                                    HG Mean
      0.948168
                      18.66309
                                    0.44739576
                                                   2.39722222
              DF
                        Type III SS
                                        Mean Square F Value
                                                            Pr > F
Source
MTRT
               2
                       42.97777222
                                        21.48888611 107.36
                                                            0.0001
              3
                        3.68801111
REP
                                         1.22933704
                                                     6.14
                                                           0.0046
Time*REP
                  6
                             2.38040556
                                                 0.39673426
                                                                1.98
                                                                        0.1218
Time
                  2
                            11.64942222
                                                 5.82471111
                                                               29.10
                                                                        0.0001
MTRT*Time
                   4
                                                  1.30344444
                              5.21377778
                                                                 6.51
                                                                        0.0020
Tests of Hypotheses using the Type III MS for MTRT*REP as an error term
Source
                 DF
                            Type III SS
                                               Mean Square
                                                              F Value
                                                                         Pr > F
MTRT
                   2
                           42.97777222
                                                21.48888611
                                                                54.16
                                                                        0.0001
```

K APPENDIX K – RELATIVE TOXICITY OF SOIL, SOIL–LIME, AND SOIL–FLY ASH LEACHATES

The following is an existing report from Environmental Toxicity Control Inc. prepared by Walter M. Koenst.

RELATIVE TOXICITY OF SOIL, SOIL/LIME, AND SOIL/FLY ASH LEACHATES

Report Date: July 28, 2000

Project No. 99047

Prepared for:

NORTHERN STATES POWER COMPANY 512 NICOLLET MALL MINNEAPOLIS, MN 55401





PROJECT: RELATIVE TOXICITY OF SOIL, SOIL/LIME, AND SOIL/FLY ASH LEACHATES

PROJECT NUMBER: 99047

INTRODUCTION:

This study was conducted to investigate the relative toxicity of soils stabilized with lime and with coal fly ash.

This study is part of a soil stabilization study conducted by the University of Minnesota for Northern States Power Company to determine water quality of runoff from the stabilized soils. Samples were provided by the University of Minnesota from their research pads and consisted of soil, soil/lime mixture and a soil/fly ash mixture. The soil/lime mixture consisted of 5% hydrated lime and the soil/fly ash mixture consisted of 12% ash by dry weight. Leachates were prepared from the soil samples and tested for toxicity.

Compacted soil without stabilizing agents was used as the control. The purpose of the study was to determine if ash stabilized soil is more toxic, that is, exhibits a greater biological risk, than the lime stabilized soil. Lime is the widely excepted soil stabilizer used for road construction; however, the biological risk of this material has not been investigated. Therefore, the relative toxicity of lime as a stabilizing agent compared to fly ash as a stabilizing agent needs to be defined to evaluate if fly ash stabilization poses greater risk to the environment.

The chemicals in the stabilizing agents become bioavailable as a leachate after contact with rainfall, surface water or groundwater. Therefore, the toxicity testing reported herein was performed on leachates from the materials in question. Side-by-side bioassays can compare the relative toxicity of the leachates and determine if the ash addition increases, decreases, or does not alter the environmental risk of the stabilizing agent.

The following tests were performed on the three leachates:

- 1. 7-Day Fathead Minnow, *Pimephales promelas*, chronic test measuring survival and growth,
- 2. 7-Day invertebrate, Ceriodaphnia dubia, chronic test, measuring survival and reproduction,
- 3. 4-Day Alga, Selenastrum capricornutum, growth test,
- 4. 14-Day earthworm, Eisenia foetida, chronic test, measuring survival and weight loss, and
- 5. 4-Day frog teratogenesis assay, using *Xenopus laevis*.

This study was started on November 6, 1999 with the start of the 7-day leachate preparation.

SUMMARY:

Leachates from soil, soil/lime and soil/fly ash were analyzed for toxicity to representative species of fish (*Pimephales promelas*), aquatic invertebrates (*Ceriodaphnia dubia*), Algae (*Selenastrum capricornutum*), amphibians (*Xenopus laevis*), and terrestrial Annelids (*Eisenia foetida*), Table 1.

Both soil/lime and soil/fly ash leachates exhibited toxicity to all tested species except the earthworm, *Eisenia foetida*. The soil/lime leachate was more toxic than the soil/fly ash leachate to fathead minnows (Pimephales promelas) and algae, *Selenastrum capricornutum*. The soil/fly ash leachate was slightly more toxic than the soil/lime leachate to *Ceriodaphnia dubia*. Toxicity of the two leachates to frog (Xenopus laevis) embryos was similar.

MATERIALS AND METHODS:

Testing Methods

Bioassay methodologies used in this study were as follows:

- 1. Fathead Minnow, *Pimephales promelas*, Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, EPA/600/4-91/002, July, 1994, Method 1000.0.
- 2. Water Flea, *Ceriodaphnia dubia*, Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, EPA/600/4-91/002, July, 1994, Method 1002.0.
- 3. Algae, *Selenastrum capricornutum*, Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, EPA/600/4-91/002, July, 1994, Method 1003.0.
- 4. Frog embryo, *Xenopus laevis*, Standard guide for Conducting the Frog Embryo Teratogenesis Assay-Xenopus (FETAX). ASTM E 1439, American Society for Testing and Materials.
- 5. Earthworm, *Eisenia foetida*, Standard Guide for Conducting a Laboratory Soil Toxicity Test with Lumbricid Earthworm *Eisenia Foetida*. ASTM E 1676, American Society for Testing and Materials.

Test Species

Ceriodaphnia dubia used for testing were acquired from Environmental Toxicity Control's (ETC) in-house cultures and were <24 hours old and all within 8 hours of age at test initiation.

Pimephales promelas were obtained from ETC's in-house cultures and were < 24 hours old at test initiation.

Selenastrum capricornutum were obtained from ETC's in-house cultures. The cells were cultured using the Woods Hole medium, and test cells used to inoculate the test dilutions were taken from a stock culture that was started seven days prior to test initiation. The Woods Hole medium nutrient list is shown in Table 2.

Eisenia foetida were obtained from the Carolina Biological Supply Company, Burlington, North Carolina. The earthworms were received on November 30, 1999, and were placed in 2 culture containers each consisting of 5 kg artificial soil (70% silica sand, 20% Kaolin clay, 10% sphagnum peat moss), 1.8 L laboratory water, and 1.5 kg composted cow manure.

Adult frogs (*Xenopus laevis*) were obtained from ETC's in-house culture. The original stock were acquired from the Carolina Biological Supply Company, Burlington, North Carolina on September 3, 1998. Males and females were kept separately in 20 L culture tanks containing laboratory water at a depth of 10 cm. The frogs were fed ground beef liver fortified with the following vitamins: Vitamin A, 1500 IU/ml; Vitamin D, 400 IU/ml; Vitamin E, 5 IU/ml; Vitamin C, 35 mg/ml; Thiamine, 0.5 mg/ml; Riboflavin, 0.6 mg/ml; Niacin, 8 mg/ml; Vitamin B6, 0.4 mg/ml; and, Vitamin B12, 2μ g/ml. The liquid multiple vitamins were mixed into the ground liver at a rate of 0.05 ml/5 g.

Test Materials

The three test materials were:

- 1. Silty clay soil originally collected from a construction site,
- 2. A 5% mixture (by dry weight) of hydrated lime (Ca(OH)₂) and the soil (material 1 above), and
- 3. A 12% mixture (by dry weight) of coal ash and soil (material 1 above). The coal ash consisted of fly ash from NSP's Allen S. King Plant. This fly ash is from the cyclone boiler burning a blend of north and south Powder River basin coals plus about 10% (by weight) petroleum coke.

