EVALUATION OF TESTING PROTOCOLS FOR THE ENVIRONMENTAL ASSESSMENT OF FLY ASH STABILIZED SOILS

(RMRC PROJECT #50)

Final Report Submitted to Federal Highway Administration

Recycled Materials Resource Center

by

Ahmet H. Aydilek, Ph.D.

August 18, 2011

Department of Civil and Environmental Engineering
University of Maryland
College Park, Maryland 20742

EXECUTIVE SUMMARY

Beneficial reuse of coal combustion byproducts requires an evaluation of metal leaching potential. A comprehensive laboratory study was conducted to evaluate the trace metal leaching from fly ash stabilized soils in a highway environment. The study had two parts. The first part focused on metal leaching in from fly ashes in highway bases and embankments and comprised both laboratory analysis and numerical simulations. The second part of the study had a deeper focus on chemical processes with a critical discussion of the three commonly used leaching testing procedures, namely the water leach test (WLT), the Toxicity Characteristic Leaching Procedure (TCLP), and the column leach test (CLT). The effect of test methodology and pH on several metals was examined. Based on these results, a combined WLT and CLT leaching protocol for testing fly ash mixtures is presented.

TRACE METAL LEACHING FROM HIGH CARBON FLY ASH MIXED SOILS

TABLE OF CONTENTS

1 INTRODUCTION

According to ACAA, the 45% of the electricity consumed in the United States in 2009 were supplied from the power plants that burn coal. Approximately 92.8 million of tons of coal combustion byproducts (CCBs) are produced in the United States each year as a result of burning coal at the electric power plants (ACAA 2008). As of 2009, 78% of these CCBs are fly ashes, and 42.3 million tons of fly ash is landfilled. American Coal Association Agency estimates that this landfilled or stockpiled amount will be increasing each year.

Fly ash production causes two main problems: impacts to the environment and occupying valuable landspace. The first one is particularly important as fly ashes may contain high concentrations of important trace elements such as Arsenic, Boron, Chromium, Copper, Zinc, Vanadium, and Nickel among many others. Disposing large amounts of fly ashes into landfills can cause leaching of these heavy metals to the groundwater through the soil vadose zone and may threaten the aquatic life and environment as well as human health.

There have been significant efforts on reusing of fly ash materials in construction and decreasing the disposing rate of fly ash as residues. Fly ash is siliceous or alumino-siliceous pozzolanic material that can form cementitious compounds in the presence of water. The physical, chemical and mineralogical properties of the fly ash are strongly dependent on the type of the coal burning, type of combustion process, type of pollution control facilities and handling (Komonweeraket et al. 2010). Fly ash is classified into two classes, F and C, based on the chemical composition of the fly ash, and the C (self-cementitious) type fly ashes are readily and F type ashes are commonly reused as concrete additive or in cement production. However, fly ashes produced by several power plants in United States in the last 5 years occasionally contains significant amounts of unburned carbon (i.e., high loss on ignition) due to the increasingly common use of low nitrogen oxide (NO_x) and sulphur oxide (SO_x) burners. This ash, called high carbon fly ash (HCFA), has a carbon content of 12-25%, cannot be efficiently re-burnt by using current technology, and has no value as a concrete additive as the unburned carbon tends to adsorb the air entrainment admixtures that are added to the cement to prevent crack formation and propagation. These ashes are typically classified as off-spec fly ashes meaning that they do not meet the physical and chemical requirements criteria outlined in ASTM C618 and are landfilled at large percentages.

The fly ashes produced by several power plants in Maryland and elsewhere occasionally contains significant amounts of unburned carbon (i.e., high loss on ignition), and cannot be used in concrete production. On the other hand geotechnical applications pose great potential for beneficial reuse of the fly ashes. In the current study, the applications of reusing of fly ash in construction of highway base layers (Section 3) and embankments (Section 4) will be discussed.

Several studies have conducted on leaching behavior of metals from coal combustion by-products and mechanisms that control the release of these metals (Wang et al. 2006, Bin-Shafique et al. 2006, Chen et al. 2006, Goswami and Mahanta 2007, Gosh 2008, Vitkova et al. 2008, Srivastava et al. 2008, Deng et al. 2008, Dutta et al. 2009, Komonweeraket et al. 2010).However, there is lack of information on leaching of these contaminants from high carbon fly ash mixtures. The environmental risks associated with fly ash stabilization may be reduced when HCFAs are used as a stabilizing agent (e.g., unburned carbon or activated carbon is often used for pollution control). The high organic carbon content of HCFA may act as a sorbent to the heavy metals in the fly ash, and reduce the amount of metals that are released into the environment. Because of enhanced adsorption of metals by the unburned carbon, metal concentrations are likely to decrease to much lower values than the ones experienced in previous field applications. The environmental benefits of the high carbon content may also result in a broader range of permissible reuse applications for fly ash.