The fly ash is similar to an ASTM C-618 "Class C" ash in that it is self-cementing and it performs well for soil stabilization uses. However, co-firing low-sulfur, subbituminous coals with petroleum coke increases the sulfur, nickel, molybdenum, and vanadium levels in the fly ash above what would otherwise be expected. The co-firing conditions and/or the relatively high carbon levels in the fly ash may also be factors in the relatively higher level of mercury than is otherwise expected in typical subbituminous coal fly ash. The elevated levels of these trace elements was the primary "environmental" reason this fly ash was chosen for the biotoxicity and run-off demonstrations.

Leachate Preparation

Leachates were prepared following procedures outlined in <u>Ecological Evaluation of Proposed Discharge of Dredged Material in Ocean Water</u>, EPA/USACE, 1977. One part of test material was leached with 4 parts water on a volume basis. For each leachate preparation, 15 L of test material was combined with 60 L of test dilution water in a 200 L Nalgene cylindrical tank and leached for 7 days. All three leachates were stirred daily for 10 minutes with a mechanical stirrer. Daily measurements of temperature, dissolved oxygen, pH, and conductivity were made prior to stirring. Upon completion of the 7 day extraction, 40 L of leachate was siphoned from each tank and stored at 4°C until testing.

The soil/lime and soil/fly ash leachates were basic (pH >9.0) and were neutralized with 2N hydrochloric acid to a pH of 7.50 to 7.60 prior to testing. Only portions used for testing and subsequent daily renewals were neutralized each day. A sample of each leachate was sent to

Northern States Power Company's chemistry laboratory for analysis. The samples were analyzed both before and after neutralization.

Dilutions

Dilution water used for leaching and testing was a soft reconstituted water prepared to a Total Alkalinity of 30-35 mg/L as CaCO3. Chemical constituents for the preparation of soft reconstituted water are shown on Table 3.

Toxicity test treatments consisted of a dilution water control and leachate concentrations of 6.3, 12.5, 25, 50, and 100%. Dilutions were prepared daily for renewals. The *Selenastrum capricornutum* test required the addition of nutrients to the test treatment. Woods Hole nutrients (except stock 6, EDTA solution) were added to each of the test concentrations and control at the start of the test.

Toxicity Tests

Pimephales promelas

The test was conducted in triplicate in 500 ml beakers each containing 250 ml of test water and 10 fish. The beakers were placed in a temperature controlled water bath and were covered with a sheet of glass. Test solutions were renewed each day and routine chemistries were performed on both the "old" water and the renewal water. Tests were conducted at 25 ± 1 °C with a 16:8 h light and dark photoperiod. Fish were fed 0.15 ml of newly hatched brine shrimp nauplii twice per day at 6 hour intervals. Brine shrimp were concentrated so that fish were fed an excess of nauplii. Fish larvae were not fed on the final day of testing. At the end of the 7-day testing period, surviving fish were removed from the test beakers, rinsed with clean deionized water, placed in pre-weighed aluminum pans, and dried at 100 °C in a drying oven for four hours, cooled and weighed.

Ceriodaphnia dubia

Ceriodaphnia tests were conducted in 30 ml plastic cups each containing 15 ml of test water and one test organism. The cups were placed in a Plexiglas board that held a total of 60 cups, 10 cups for each treatment and a control. The board was placed in a temperature controlled water bath and covered with a sheet of glass. Test organisms were transferred each day to newly prepared solutions on a new board and the number of young produced by each test organism were counted. Test organisms were fed immediately after each renewal with 0.1 ml YCT and 0.1 ml of an algal suspension containing 3.5×10^7 cells of Selenastrum capricornutum. Routine chemistries were performed on both "old" and renewal dilutions.

Selenastrum capricornutum

The *Selenastrum* tests were conducted in triplicate in 250 ml Erlenmeyer flasks. Test treatments consisted of the 6.3% - 100% leachate treatments and a control nutrified with media. The media used in the test treatments consisted of Woods Hole media without Stock 6 (see Table 2). One liter of each concentration was prepared prior to nutrient addition. The nutrients were added at the same concentration as in the culture media. Each replicate flask received 150 ml of leachate treatment and was inoculated with 7-day-old algae cells to provide an initial cell density of 1.0 x 10⁶ cells/ml. Flasks were stoppered with a foam plug to allow for gas exchange. Test flasks were placed in an

incubator at 25 ± 1 °C with continuous light and were manually shaken twice per day during the test. After the 96-hour exposure period cells were counted from each test vessel using a hemacytometer.

Eisenia foetida

The *Eisenia* test was conducted in triplicate in 350 ml plastic cups containing approximately 300 ml of test soil. Test soils were hydrated with test leachate concentrations and allowed to equilibrate overnight. The test soil was prepared to a 25% moisture content by adding 214 ml of each leachate concentration or control to 600 gm of artificial soil medium. For each leachate concentration, moisture content was measured at the beginning and soil pH was measured at the beginning and end of the test. Tests were conducted in an incubator at 20 + 1°C and 24 hours continuous light.

Test earthworms were removed from culture media and kept for a 24-hour period in moist paper towels to purge their stomach contents. At test initiation, ten earthworms were randomly distributed into 30 ml plastic cups, weighed, and then placed in the test soil chambers. Weights and survival counts were performed on days 7 and 14.

Xenopus laevis

The frog test consisted of using separate egg clutches from three pairs of frogs. Three separate pairs of frogs were induced into mating. The pairs were kept in separate breeding containers and egg clutches were harvested and kept separate throughout the test since embryos from a mating pair may develop poorly after acceptable development was observed at the time of test initiation. The frogs were induced into mating by injection of human chorionic gonadotropin 14 to 16 hours prior to test initiation. The adult frogs during mating and their resulting egg clutches were kept in FETAX solution water prior to testing. Formulation for FETAX solution is shown in Table 4. The FETAX solution was also used as a method control.

Frog embryos were dejellied with 2% w/v L-cysteine solution prepared in FETAX solution and adjusted to pH 8.1 with 1N NaOH. Normally cleaving embryos at stage 8 (Midblastula) to stage 11 (Early Gastrula) were used to start the test. Each of the three clutches of eggs was treated as a separate test. The embryos were replicated twice for each leachate concentration and four times for each of the controls, dilution water and FETAX solution. Test chambers consisted of covered 55 mm polystyrene Petri dishes each containing 10 ml test solution and 25 embryos. Test solutions consisted of leachate diluted with soft reconstituted water at concentrations of 6.3% to 100%. Test solutions were renewed each day and survival counts were made at renewals. At the end of the 96-h test period, surviving embryos were preserved in 3% formalin and later inspected for abnormalities.

Data Analysis

Acute toxicity data (LC50) were analyzed using the Trimmed Spearman-Karber Test. Chronic toxicity was analyzed for the NOEC and the IC25. The NOEC was determined using Dunnetts Test. And IC25s and IC50s were calculated using EPA's "A Linear Interpolation Method for Sublethal Toxicity: The Inhibition Concentration (ICp) Approach, Version 2.0. If a difference in end point was noted, then a t-test was applied at individual treatment concentrations for comparison.

RESULTS AND DISCUSSION:

Chemical Analysis

Chemical analysis results are shown in Table 5 (pre neutralization) and Table 6 (post neutralization). No significant changes in chemistries were noted due to neutralization with hydrochloric acid.

The chemistry results were compared to the state of Minnesota's end-of-pipe toxicity-based standards, also known as final acute values (FAVs), and ambient standards based on chronic aquatic toxicity or based on drinking water or irrigation needs where established for Class 1A/2Bd/4A waters (Table 7) as found in Minnesota Rules 7050. For hardness dependent parameters, a total hardness of 100 mg/l was utilized to derive a conservatively low standard for state waters. Class 2Bd waters are protected for cool and warm water sport or commercial fish and associated aquatic life and are also protected for aquatic recreation including bathing and as a source of drinking water. Class 4A waters are protected for their use for irrigation without any significant damage or adverse effects upon any crops or vegetation usually grown in the waters or area. Some chemical constituents of the leachates exceeded standards, possibly an indication of their contribution to the toxicities exhibited during the testing. However, results from only two parameters, aluminum and copper, exceeded FAVs and only in soil/lime leachate samples. The copper results were above the FAV for all soil/lime leachate samples, and the aluminum result was above the FAV for only the November 1999 soil/lime leachate sample. The soil/fly ash leachate chromium results were near or above the FAV for chromium +6 ion, but the results were not speciated to the chromium ions. As a reference, the results were well below the FAV for the chromium +3 ion. Regarding ambient standards, results from the soil leachate sample from only November 1999 exceeded ambient standards for aluminum and iron. Results from the soil/lime leachate exceeded ambient standards for ammonia, arsenic, and specific conductance in all samples and exceeded ambient standards for fluoride, iron, and mercury only in the November 1999 samples. Results from the soil/fly ash leachate exceeded ambient standards for ammonia, arsenic, boron, copper, selenium, specific conductance, and sulfate in all samples; exceeded the aluminum ambient standard only in the November 1999 sample; and exceeded the cadmium ambient standard only in the April 2000 sample. The boron and specific conductance standards are based on irrigation needs as defined by the beneficial use designation of Class 4A waters. Although a boron FAV is not established in Minnesota Rules 7050, the soil/fly ash leachate boron results were all below an FAV derived from available toxicity data to provide a basis for performance measures in a solid waste permit for an NSP ash site. The iron and fluoride references are based on secondary drinking water standards. Additionally the chronic toxicity-based ammonia standard of 0.040 mg/l used as a reference is for un-ionized ammonia, and the analysis was for total ammonia. The un-ionized ammonia concentrations are dependent on temperature and pH and range from .026% to 32.6% of the total ammonia at a temperature range of 15 to 26°C and a pH range of 6.0 to 8.9.

Bioassay Results

Pimephales promelas

Toxicity test results are shown in Table 8 and Figures 1 and 2; and test conditions are summarized in Table 9.

Fathead minnow survival was reduced at the 100% concentration for both soil/lime and soil/fly ash leachates after seven days of exposure. However, no 96-hour LC50 was determined since survival was above 50% in both leachate tests at the 100% leachate concentration. Survival after seven days was reduced to 53% in the soil/lime leachate and 47% in the soil/fly ash leachate. The No-Observable-Effect-Concentration (NOEC) for survival was determined to be 50% for both soil/lime and soil/fly ash leachates. No differences were noted between the soil leachate concentrations and the control.

Growth of fish exposed to the soil/lime and soil/fly ash leachates was significantly reduced when compared to the control. The soil/lime leachate appeared to be more toxic than the soil/fly ash leachate. The NOEC for fathead minnow growth was 25% soil/lime leachate and 50% soil/fly ash leachate. The 25% Inhibition Concentration (IC25), the calculated concentration where the measured effect is reduced by 25% from the control, for minnow growth was determined to be 20.4% soil/lime leachate and 75.4% soil/fly ash leachate.

Ceriodaphnia dubia

Toxicity test results are shown in Table 10 and Figures 3 and 4; and test conditions are summarized in Table 11.

Ceriodaphnia dubia survival was not inhibited in the soil and soil/lime leachates. However, survival was significantly reduced over the 7-day test period in the 100% and 50% soil/fly ash leachate. No 48-hour LC50 was calculated since most mortality occurred later in the test period. The NOEC for survival after a 7-day exposure was 100% for the soil/lime leachate and 25% for the soil/fly ash leachate.

Young production was significantly reduced in both the soil/lime and soil/fly ash leachates. A reduction in the number of young produced occurred in the 25%, 50% and 100% leachate concentrations for both the soil/lime and soil/fly ash leachates. The decrease in the number of young in the soil/lime and soil/fly ash leachates was similar. The IC25 for the soil/lime and soil/fly ash leachates was 19.2% and 22.6%, respectively. The NOEC for young production was 12.5% for both leachates.

The soil leachate appeared to enhance *Ceriodaphnia* reproduction when compared to the soft reconstituted water control. The number of young increased with an increase in soil leachate concentration.

Selenastrum capricornutum

Toxicity test results are shown in Table 12 and Figure 5; and test conditions are summarized in Table 13.

Cell density was significantly reduced in all soil/lime leachate concentrations from 6.3% to 100%. The NOEC for the soil/lime leachate was < 6.3% and the IC50, the 50% inhibition concentration or the concentration reducing cell density to 50% of the control density, was determined to be 21.7% leachate. The soil/fly ash leachate showed no effect on algal cell growth when compared to the soft water control. Cell density increased in the soil only leachate.

Eisenia foetida

Toxicity test results are shown in Table 14 and Figures 6 and 7; and test conditions are summarized in Tables 15 and 16.

The leachates had no significant effect on worm survival in a 14 day test. Survival at the 100% leachate concentrations was not significantly different from the soft reconstituted water control, nor was it different from the soil leachate survival rates. In addition, weight loss of *Eisenia foetida* was not significantly different from the control group in both leachate tests. The NOEC was 100% for both soil/lime leachate and soil/fly ash leachate.

Soil pH was measured in all leachate treatments and in the control at the beginning and end of the test (Table 16). The pH was similar between treatments and showed no significant change at the end of the 14-day test period.

Xenopus laevis

Toxicity test results are shown in Table 17 and Figure 8; and test conditions are summarized in Table 18.

Test results were based on embryos from two clutches of eggs since one of the three initial egg clutches showed poor embryo development in the control and according to standard test procedures was discarded after 24 hours. Survival was reduced in the 100% concentration for both the soil/lime leachate and soil/fly ash leachate. No effect on survival was observed at leachate concentrations of 50%. The NOEC for survival was determined to be 50% soil/lime leachate and 50% soil/fly ash leachate. The 96-hour LC50s were 70.4% soil/lime leachate and 76.8% soil/fly ash leachate for the egg clutch from the first mating pair, and 69.7% soil/lime leachate and 78.8% soil/fly ash leachate for the egg clutch from the second mating pair.

The leachates showed little effect on abnormality formation in the surviving embryos in concentrations of 50% and less. All survivors in the 100% concentrations of both the soil/lime leachate and soil/fly ash leachate were abnormally developed.

CONCLUSIONS:

No detrimental effects were observed in the tests with soil only leachates for any species. However, both soil/lime and soil/fly ash leachates exhibit some toxicity to all the test organisms except the earthworm, *Eisenia foetida*. All aquatic toxicity tests exhibited measurable responses from both leachates. However, when comparing one leachate to the other, slight differences were observed. Some tests showed soil/lime leachate to be less toxic, while others showed soil/fly ash leachate to be less toxic. And some tests showed no difference between the two leachates.

Testing on the fathead minnow (*Pimephales promelas*) showed a higher NOEC and IC25 for growth in the soil/fly ash leachate than in the soil/lime leachate.

The water flea (*Ceriodaphnia dubia*) test showed a lower NOEC for survival in the soil/fly ash leachate. However, there was no difference between the two leachates in the NOEC and IC25 for reproduction.

The algae (*Selenastrum capricornutum*) test showed a lower cell density in the soil/lime leachate while no detrimental effects were observed in the soil/fly ash leachate.

The frog (*Xenopus laevis*) test showed no significant differences in the 96-hour LC50s and the NOEC between the two leachates.

QUALITY ASSURANCE AND QUALITY CONTROL:

Satisfactory laboratory performance on an ongoing basis is demonstrated by conducting acceptable toxicity tests with a reference toxicant. Reference tests were performed for all test species used in this study. Test methods and procedures are documented in ETC's Standard Operating Procedures (SOPs). Test and analysis protocols are reviewed by ETC's Quality Assurance/Quality Control Officer. Procedures are documented and followed as written. Any deviation from a QA/QC procedure is documented and kept in the project file. Additionally, the laboratory is an active participant in EPA's NPDES DMR QA Studies.