The objective of the proposed study is to evaluate the leaching potential of borrow materials mixed with HCFAs relative to those stabilized with conventional additives (low carbon fly ashes), and to evaluate the potential groundwater and soil vadose zone impacts. The experimental program consisted of the following tasks:

1) Determining the concentrations of minor, major and trace elements and other chemical properties of interests, speciation in leachates from fly ashes and soil alone and soil – fly ash mixtures.
2) Running batch (small-scale) water leaching tests for a quick estimate of estimates about the leaching behavior of the soil mixtures
3) Running long term column leaching tests to study leaching behavior and controlling mechanisms of the trace metals form soil-fly ash mixtures.
4) Comparing the results of WLTs and CLTs and try to obtain a relationship between these two tests to estimate the metal concentrations quickly in the field.
5) Determining the groundwater impacts by using computer modeling called WiscLEACH.
6) Predicting the species of the trace metals that could occur under the corresponding pH and oxidation – reduction values with the help of MINTEQA2.

2 LITERATURE REVIEW

Previous studies showed that high carbon fly ashes (HCFA) could be used in variety of applications, including as a barrier in the remediation of contaminated groundwater (Demirkan et al. 2006), and bulk fill material in geotechnical fills and highway bases (Cetin et al. 2009). The advantages of using fly ash as a bulk fill material include low cost, low unit weight, and good strength. Furthermore, roadways and embankment constructions have high potential for large volume use of HCFA. Using this fly ash as a part of base course material in highways and embankment is one of the most beneficial ways of utilizing the already disposed fly ash. On the other hand, the leachability of heavy metals from the fly ash into soil and groundwater is a significant concern, creating environmental health problems due to their high potential for cumulative build-up and long life in the environment (Ghosh and Subbarao 1998, Wang et al. 2006, Bin-Shafique et al. 2006, Chen et al. 2006, Goswami and Mahanta 2007, Sushil and Batra et al. 2008, Vitkova et al. 2008, Srivastava et al. 2008, Dutta et al. 2009).

Naik et.al (2001) evaluated the performance and leaching of controlled low strength materials incorporating fly ash and foundry sand. The concentrations of heavy metals were below the enforcement standards of State of Wisconsin, and were not significantly affected by the type and source of fly ash or foundry sand. Bin-Shafique et.al (2006) showed that water leaching and column leaching tests yielded similar trends with fly ash content, leachate pH, and soil properties. The column tests provided a good indication of the conditions likely to occur in the field, whereas water leaching tests were used to estimate the initial concentrations of Cd, Cr, Se, and Ag in the field. Fly ashes were used as a pre-filter material for the retention of Pb ions by

Pandian et al. (1996) and leaching of Pb ions was observed to be the highest at extreme pH conditions. Similarly, Wang et al. (2008) also demonstrated the metal adsorption capability of Class F fly ashes and its relation to the carbon content. Jo et al. (2007) looked at the environmental feasibility of using fly ash as a fill material and showed that all metals except Mn were below the EPA limits. It has been shown that fly ash can also be used in the stabilization of residual lateric soils (Goswami and Mahanta 2007). In such applications, calcium content of fly ash affects the pH of soil significantly and leaching behavior of metals is highly dependent on the pH of the aqueous solution. A study carried out by Baba et al. (2008) revealed that the heavy metal concentrations increase with increasing acidity and temperature of the aqueous environment. Chen et al. (2006) studied the leaching potential of Cd, Ni, Pb, Cu and Zn from acidic sandy soil amended with dolomite phosphate rock (DPR) fertilizers and determined that the maximum leachate concentrations of all five metals were below drinking water guidance limits set by the Florida Department of Natural Resources. Suzuki and Ono (2008) researched the leaching characteristics of stabilized/solidified fly ashes and observed pH-dependent concentrations for Pb, Cu and Zn. Stabilization of Zn, Fe and Mn were achieved at neutral pH conditions in another study conducted by Srivastava et al. (2008).

Despite the leaching of heavy metals, cementitious properties and low cost of fly ash makes it a good candidate for improving the mechanical properties of soils. In the last decade, significant efforts have been made to understand leaching characteristics of heavy metals from soil-fly ash mixtures; however, lack of information exists on leaching of HCFA or off-spec fly ashes especially when they are amended with an activator rich in CaO. It is well known that the high pH may fix some of the heavy metals within the stabilized soil mixtures (Bin-Shafique et al. 2006, Dutta et al. 2009). In addition, the alkalinity and calcium content of the stabilized soil affect the leaching characteristics of heavy metals significantly by increasing the pH of soil and decreasing the leaching potential of metals (Goswami and Mahanta 2007, Dutta et al. 2009). On the other hand, a significant increase in the pH of the aqueous solutions is likely to increase the solubility of anionic metal species like Al, Cr, As and Se which are also critical metals in threatening aquatic life and human health (Al-Abed 2006, Morar 2007, Wang et al. 2007, Malferrari et al. 2008, Wang et al. 2008, Wang et al. 2009). Thus, there is an emerging need to evaluate the environmental solubility of fly ash-stabilized soils amended with calcium-rich agents.