This Report Has Been

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APPENDIX A

TABLES

Table 1. Summary of Results of Toxicity Tests Performed on the Soil, Soil/Lime and Soil/Ash Leachates.

		% Leachate	
Test Species and Endpoint	Soil	Soil/Lime	Soil/Fly Ash
Fathead Minnow (Pimephales pro	melas)		
96-hr LC50	>100%	>100%	>100%
NOEC Growth	100%	25%	50%
NOEC Survival	100%	50%	50%
IC25 Growth	>100%	20.4%	75.4%
Water Flea (Ceriodaphnia dubia)			
48-hr LC50	>100%	>100%	>100%
NOEC Reproduction	100%	12.5%	12.5%
NOEC Survival	100%	100%	25%
IC25 Reproduction	>100%	19.2%	22.6%
Algae (Selenastrum capricornutum	ı)		
IC50	>100%	21.7%	>100%
NOEC Growth	100%	<6.3%	100%
Earthworm (Eisenia foetida)			
NOEC Survival	100%	100%	100%
NOEC Weight Loss	100%	100%	100%
LC50	>100%	>100%	>100%
Frog (Xenopus laevis)			
96-hr LC50	>100%	70.1%	77.8%
NOEC Survival	100%	50%	50%
NOEC Abnormalities	100%	50%	50%

NOEC = No Observable Effect Concentration

LC50 = Median Lethal Concentration, Calculated Concentration that is Lethal to 50% of the Test Organisms

 $IC50 = Median\ Inhibition\ Concentration, Calculated\ Concentration\ where\ the\ Measured\ Effect\ (Cell\ Growth)\ was\ 50\%$ of the Control\ Group

IC25=25% Inhibition Concentration, Calculated Concentration where the Measured Effect was 25% less than the Control Group

 Table 2.
 Nutrient Composition Used in Woods Hole Media.

Stock Number	Compound	g/L
1	$CaCl_2$	36.76
	NaNO ₃	80.02
2	$MgSO_4 \bullet 7 H_2O$	36.97
3	NaHCO ₃	12.60
4	K_2HPO_4	8.71
5	$Na_2SiO_3 \bullet 9 H_2O$	28.42
6	Na_2EDTA	4.36
	CuSO ₄ • 5 H ₂ O	0.01
	CoCl ₂ • 6 H ₂ O	0.01
	$ZnSO_4 \bullet 7 H_2O$	0.022
	$MnCl_2 \bullet 4 H_2O$	0.18
	$NaMoO_4 \bullet 2 H_2O$	0.006
	H_3BO_3	1.0
7	FeCl ₂ • 6 H ₂ O	3.15

1 ml of stock Nos. 1, 2, 3, 4, 6 and 2 ml of stock No. 7 per liter of media.

¹ ml of stock No.5 per liter of media.

Table 3. Reagent Composition of Soft Reconstituted Water Used as Dilution Water in This Study.

Reagents Added to Dei	ionized Water	
Reagent		mg/L
NaHCO ₃		48.0
CaSO ₄ •2H ₂ 0		30.0
MgSO ₄		30.0
KCl		2.0
	Final Wat	er Quality
	рН	7.2 - 7.6
	Hardness	40 - 48
	Alkalinity	30 - 35

 Table 4.
 Nutrient Composition of FETAX Water Used in the Frog Test.

Reagent	mg/L
NaCl	625
NaHCO ₃	96
KCl	30
$CaCl_2$	15
CaSo₄·2H₂O	60
${ m MgSO}_4$	75

Table 5. Chemical Analysis of Soil, Soil/Lime, and Soil/Fly Ash Leachates Before Neutralization With 2N HCl.

Sample Description			Soil	Soil/Lime	Soil/Ash
Sample 2 escription			Leachate	Leachate	Leachate
Date Sampled			11/18/99	11/18/99	11/18/99
Date Sampred			11,10,77	11,10,75	11,10,77
Alkalinity	EPA 310.1	mg/L CaCO3	136	573	70
Aluminum	EPA 200.7	μg/L Al	506	2921	537
Ammonia	Orion probe	mg/L N	-0.03	2.87	0.56
Antimony	EPA 200.8	μg/L Sb	0.23	0.76	1.37
Arsenic	EPA 200.8	μg/L As	1	5	12
Barium	EPA 200.7	μg/L Ba	55	55	261
Beryllium	EPA 200.8	μg/L Be	-0.1	-0.1	-0.1
BOD	EPA 405.1	mg/L O2	4	4	4
Boron	EPA 200.7	μg/L B	35	69	2578
Cadmium	EPA 200.8	μg/L Cd	-0.06	0.06	0.09
Calcium	EPA 200.7	mg/L Ca	44.7	229.4	244.9
Chloride	EPA 300.0	mg/L Cl	3	4	2
Chromium	EPA 200.8	μg/L Cr	1.2	10.1	36.1
Cobalt	EPA 200.8	μg/L Co	0.32	2.69	0.83
COD	Hach ampule	mg/L O2	13	83	15
Copper	EPA 200.8	μg/L Cu	5.7	70.9	21.4
Fluoride	EPA 300.0	mg/L F	0.6	3.1	0.8
Hardness, Total	EPA 200.7	mg/L CaCO3	164	575	613
Iron	EPA 200.7	μg/L Fe	483	805	99
Lead	EPA 200.8	μg/L Pb	0.40	0.91	0.34
Magnesium	EPA 200.7	mg/L Mg	12.7	0.6	0.4
Manganese	EPA 200.7	μg/L Mn	6	12	-1
Mercury	EPA 200.8	μ g/L Hg	-0.01	0.04	0.32
Molybdenum	EPA 200.8	μg/L Mo	5	15	1430
Nickel	EPA 200.7	μ g/L Ni	5.6	57.5	17.1
Nitrate+Nitrite	EPA 353.2	mg/L N	0.34	0.32	0.30
pН	EPA 150.1		8.00	11.98	10.20
Phosphorous, total	EPA 365.3	mg/L P	0.11	0.09	0.13
Potassium	EPA 200.7	mg/L K	1.1	1.5	6.3
Selenium	EPA 200.8	μ g/L Se	1	4	26
Silver	EPA 200.8	μ g/L Ag	-0.1	-0.1	-0.1
Sodium	EPA 200.7	mg/L Na	12.6	11.8	133.2
Solids, Total Suspended	EPA 160.2	mg/L	2	25	-1
Specific Conductance	EPA 120.1	μmhos/cm@25C	359	2350	1523
Sulfate	EPA 300.0	mg/L SO4	38	25	716
Thallium	EPA 200.8	μ g/L Tl	0.04	0.02	-0.01
Tin	EPA 200.7	μg/L Sn	-30	-30	88
Titanium	EPA 200.7	μ g/L Ti	7	10	3
TOC	EPA 415.1	mg/L C	7.9	27.9	7.8
Zinc	EPA 200.8	μg/L Zn	4	5	6

Negative values indicate None Detected and the absolute value is the Method Detection Limit.

Table 6. Chemical Analysis of Soil, Soil/Lime, and Soil/Fly Ash Leachates After Neutralization with 2N HCl.