3 METAL LEACHING FROM HCFA STABILIZED BASE LAYERS

3.1 Introduction

Using fly ash in highway applications is gaining importance due to its potential to solve the landfilling problems and provide good strengthen material. The most important problem in highway constructions is building the suitable base layer that can provide enough support to the asphalt layer. The two conventional methods to stabilize the base layer are removing the soft soil and replacing it with a stronger material, such as granular materials (gravel), or in situ stabilization of the soil via physical and chemical techniques. However, these conventional methods can be costly and time consuming, and alternative approaches such as fly ash amendment could be very practical and provide an economical solution for stabilization of the existing soil (Cetin et al. 2010). Leaching of the metals from HCFA-stabilized soil layers is, on the other hand, the main concern for construction applications (Bin Shafique et al. 2002, Sauer et al. 2005, Goswami and Mahanta 2007).

In order to evaluate the environmental suitability of fly ash-stabilized soils for potential highway applications, a series of short term batch water and long term column leaching experiments were conducted. These mixtures were selected based on strength and moduli determined in an earlier study by Cetin et al. (2010). Results were used to determine leaching patterns and relationships between concentrations from the two laboratory tests. Numerical modeling tools were also utilized to predict concentrations at different times and locations in the field.

3.2 Materials

An unpaved road material and three fly ashes were used in this study. The unpaved road material (URM) was soil – fly ash – lime kiln dust mixtures in all tests as well as a reference material was utilized in both column leach and water leach tests. The URM was collected from a highway construction site in Caroline County, Maryland. Any debris and foreign materials in the soil were removed by hand and, by sieving through a U.S. ¾ inches (19 mm) sieve. The soil is classified as poorly graded sand with gravel (SP) according to the Unified Soil Classification System (USCS), and A-1-b according to the American Association of State Highway and Transportation Officials (AASHTO) Classification System.

URM material was chosen as it satisfied the gradation as well as maximum dry unit weight requirements by the Maryland State Highway Administration (MDSHA). The URM was collected in airtight buckets to preserve its natural water content. Physical properties of the unpaved road material are summarized in Table 3.1.

The fly ashes used in this study were obtained from three power plants in Maryland: Brandon Shores (BS), Paul Smith (PS) and Dickerson Precipitator (DP). All of the fly ashes consisted primarily of silt-size particles and contained 80 to 94% fines (passing the 75-µm sieve). Particle size distribution curves for the unpaved road material and fly ashes are shown in Figure 3.1. Specific gravity of fly ashes ranged between 2.17 and 2.37 per ASTM D 854. The physical properties and chemical compositions of the materials are summarized in Tables 3.1 and 3.2, respectively. The fly ashes investigated in this study were classified as off-specification fly ashes (neither C nor F type according to ASTM C 618) due their high loss on ignition values (LOI > 6), and high (SiO_2 (%) + Al_2O_3 (%) + Fe_2O_3 (%) (>70 %) and very low lime (CaO) contents (0.7-7.8 %). The LOI data along with the pH measurements were conducted according to EPA Method SW-846 Method 9045 are also presented in Table 3.2. Since the three fly ashes do not have high cementing potential, lime kiln dust (LKD) was used to initiate pozzolanic reactions for stabilization of the soil. LKD was obtained from Carmeuse Lime and Stone Company, Pittsburgh, Pennsylvania and contained approximately 60% CaO by weight. The specific gravity (G_s) of LKD is 2.97. Total elemental analyses of the three fly ashes and URM were conducted following the procedures outlined in EPA SW-846 Method 6800 and summarized in Table 3.3.

3.3 METHODS

3.3.1 Batch Water Leach Test (WLT)

Batch water leach tests were conducted on the soil, fly ashes and soil mixtures using different percentages of fly ashes and lime kiln dusts in accordance with ASTM D 3987. Two modifications were made on the standard method. First, instead of using 2-L, a 50-mL mixture of leachant/solid volume was used because of the size of centrifuge machine employed in the current study. Second, a constant liquid-to-solid (L:S) ratio of 20:1 was used for all materials. The air dried soil was crushed and sieved from U.S. No. 4 sieve (4.75 mm), and the soil was mixed homogeneously with fly ash and lime kiln dust at different percentages. Each specimen was cured for 7 days in plastic bags in a moisture controlled humidity chamber (21 C^o and 100% relative humidity). After curing, 2.4 g of soil mixture was added to a 50-mL plastic centrifuge tube followed by 48 mL leachant (i.e., the 0.1 M NaBr solution). The soil mixtures were rotated continuously on a rotator at 29 revolutions per minute, room temperature (19 C^o - 25 C^o) for 18 hours for equilibration. After equilibrium, the specimens were settled for 5 minutes and placed in the Beckman GPR centrifuge machine. The mixtures were centrifuged at 3000 rpm for 20 minutes. Next, the suspended solids were filtered through the 0.2-µm pore size, 25 mm diameter membrane disk filters fitted in a 25-mm Easy Pressure syringe filter holder by using a 60-mL plastic syringe. After filtration, pH, electrical conductivity and oxidation reduction values were recorded. Then, the filtered samples were acidified to pH < 2 using high-purity nitric acid and stored in 15 mL high density polyethylene centrifuge tubes. Before use, the sample bottles were washed with acid (2 % HNO_3) and rinsed with deionized water. All samples were stored at 4 Cº for chemical analysis. Triplicate WLTs were conducted on all soil mixtures using each soil solution.