Sample Description			Soil	Soil/Lime	Soil/Lime	Soil/Ash	Soil/Ash
			Leachate	Leachate	Leachate	Leachate	Leachate
					Neutralized		Neutralized
Date Sampled			4/18/00	4/18/00	4/18/00	4/18/00	4/18/00
•							
Alkalinity	EPA 310.1	mg/L CaCO3	144	509	34	46	16
Aluminum	EPA 200.7	mg/L Al	-0.01	0.81	0.65	0.15	0.11
Ammonia	Orion probe	mg/L N	-0.03	2.98	2.95	0.64	0.63
Antimony	EPA 200.8	μg/L Sb	0.23	0.67	0.63	1.19	1.27
Arsenic	EPA 200.8	μ g/L As	-1	5	5	9	9
Barium	EPA 200.7	mg/L Ba	0.045	0.049	0.049	0.179	0.177
Beryllium	EPA 200.7	mg/L Be	-0.001	-0.001	-0.001	-0.001	-0.001
Boron	EPA 200.7	mg/L B	0.06	0.07	0.07	2.30	2.45
Cadmium	EPA 200.8	μg/L Cd	-0.1	-0.1	-0.1	1.9	2.0
Calcium	EPA 200.7	mg/L Ca	45.0	232	227	234	226
Chloride	EPA 325.2	mg/L Cl	6	6	356	6	21
Chromium	EPA 200.8	μg/L Cr	0.3	9.8	9.3	31.1	34.4
Cobalt	EPA 200.8	μg/L Co	0.19	2.28	2.24	0.46	0.50
COD	Hach amp.	mg/L O2	-6	68	78	13	13
Copper	EPA 200.7	mg/L Cu	0.005	0.087	0.090	0.018	0.017
Fluoride	EPA 300.0	mg/L F	0.5	-0.1	-0.1	0.7	0.7
Hardness, Total	EPA 130.2	mg/L	167	580	568	586	567
,		CaCO3					
Iron	EPA 200.7	mg/L Fe	0.031	0.154	0.158	0.008	-0.006
Lead	EPA 200.8	μg/L Pb	0.13	0.26	0.31	0.16	0.14
Magnesium	EPA 200.7	mg/L Mg	13.2	-0.1	-0.1	0.4	0.4
Manganese	EPA 200.7	mg/L Mn	-0.001	-0.001	0.001	-0.001	-0.001
Mercury	EPA 245.1	mg/L Hg	-0.0002	-0.0002	-0.0002	-0.0002	-0.0002
Molybdenum	EPA 200.8	μg/L Mo	5	17	16	1493	1590
Nickel	EPA 200.8	μg/L Ni	5	62	59	12	13
Nitrate+Nitrite	EPA 353.2	mg/L N	0.38	0.32	0.32	0.46	0.45
pН	EPA 150.1		8.17	11.82	8.21	9.68	7.46
Selenium	EPA 200.8	μg/L Se	-1	4	4	22	23
Silver	EPA 200.7	mg/L Ag	-0.005	-0.005	-0.005	-0.005	-0.005
Solids, Total	EPA 160.2	mg/L	-1	16	-1	-1	-1
Suspended		8					
Specific	EPA 120.1	μmhos/cm	336	2020	1252	1376	1480
Conductance		@25C					
Sulfate	EPA 300.0	mg/L SO4	41	20	21	716	736
Thallium	EPA 200.8	μg/L Tl	0.01	-0.01	-0.01	0.02	-0.01
Tin	EPA 200.8	μg/L Sn	-0.1	-0.1	-0.1	0.2	-0.1
Titanium	EPA 200.7	mg/L Ti	-0.001	-0.001	-0.001	-0.001	0.001
TOC	EPA 415.1	mg/L TI	8	33	33	10	10
Zinc	EPA 200.7	mg/L Zn	-0.01	0.01	-0.01	-0.01	-0.01

Negative values indicate None Detected and the absolute value is the Method Detection Limit.

 Table 7.
 Table of Minnesota Water Quality Standards.

		FAV Final Acute	Chronic Toxicity	Drinking Water or
		Value	Based Stds.	Irrigation Stds.
		Discharge Stds.	Ambient Stds.	Ambient Stds.
Alkalinity	mg/L CaCO3			
Aluminum	mg/L Al	2.145	0.125	
Ammonia	mg/L N			0.04
Antimony	mg/L Sb	0.18	0.0055	
Arsenic	mg/L As	0.72	0.002	
Barium	mg/L Ba			2
Beryllium	mg/L Be			0.004
Boron	mg/L B			0.5
Cadmium *	mg/L Cd	0.067	0.0011	
Calcium	mg/L Ca			
Chloride	mg/L Cl	1720	230	
Chromium (+3) *	mg/L Cr	3.469	0.207	
Chromium (+6) *	mg/L Cr	0.032	0.011	
Cobalt	mg/L Co	0.872	0.0028	
Copper *	mg/L Cu	0.035	0.0098	
Fluoride	mg/L F			2
Iron	mg/L Fe			0.3
Lead *	mg/L Pb	0.164	0.0032	
Magnesium	mg/L Mg			
Manganese	mg/L Mn			0.05
Mercury	mg/L Hg	0.0049	0.0000069	
Molybdenum	mg/L Mo			
Nickel *	mg/L Ni	2.836	0.158	
Nitrate+Nitrite	mg/L N			1 to 10
рН			6 to 9	
Phosphorous, total	mg/L P	1		1
Potassium	mg/L K			
Selenium	mg/L Se	0.04	0.005	
Silver *	mg/L Ag	0.0041	0.001	
Sodium	mg/L Na			
Conductivity	μmhos/cm@25C			1000
Sulfate	mg/L SO4			250
Thallium	mg/L Tl	0.128	0.00028	
Tin	mg/L Sn			
Titanium	mg/L Ti			
TOC	mg/L C			
Zinc *	mg/L Zn	0.234	0.106	

^{*} Standards that vary with total hardness, conservatively used a hardness of 100 mg/L

Table 8. Percent Survival and Growth of Fathead Minnows (*Pimephales promelas*) Exposed to Soil, Soil/Lime, and Soil/Fly Ash Leachate.

	So	oil Leacha	te	Soil/l	Lime Lea	chate	Soil/F	ly Ash Le	achate
Leachate Conc.	Growth	% Su	ırvival	Growth	% Sı	ırvival	Growth	% Su	ırvival
	(mg)	7-day	96-hour	(mg)	7-day	96-hour	(mg)	7-day	96-hour
Control	.556	97	97						
6.3%	.534	97	97	.452	90	100	.537	83	90
12.5%	.493	90	93	.493	73	93	.447	100	100
25%	.505	97	97	.385	87	93	.536	93	93
50%	.498	90	90	.284	77	87	.520	87	97
100%	.587	87	90	.225	53	63	.336	47	70
NOEC	100%	100%	-	25%	50%	-	50%	50%	-
96h-LC50	-	-	>100%	_	-	>100%	-	-	.1005
IC25	>100%	-	-	20.4%	-	-	75.4%	-	-

Table 9. Ranges of Chemical and Physical Data of the 7-Day Fathead Minnow Tests.

% Leachate	рН	Dissolved Oxygen (mg/L)	Temperature (°C)	Total Hardness (mg/L)	Total Alkalinity (mg/L)	Conductivity (µmhos/cm)
Control	7.04 - 7.52	4.8 - 8.4	25	36	32	160
Soil 6.3	6.99 - 7.58	4.4 - 8.7	25			
Soil 12.5	6.96 - 7.54	4.5 - 8.7	25			
Soil 25	7.00 - 7.58	4.5 - 9.0	25			
Soil 50	7.04 - 7.61	4.4 - 9.7	25			
Soil 100	7.28 - 7.70	4.8 - 10.8	25	184	128	360
Lime 6.3	7.08 - 7.67	4.5 - 8.4	25			
Lime 12.5	7.02 - 7.59	4.4 - 8.8	25			
Lime 25	6.99 - 7.60	4.4 - 9.0	25			
Lime 50	6.94 - 7.68	4.2 - 9.7	25			
Lime 100	6.92 - 7.80	4.2 - 10.7	25	532	40	1220
Ash 6.3	7.07 - 7.53	4.7 - 8.5	25			
Ash 12.5	7.01 - 7.50	5.0 - 8.8	25			
Ash 25	6.95 - 7.51	4.5 - 9.0	25			
Ash 50	6.90 - 7.61	4.8 - 9.5	25			
Ash 100	6.89 - 7.71	5.1 - 10.6	25	580	28	1518

Table 10. Percent Survival and Reproduction of *Ceriodaphnia dubia* Exposed to Soil, Soil/Lime, and Soil/Fly Ash Leachate.