3.3.2 Column Leach Tests

The column leach test (CLTs) were conducted on soil, fly ashes alone and soil mixtures to provide more realistic results about leaching behavior and transport parameters of heavy metals. The soils, fly ashes their mixtures prepared for CLTs tests were the same materials prepared for WLTs. Air-dried soil was sieved from U.S. No.4 (0.425mm) sieve. All specimens were compacted in a PVC mold having 101.6 mm diameter and 116.4 mm height by using standard Proctor compaction effort (ASTM D 698). Table 3.4 provides the optimum moisture contents (OMCs) and maximum dry unit weights (γ_{dm}) of the mixtures based on compaction tests. PVC molds were preferred to minimize the outside effects on effluent metal concentrations. All soil mixtures were cured for 7 days in a humidity chamber with 100% relative humidity and 21 Cº following compaction.

After curing, the CLTs were started immediately. The columns were operated in an up-flow mode with flow provided by a peristaltic pump on the influent line. The polypropylene (PP) influent lines were connected to a polyethelene reservoir tank which was filled with the 0.1 M

NaBr solution with adjusted pH (pH 6.5~7). On the effluent end of the column, polytetrafluoroethylene (PTFE) tubing transferred the effluent solution into the collection bottle. A sketch of the column test set up is shown in Figure 3.2. An inflow rate of 60 mL/hr was used for all tests following the recommendations of Gelhar et al. (1992) and Morar (2007).

A 0.1 M NaBr solution was used to provide influent with an ionic strength comparable to that of percolating water (Papini et al. 1999, Bin-Shafique 2006). The solution was prepared with NaBr salts dissolved in ASTM Type II water. Br was selected because it is a non-reactive tracer. pH of the influent solution was open to atmosphere and adjusted by adding NaOH solution to stay between 6.5 and 7.

During the first three days of testing, frequent sampling (every 4 hours) was necessary in order to catch the breakthrough curve describing the leaching of each metal studied. After 72 h, the sampling frequency was decreased to twice a day for two days, and 2 to 7 times a week as the temporal changes in the metals concentrations became less significant. pH and electrical conductivity measurements were recorded immediately after the sample collection. The protocol for sample filtration and preservation followed those employed in WLTs.

3.3.3 Chemical Analysis

pHs of the leachate samples collected from the CLTs and WLTs were determined following the methods outlines in ASTM D1293. pHs of the fly ashes were determined by using SW-846 Method 9045. Three replicate samples were measured for each sample and the mean values were reported. The metals selected for analysis were Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Si, Sr, TI, V, Zn. The selection was based on the total elemental analyses presented in Table 3.3. However, initial spectroscopy analyses showed effluent concentrations below the detection limits for all metals, except Al, Cr, Cu, Fe, Mn, Sb, V, Zn. These eight metals pose health concerns based on the recommendations of the U.S. Environmental Protection Agency, and therefore, included in further analyses. The metals also represent different mobilities. For instance, at the pHs typical of soil-fly ash mixtures (10-12.5), Cr forms oxyanions that can be very mobile, whereas Al forms hydroxyl compounds and their attachment to the soil surface depends on the solubility level.

The concentrations of all metals were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Varian Vista-MPX CCD Simultaneous ICP-OES instrument. All sampling equipment that contacted the leachate samples was acid cleaned, dried, and bagged in clean and sealed bags. Blanks were run every 10-20 analyses and the calibration was verified every 10 analyses. A reagent blank was tested every 20 samples and a spiked sample was analyzed every 10 samples. Minimum detection limits (MDLs) for ICP-OES were determined for each metals and a set of calibration standards according to the U.S. Code of Federal Regulations Title 40. The MDLs for Al, Cr, Cu, Fe, Mn, Sb, V, and Zn metals were determined as 2.5 ppb, 0.5 ppb, 0.7 ppb, 3.2 ppb, 0.05 ppb, 3 ppb, 0.1 ppb, and 1 ppb, respectively.

3.4RESULTS

3.4.1Water Leach Tests

Triplicate batch water leach tests (WLTs) using two leaching solutions were conducted on different combinations of mixtures. These included URM only, fly ash only, and several unpaved road material (URM)-fly ash- lime kiln dust (LKD) mixtures. Table 3.5 summarizes the pH and electrical conductivity of the specimens tested.