	Soil Lead		te	Soil/l	Lime Lea	chate	Soil/Fl	y Ash Le	achate
Leachate Conc.	Mean #	% Su	rvival	Mean #	% Su	ırvival	Mean #	% Sı	ırvival
	Young - Produced	7-day	48-hour	Young Produced	7-day	48-hour	Young Produced	7-day	48-hour
Control	24.6	100	100						
6.3%	28.1	90	100	30.1	90	100	25.3	90	100
12.5%	29.1	100	100	26.2	90	100	22.9	90	100
25%	29.0	90	100	15.6	100	100	17.7	90	100
50%	32.4	100	100	7.7	80	100	2.3	0	100
100%	31.6	100	100	0.8	80	100	0	0	90
NOEC	100%	100%	-	12.5%	100%	-	12.5%	25%	-
48h-LC50	-	-	>100%	-	-	>100%	_	-	>100%
IC25	>100%	_	_	19.2%	-	_	22.6%	-	-

Table 11. Ranges of Chemical and Physical Data of the 7-Day Ceriodaphnia dubia Test.

% Leachate	рН	Dissolved Oxygen (mg/L)	Temperature (°C)	Total Hardness (mg/L)	Total Alkalinity (mg/L)	Conductivity (µmhos/cm)
Control	7.32 - 7.80	8.3 - 8.6	25	40	32	154
Soil 6.3	7.33 - 7.82	8.3 - 8.8	25			
Soil 12.5	7.35 - 7.84	8.3 - 8.8	25			
Soil 25	7.41 - 7.88	8.4 - 8.9	25			
Soil 50	7.47 - 7.98	8.4 - 9.7	25			
Soil 100	7.55 - 8.18	8.3 - 10.8	25	192	160	329
Lime 6.3	7.36 - 7.65	8.3 - 8.6	25			
Lime 12.5	7.40 - 7.69	8.3 - 8.8	25			
Lime 25	7.41 - 7.67	8.1 - 9.0	25			
Lime 50	7.46 - 7.64	8.0 - 9.7	25			
Lime 100	7.32 - 7.73	7.2 - 10.7	25	536	48	1380
Ash 6.3	7.36 - 7.64	8.3 - 8.6	25			
Ash 12.5	7.36 - 7.65	8.3 - 8.8	25			
Ash 25	7.38 - 7.63	8.3 - 9.0	25			
Ash 50	7.41 - 7.66	8.3 - 9.5	25			
Ash 100	7.40 - 7.71	8.3 - 10.5	25	580	48	1560

Table 12. Cell Growth of Algae, *Selenastrum capricornutum*, Exposed to Soil, Soil/Lime, and Soil/Fly Ash Leachate.

Leachate	Soil Leachate	Soil/Lime Leachate	Soil/Fly Ash Leachate
Concentration	Mean # Cells x 10 ⁶	Mean # Cells x 10 ⁶	Mean # Cells x 10 ⁶
Control	2.70		
6.3%	2.72	1.28	2.42
12.5%	2.50	1.59	2.63
25%	3.14	1.32	2.65
50%	3.33	0.80	2.33
100%	3.31	0.73	2.56
NOEC	100%	<6.3%	100%
IC50	>100%	21.7%	>100%

Table 13. Ranges of Chemical and Physical Data of the 96-Hour *Selenastrum capricornutum* Test.

% Leachate	рН	Dissolved Oxygen (mg/L)	Temperature (°C)	Total Hardness (mg/L)	Total Alkalinity (mg/L)	Conductivity (μmhos/cm)
Control	8.82 - 8.54	8.4	25	96	52	369
Soil 6.3	8.46 - 8.79	8.1	25			
Soil 12.5	8.43 - 8.71	8.2	25			
Soil 25	8.30 - 8.61	8.4	25			
Soil 50	8.20 - 8.46	8.8	25			
Soil 100	8.25 - 8.30	9.6	25	628	56	567
Lime 6.3	8.53 - 8.76	8.4	25			
Lime 12.5	8.48 - 8.73	8.3	25			
Lime 25	8.34 - 8.65	8.3	25			
Lime 50	7.98 - 8.56	8.6	25			
Lime 100	7.71 - 8.47	9.0	25	596	64	1250
Ash 6.3	8.68 - 8.79	8.1	25			
Ash 12.5	8.54 - 8.72	8.2	25			
Ash 25	8.41 - 8.62	8.3	25			
Ash 50	8.32 - 8.49	8.6	25			
Ash 100	8.16 - 8.32	9.2	25	232	160	1500

Chemical measurements taken after pH adjustment and nutrient addition. Soil=Soil only leachate, lime=soil/lime leachate, and ash =soil/fly ash leachate

Table 14. Percent Survival and Weight Loss of *Eisenia foetida* Exposed to Soil Leachate, Soil/Lime Leachate, and Soil/Fly Ash Leachate.

	Soil Leachate		Soil/Lime	Leachate	Soil/Fly Ash Leachate		
Leachate Conc.	% Weight Loss	% Survival	% Weight Loss	% Survival	% Weight Loss	% Survival	
Control	47.15	90					
6.3%	29.68	83	29.63	80	43.15	80	
12.5%	29.83	77	46.53	83	41.19	90	
25%	24.77	90	34.18	90	40.72	80	
50%	29.91	90	42.46	83	37.32	97	
100%	35.41	83	46.25	87	38.88	90	
NOEC	100%	100%	100%	100%	100%	100%	
IC25	>100%		>100%		>100%		

Table 15. Initial Chemical and Physical Data of Leachates Prior to Addition to Artificial Soil.

% Leachate	рН	Temperature (°C)	Total Hardness (mg/L)	Total Alkalinity (mg/L)	Conductivity (µmhos/cm)
Control	7.30	25	44	32	157
Soil 6.3	7.31	25			
Soil 12.5	7.38	25			
Soil 25	7.44	25			
Soil 50	7.50	25			
Soil 100	7.62	25	196	140	363
Lime 6.3	7.65	25			
Lime 12.5	7.58	25			
Lime 25	7.50	25			
Lime 50	7.45	25			
Lime 100	7.44	25	536	40	1378
Ash 6.3	7.70	25			
Ash 12.5	7.60	25			
Ash 25	7.54	25			
Ash 50	7.56	25			
Ash 100	7.61	25	588	36	1535

Table 16. Test Conditions of *Eisenia foetida* Soil Toxicity Test.

% Leachate Concentration	Initial pH	Final pH	% Moisture Content
Control	7.12	7.70	25.9
Soil 6.3	7.15	7.69	26.1
Soil 12.5	7.15	7.66	25.5
Soil 25	7.19	7.66	25.6
Soil 50	7.24	7.69	26.1
Soil 100	7.23	7.70	26.1
Lime 6.3	7.22	7.62	26.7
Lime 12.5	7.24	7.68	26.6
Lime 25	7.21	7.61	25.2
Lime 50	7.18	7.53	25.9
Lime 100	7.08	7.46	25.1
Ash 6.3	7.22	7.63	26.0
Ash 12.5	7.23	7.58	26.0
Ash 25	7.26	7.60	25.0
Ash 50	7.21	7.55	24.7
Ash 100	7.14	7.49	26.2

Table 17. Percent Survival and Abnormalities of *Xenopus laevis* to Exposed to Soil Leachate, Soil/Lime Leachate, and Soil/Fly Ash Leachate.