Figure 3.3 shows that the rate of increase in pH was initially high and addition of LKD above 2.5% by weight did not affect pH significantly. It is speculated that an increase in LKD amount increased the release of free lime (CaO), hydrated calcium silicate (C-S-H) and portlandite ($Ca (OH_2)$) which resulted in increase in pH values. The fly ash, as compared to LKD, had little effect on the resulting pH of the mixture due to its relatively lower calcium content (Table 3.5). All three fly ashes except Brandon Shores (BS) fly ash used in this study had calcium contents of less than 5% compared to a calcium content of approximately 60% for LKD. Such calcium contents resulted in high pH contents for the mixtures, the values being higher than 8.5, the allowable limit in various states including Maryland.

Table 3.6 shows the concentrations of eight metals for several different soil mixtures compared to the U.S. EPA maximum concentration limits for drinking waters (MCLs), EPA water quality limits (WQLs) for protection of aquatic life and human health, and Maryland aquatic toxicity limits (ATLs) for fresh water. The results show that, except for Zn, higher concentrations were obtained for fly ashes alone than URM–fly ash–LKD mixtures. Of the three fly ashes tested, generally the soil mixture blended with Brandon Shores (BS) fly ash yielded the highest metal concentrations followed by the mixtures prepared with Dickerson Precipitator (DP) and Paul Smith fly ashes. Trace metal contents were also generally the highest in Brandon Shores fly ash based on total element analysis (Table 3.3). However, regardless of the increase in metal concentrations, except Al, all trace metal concentrations were below the MCL, WQL and Maryland ATL.

The variation in concentrations of these eight metals was plotted against fly ash content for mixtures prepared with 5% LKD in Figure 3.4. Al, Cr, V, Sb, Mn and Cu show similar trends. The concentrations of these metals generally increased with an increase in fly ash content. The rate of increase of these six metals concentrations, however, was different without a recognizably consistent variation. For generally all metals the rate of increase in concentration was high initially as fly ash amount was increased from 0% to 10% by weight, but the rate generally decreased when the fly ash amount was increased from 10% to 20%.

The effluent concentrations of all metals, except Zn, were higher for the fly ash alone than the soil alone. For the soil-fly ash-LKD mixtures, a higher fly ash contents generally yielded higher effluent concentrations of metals, which is consistent with the higher values for fly ash alone. However, the increase in metal concentrations was not linear with fly ash content, even though the mass of metals in soil mixture increases approximately linearly with increasing fly ash content. Therefore, the use of linear dilution calculations will underestimate the resulting concentrations of metals from soil mixtures.

The fly ashes were richer in Cr, Cu, V, Mn and Sb metals than the URM alone based on total elemental analyses (Table 3.3). Thus, an increase in Cr, Cu, V, Mn and Sb concentrations with the incremental increase of fly ash content in soil mixture observed in Figure 3.4 is expected.

High concentrations of Al were observed in the effluent leachates. As with Cr, the solubility of Al is highly dependent on pH of the aqueous solution. The solubility of Al is minimum at a pH of about 6.5 and increases with increasing pH values (Lim et al. 2004, Komonweeraket et al. 2010). As seen in Table 3.6, the aluminum concentration in fly ashes alone was at least 30 times lower than that of the mixtures. The addition of the LKD is most probably responsible for leaching of Al. Aluminum produces anionic species and cannot be absorbed by the negatively charged surface. High pH values may have showed a significant change in the size of negatively charged particle surface occupied by the hydrogen ions, causing a serious space decrease for Al and other metals (Sparks 2003). Figure 3.4 shows that an increase in fly ash content caused a decrease in Zn concentration as URM contains higher amounts of Zn than all the three fly ashes based on total elemental analyses. On the other hand, an increase in LKD content from 2.5% to 5% LKD caused an increase in Zn concentrations in the aqueous solution. Goh and Tay (1993) and Ghosh and Subbaroa (1998) also showed that Zn concentration increased when pH was increased from 9 to 12 which is controversial with the findings in the current study. The reason for that could be explained as the main metal resource is the dominant parameter that affects the leaching of Zn in this situation.

3.4.2 Column Leach Tests

pH Measurements

Figure 3.5 shows the variation of effluent pH of the URM alone, fly ash alone and soil mixtures as a function of pore volumes of flow. All tests were continued until a minimum of 200 pore volumes of flow were obtained to examine the behavior and persistency of pH of the soil mixtures. In all cases, pH initially decreases during the first 20 – 50 pore volumes of flow with few exceptions followed by an essentially constant pH. Even though the pH of the influent solutions were kept between 6.5 and 7, the stabilized pH of the effluent solutions were still relatively high (pH>11) due to the buffering capacities of the fly ashes and LKD.

URM alone had the lowest pH values. When either fly ash or LKD were added, pH increased regardless of the percentage of admixture (Figure 3.5). As with the WLT, the addition of LKD appears to have a greater effect on pH than the addition of fly ash since the CaO content of LKD (60%) is much higher than that of all three fly ashes utilized in this study. The pH values can also be correlated with the Ca content of the ash. For instance, Paul Smith (PS) fly ash has lower pH than Brandon Shores (BS) fly ash (Table 3.2), which yielded in relatively lower stabilized pH values in CLTs (Figure 3.5).

3.4.3 Metal Leaching

Table 3.7 shows that the peak concentrations of all metals in all soil-fly ash mixtures except Al concentrations or other metal concentrations were below the groundwater quality limits. It should be noted that Al is on the EPA list of secondary drinking water regulations, and there are no limits for Al specified in Maryland groundwater protection guidelines.

Figures 3.6 and 3.7 show a series of CLT elution curves. All elution curves for each metal for all specimens are in the Appendix B. The curves suggest a high initial leaching of the metals followed by a sharp decrease to near constant concentrations after approximately 50 pore volumes of flow, with few exceptions. This type of leaching behavior is called first flush pattern and occurs due to release of the metals from the water soluble fraction as well as from the sites with low adsorption energies. The initial pH values of the effluent solution are another potential explanation for the first flush pattern leaching of Al and Cr metals. The range of effluent (pH= 10-12) observed in the current study suggests that, Al and Cr are likely to be available in their anionic species in the environment. In this pH range the dominant Al species are $Al(OH)_4^-$ and $Al(OH)_5^{-2}$, and the Cr species are $HCrO_4^-$ and CrO_7^{-2}, CrO_4^{-2}. Cr (VI) is a toxic Cr species and an acute irritant for living cells and can be carcinogenic to humans via inhalation (Whalley et al. 1999). Of the eight metals considered, Cr ,Zn and Al are the only metals that increase with increasing pH. While anionic species of Cu, Fe, Sb, Mn and V may exist in the environment, the pH range observed in the current study is most conducive to the existence of their cationic species. At basic pHs, the availability of deprotonated (negatively charged) surface increases

(Stumm and Morgan1996). This may have led to an increase in adsorption of cationic species and caused a decrease in the concentrations of Cr, Cu, Fe, V, Sb and Mn into the solution. Since the initial pH of the effluent was high, it probably enhanced the solubility of anionic species of these Cr, Al, Zn metals due to unavailability of positively charged surface species for complexation. However, the pH values decreased from pH~12 to pH~10.5 after nearly 50 pore volumes of flow and caused a decrease in the solubility of anionic species of Al, Zn and Cr in the effluent solution.

The solubility of some metals is highly dependent on the pH of the solution. Table 3.5 shows that the pH of the soil mixtures was very high (pH> 11.5), indicating a very basic effluent solution. It is well-known that the solubility of Cu decreases significantly with increasing pH (Ricou et al. 1999, Yan et al. 2001, Goswami and Mahanta 2007). It is assumed in alkaline conditions that Cu metals are either included in low-solubility minerals or fixed in precipitates (Wehrer and Totsche 2008), which is consistent with the findings obtained in this study. Wang et al. (2006) related ammonia content of fly ashes to Cu adsorption capability. Their results indicated that the Cu concentration increased between a pH of 7 to 10 and then began to decrease at a pH greater than 10. The variations in Cu concentrations as a result of LKD addition in this study (Table 3.7) are consistent with the findings of Wang et al. (2006).

Table 3.7 shows that the Cu in the leachate generally decreased with increasing pH. As seen in Table 3.5, an increase in LKD amount from 2.5 % to 5 % by weight caused an increase in pH of the effluent solution, which may have resulted in a reduction in Cu concentrations in the aqueous solution due to the more adsorption of Cu metals to the soil surface (Sparks 2003). Jegadeesan et al. (2008) also showed that the leaching of cationic metals such as Cu can be very low in alkaline conditions (pH > 10). Material amendments into soils that include Fe oxides and alkaline materials can also reduce the mobility and availability of metals in soil by adsorption, complexation, precipitation or combination (Kumpiene et al. 2007). Brown at al. (2005) showed that iron oxides have a high sorptive capacity for metals that help decrease metal concentrations and X-ray diffraction analyses conducted on fly ashes tested in the current study revealed significant amounts of Fe_2O_3 (3.2 – 5.8 % by weight).

The leaching of aluminum from the soil fly ash mixtures is controlled by the solubility of aluminum hydroxides (Roy 1984, Komonweeraket 2007). The leaching behavior of Al shows an amphoteric pattern which represents higher leaching concentrations at extreme pH levels and lesser leaching concentration at neutral pH (Langmuir 1997, Kenkel 2003). Tables 3.6 and 3.7 show that the Al concentrations rise with an increase in LKD and fly ash contents suggesting that Al leaching also reflects an amphoteric pattern. Aluminum is very insoluble at neutral pH (Sparks 2003) and its solubility is controlled by dissolution-precipitation oxide and hydroxide minerals (Komonweeraket et al. 2010). The behavior of Al leaching is good agreement with other studies which shows that Al leaching is the lowest at neutral pH and highest at very basic pH (Lim et al.2004, Komonweeraket et al.2010).