Leachate Conc.	Soil Leachate			Soil/Lime Leachate			Soil/Fly Ash Leachate					
	% Survival		% Abnormal		% Survival		% Abnormal		% Survival		% Abnormal	
	Pair 1	Pair 2	Pair 1	Pair 2	Pair 1	Pair 2	Pair 1	Pair 2	Pair 1	Pair 2	Pair 1	Pair 2
Control	98	100	0	2								
6.3%	98	96	0	2	100	100	0	4	100	96	0	2
12.5%	100	94	0	4	100	92	0	0	100	90	0	0
25%	100	94	0	0	98	94	0	2	100	98	0	0
50%	94	98	2	0	100	90	4	4	98	92	0	2
100%	100	90	2	2	0	8	*	100	20	28	100	100
NOEC	100%	100%	100%	100%	50%	50%	50%	50%	50%	50%	50%	50%
LC50	>100%	>100%	-	-	70.4%	69.7%	_	-	76.8%	78.8%	-	-

^{*}No survivors

Table 18. Chemical and Physical Data of Renewal Water Used in the Xenopus Embryo Survival and Abnormality Test.

% Leachate	рН	Dissolved Oxygen (mg/L)	Temperature (°C)	Total Hardness (mg/L)	Total Alkalinity (mg/L)	Conductivity (µmhos/cm)
Fetax	7.77 - 7.90	8.1	23	128	64	1637
Control	7.33 - 7.54	8.1 - 8.3	23	48	32	162
Soil 6.3	7.28 - 7.44	8.1 - 8.4	23			
Soil 12.5	7.27 - 7.46	8.2 - 8.5	23			
Soil 25	7.31 - 7.50	8.4 - 8.5	23			
Soil 50	7.40 - 7.56	9.0 - 9.3	23			
Soil 100	7.43 - 7.71	10.2 - 11.3	23	180	140	356
Lime 6.3	7.35 - 7.66	8.2 - 8.4	23			
Lime 12.5	7.25 - 7.57	8.2 - 8.5	23			
Lime 25	7.24 - 7.52	8.3 - 8.5	23			
Lime 50	7.35 - 7.56	8.7 - 9.0	23			
Lime 100	7.48 - 7.74	9.9 - 11.1	23	520	36	1408
Ash 6.3	7.34 - 7.82	8.1 - 8.5	23			
Ash 12.5	7.31 - 7.61	8.1 - 8.4	23			
Ash 25	7.32 - 7.55	8.2 - 8.5	23			
Ash 50	7.39 - 7.56	8.8 - 9.0	23			
Ash 100	7.63 - 7.70	9.9 - 10.8	23	604	24	1554

APPENDIX B

FIGURES

Figure 1. Growth of *Pimephales promelas* exposed to soil, soil/lime, and soil/fly ash leachates.

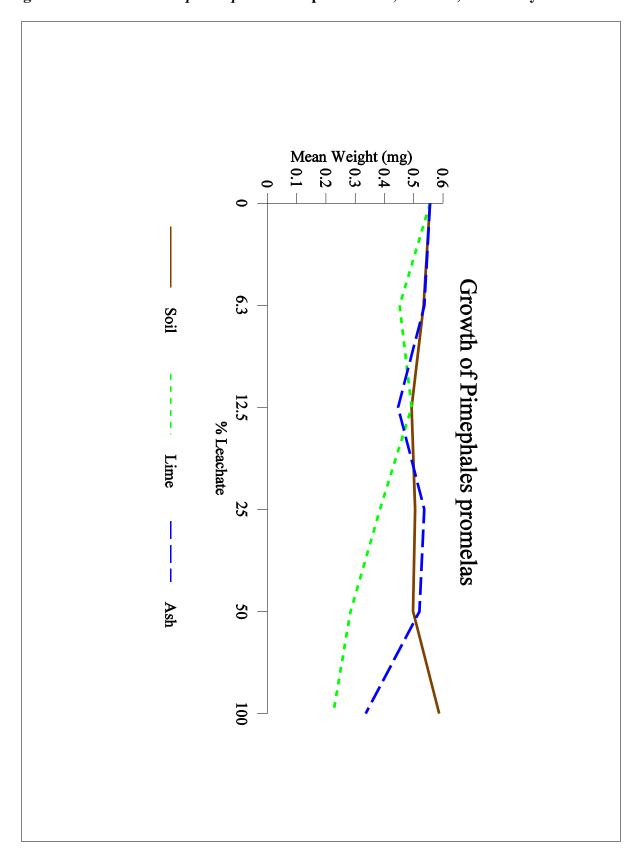


Figure 2. Survival of *Pimephales promelas* exposed to soil, soil/lime, and soil/fly ash leachates.

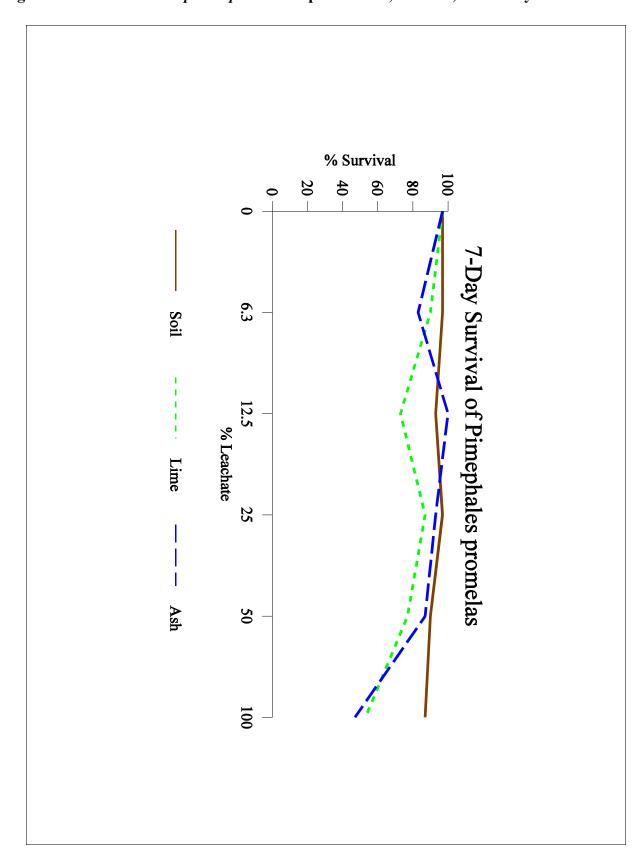


Figure 3. Reproduction of *Ceriodaphnia dubia* exposed to soil, soil/lime, and soil/fly ash leachates.

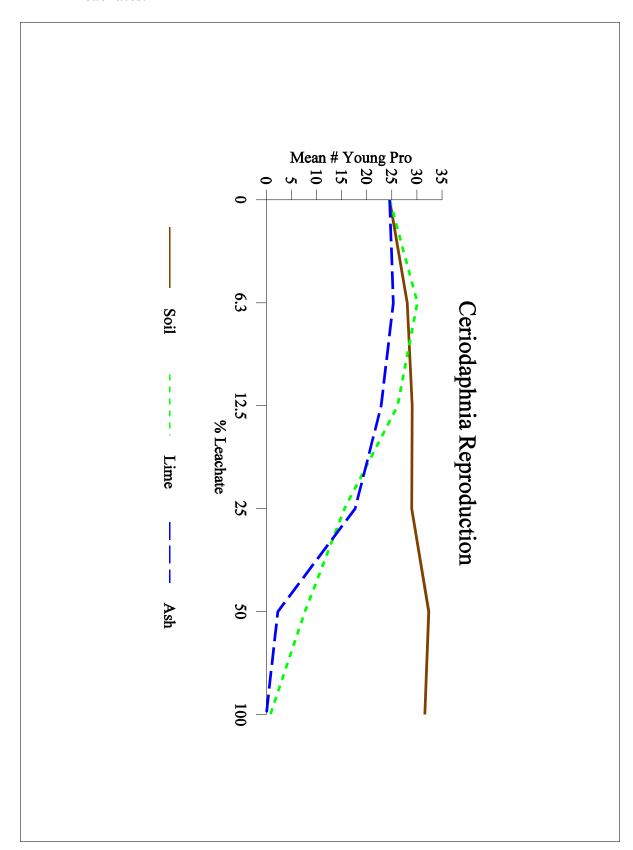


Figure 4. Survival of Ceriodaphnia dubia exposed to soil, soil/lime, and soil/ash leachates.