The amounts of metals that exist in chemical compositions of the fly ashes are also important to define the leaching behavior of the metals. The Al content, for example, is high in all three fly ashes (Table 3.3) resulting in significantly high Al concentrations in the effluent leachate. Similar to other metals studied, Al also showed the first flush leaching behavior mainly due to basic conditions at the initial pore volumes which probably enhanced the Al solubilization. Edil et al. (1992) and Chichester and Landsberg (1996) reported similar first-flush patterns for metals with high concentrations and a sharp decrease at early PVFs flowed by flattening of the elution curves during column testing of soil-fly ash mixtures. Ogunro and

Inyang (2003) also observed wash-out and detachment of Al and Cu metals by percolating solution during the initial stages of a column test. They attributed this phenomenon to an increase in the chemical potential which initiated the leaching of metals from the solid matrix into the surrounding solution. Such an increased chemical potential continued to occur until the concentration difference between the leachant and the solid material was reduced and a steady-state condition was reached.

Figure 3.7 shows that an increase in the initial Cr metal concentrations occurs with increasing fly ash content. This level of increase is due to the large amounts of Cr concentrations in the fly ash itself. At initial pore volumes of flow, relatively high levels of Cr were observed in mixtures that included 20% fly ash, however, after nearly 20 PVFs the concentrations for all mixtures were comparable. Solubility of Cr is highly dependent on pH of the aqueous solution. Cr mobility is very low at a neutral pH, but the metal is very mobile at very acidic and basic conditions. As seen in Table 3.7, an increase in LKD caused an increase in pH and Cr concentrations in the effluent leachate. At a high pH, Cr generally produces anionic species which cannot be retained on the negatively charged fly ash surfaces. No testing was conducted to identify the oxidation state of Cr speciation in the leachate, however Cornelis (2008) claimed that Cr is always hexavalent because equilibrium with insoluble Ca-Cr^{III} minerals causes $Cr(OH)^-_4$ concentrations to be very low. Cr^{III} could be found only in the soil mixtures having strong reductive capacity and low Ca contents that cause some soluble $Cr(OH)^-_4$ to exist (Cornelis 2008). Ca–Cr^{III} compounds may exist in alkaline leachates as $Ca_2Cr_2O_5$ (Jing 2006). At basic conditions, the solubility of $CaCrO_4$ is very high compared to other Cr containing compounds (Allison et al. 1991). On the other hand, most of the oxyanionic species tend to produce surface adsorption complexation with Fe oxides. Dzombak and Morel (1990) showed that desorption of Cr^{III} from Fe oxides above pH>12.5 and Cr^{VI} starts at pH >7. Pourbaix diagrams for the Cr-O-H system indicate that Cr determined in WLT leachates in the current study is likely to exist as CrO_4^{-2} or $HCrO_4^-$ for the pH conditions present (pH= 10 to 12.5) (Brookins 1988). Thus, it should be kept in mind that most of the Cr concentrations determined in the leachate are likely to be Cr^{VI} which is of concern to environmental safety (Whalley et al. 1999).

Table 3.7 shows that the leaching of antimony decreases with an increase in pH in alkaline conditions and increases with fly ash amount which is most likely due to an increase in main metal source in the soil fly ash mixture. Leaching of antimony (Sb) is significantly related to the redox potential and pH conditions of the aqueous solution. Cornelis (2008) suggests that Sb^V is more commonly found in alkaline waste leachates (pH>10). However, Leuz et al. (2006b) explained that oxidation of Sb^{III} by Fe oxides are generally faster at a high pH which is less soluble than Sb^V in alkaline conditions (Cornelis et al. 2008). Garavaglia and Caramuscio (1994) reported that no solubility-controlling solid phases exist for Sb. Jackson et al. (1999) and Komonweeraket et al. (2010) found that the leaching of Sb is the highest around neutral pH and decreases at extreme pH conditions which is in agreement with the findings of the current study.

There is growing interest in leaching behavior of Vanadium (V) over the past years. Similar to antimony, V is also very redox and pH sensitive. Some oxidation states of V can form oxyanions at very alkaline conditions which cause a desorption of V from the soil surfaces due to the negatively charged surfaces of the soil surface. Vanadium can be found as $V(OH)^+_2$, $VO(OH)^+_2$ and VO^{-3}_4 species (Cornelis et al. 2008). Pavageau et al. (2004) found only V^V in fly ash. Even though it is possible that the oxyanionic species of V desorps from the soil and fly ash particles surface, Table 3.7 shows retention of total V is higher than the release of oxyanionic V species, which may be a cause in decrease in V concentrations with an increase in LKD content from 2.5% to 5% by weight. Since the oxidation states of the both influent and effluent solutions were not constant, the oxidation states of the V may fluctuate and may not transform the oxyanionic vanadium species.