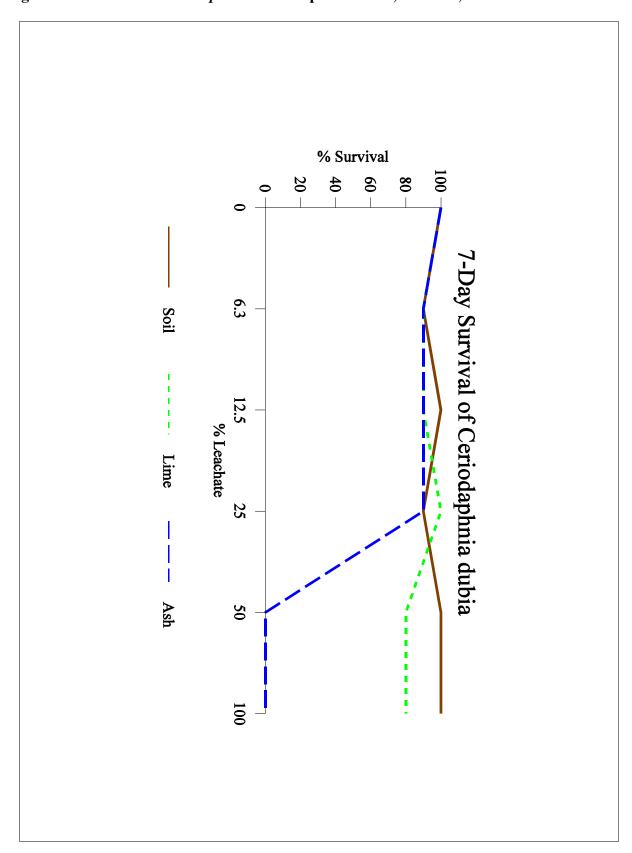


Figure 5. Cell growth of algae, *Selenastrum capricornutum*, exposed to soil, soil/lime, and soil/fly ash leachates.

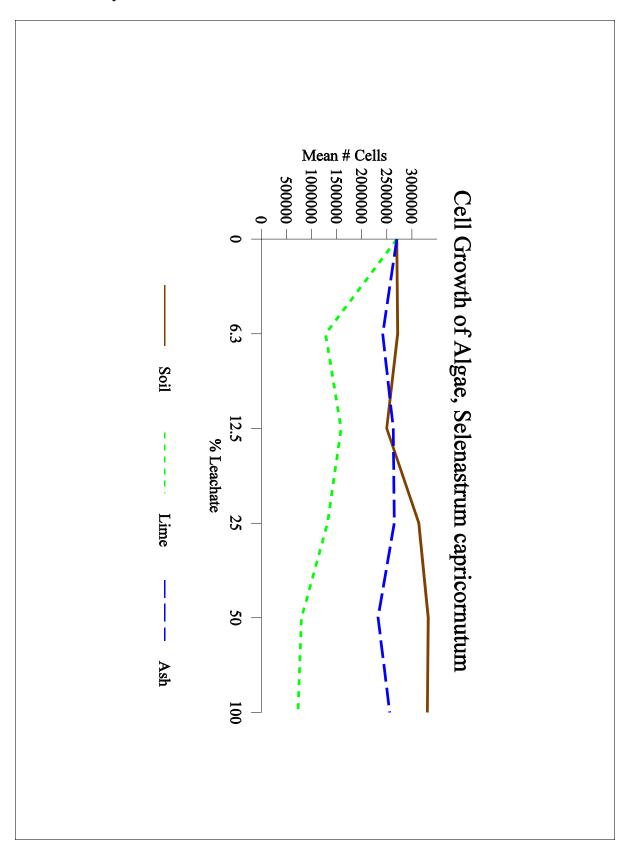


Figure 6. Percent weight loss of the earthworm, *Eisenia foetida*, exposed to soil, soil/lime, and soil/fly ash leachates.

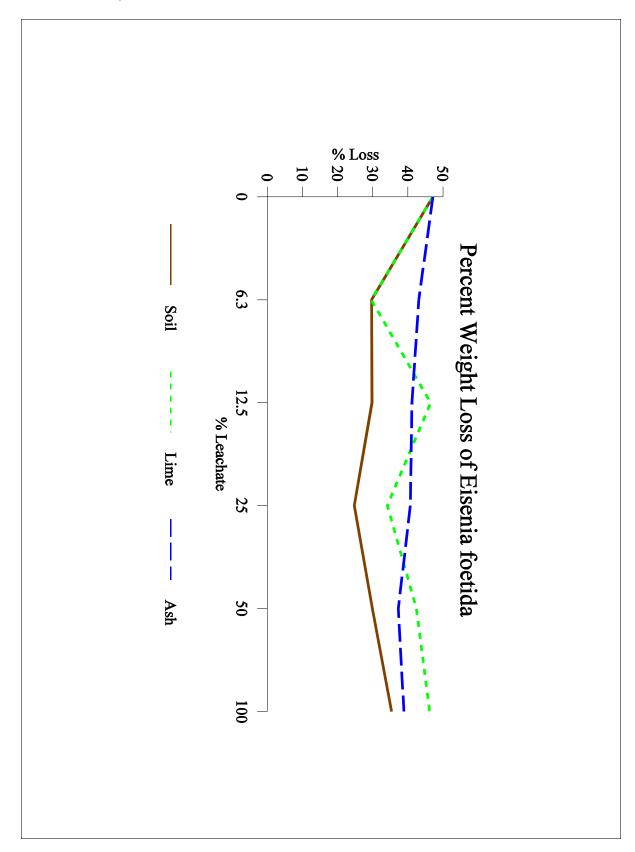


Figure 7. Percent Survival of *Eisenia foetida* exposed to soil, soil/lime, and soil/fly ash leachates.

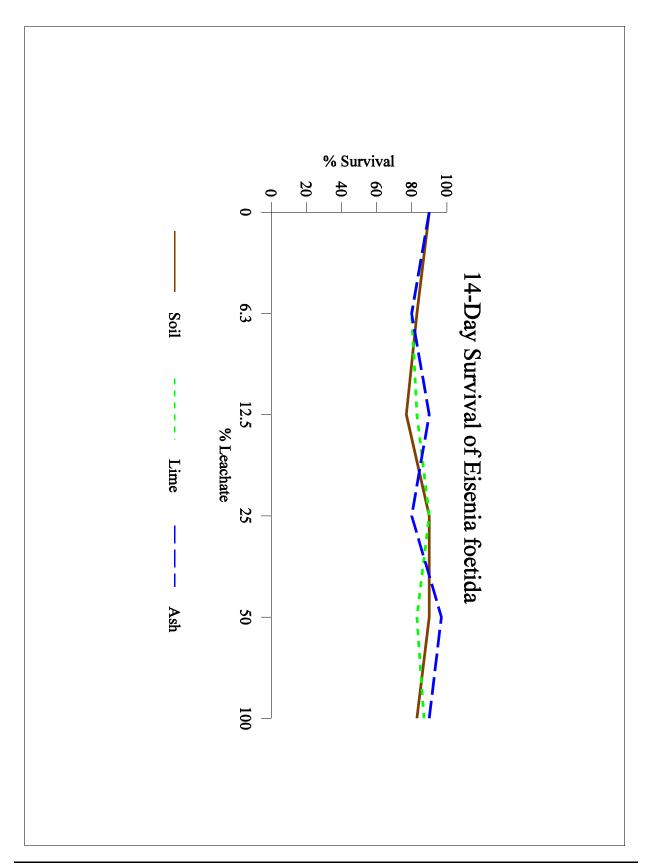


Figure 8. Percent survival of the frog, *Xenopus laevis*, exposed to soil, soil/lime, and soil/fly ash leachates.