Fe and Mn metals exhibited a similar leaching behavior (Table 3.6 and 3.7). Both Fe and Mn concentrations in the aqueous solutions tended to decrease or remain nearly the same with an increase in pH. Both Mn oxides and Fe oxides are very important for the surface complexation of the other oxyanions in the aqueous solutions (van der Hoek et al.1996, Piantone et al. 2004, Kumpiene et al. 2006). Most of the oxyanions can complex during the co-precipitation of iron metals in the vadose zone (Dixit and Hering 2003, Peacock and Sherman 2004, Jegadeesan et al. 2008, Dutta et al. 2009). Precipitation of Fe^{III} starts as Fe – (hydr)oxides after pH > 6 (Espana et al. 2005, Cornelis et al. 2008 and Dutta et al. 2009). Metal adsorption of Fe-oxide is increasing with pH (Cornell and Schwertmann 2003) which causes a decrease in the metal concentrations in the effluent solutions. The current study showed that both Mn and Fe concentrations decreases with an increase in pH, which is an agreement with the previous studies (Cornelis et al. 2008, Dutta et al. 2009 and Komonweeraket et al. 2010).

Figure 3.6 shows the variation of Zn with fly ash content. The total elemental analyses conducted on the materials showed that higher amounts of Zn exist in URM than the three fly ashes (Table 3.3). Thus, an increase in fly ash content may have caused a decrease in Zn concentration in the effluent solution. Even though an increase in fly ash content caused an increase in pH of the materials tested in the current study (Table 3.5), this effect was probably suppressed by high amounts of Zn in URM. The results presented in Table 3.7 suggest that the leaching of Zn follow an amphoteric pattern, which was also confirmed by Lim (2004), Garrabrants (2004) and Komonweeraket et al. (2010). On the other hand, Jegadeesan et al. (2008) showed that a decrease in leaching of Zn with pH is due to its surface complexation to Fe-Al-oxide or silicate material or the formation of insoluble hydroxides. Futhermore, beyond neutral pH, the Zn metals start precipitating as $Zn(OH)_2$ and dissolve completely under very alkaline conditions as $Zn(OH)_3^-$ (Cotton and Wilkinson 1999). Shrivastava et al. (1998) also mentioned that Zn may be transformed to the oxidizable forms which are more soluble in alkaline conditions and lime addition may increase the possibility of this transformation in the aqueous solutions.

3.5 Comparison of WLTs and CLTs

Attempts were made to compare the water leach and column leach test data obtained from URM alone, fly ash alone and soil- fly ash-lime kiln dust mixtures. The peak effluent concentrations from the CLTs (C_i) are plotted against the concentrations from the WLTs (C_w) in Figure 3.8. The peak concentrations found in the leachate from the column leaching tests are consistently greater than the concentrations from the water leach tests. Differences in L:S ratio between the two leaching tests (a ratio of 20:1 in WLTs versus 0.1:1 in CLTs in the initial PVFs) could be responsible for the significant metal concentration differences measured in these two leaching tests. Figure 3.8 shows that C_i for Al is 2 to 50 times higher than C_w. Similarly, C_i for Cu, Zn, V, Fe, Sb and Mn is up to 40, 30, 11, 100, 50 and 20 times higher than C_w, respectively. The only exception was for the Cr concentrations, and a 1:1 linear relationship existed between concentrations measured from CLTs and WLTs. The lack of linear relationship between the WLT concentrations and the peak concentrations from CLTs for most metals could be attributed to the variation in effluent pHs. Bin Shafique et al. (2006) made similar observations during comparison of WLTs and CLTs.

The scale factors mentioned above should be used with caution as the testing conditions between the CLT and WLT are different. First, the liquid-to-solid ratio remains constant in WLTs but varies in CLTs (Ogunro and Inyang, 2003). A second issue of concern is the difference in duration of the tests. CLT is a dynamic test and the data fluctuates for an extended period of time, while WLTs are finalized in 24 hours. The peak concentrations in CLTs typically occur in the transient stage, and may be different than the ones observed in WLTs. Third, the water flows smoothly through the column set-up while in the WLTs the samples are agitated aggressively, likely enhancing the surface contact of the leaching solution and the solid particulates. This may result in both a higher leaching rate of the metals and a shorter period of time to the equilibrium state between the liquid and solid phases. The pH conditions may also be influenced by this agitation as well as by the dissolution of the mineral components of the metals that were tested. Because the speciation of Al, Cr, V and Sb are highly dependent on redox conditions, the different environments of the two tests are likely to contribute to the difference in the test results.

3.6. CHEMICAL TRANSPORT MODELING

3.6.1 Numerical Model

The flow and transport problem was simulated using WiscLEACH, a recent and verified windows-based software package for simulating water and solute movement in two-dimensional variably saturated and unsaturated media. Three analytical solutions to the advection-dispersionreaction equation are combined in WiscLEACH to develop a method for assessing impacts to groundwater and the soil vadose zone caused by leaching of trace elements from fly ashes used in highway layers.

WiscLEACH simulations were conducted to study the locations of maximum soil vadose zone and groundwater concentrations (e.g., at the centerline of the pavement structure, at the vicinity of point of compliance) and contours of trace metals are predicted at different years as a function of depth to groundwater, thickness of the base layer, percent fly ash by weight, hydraulic conductivity of the least conductive layer in the vadose zone, hydraulic conductivity of the aquifer material and the initial concentration in the fly ash.

Flow Simulation

Input to the model consists of the annual precipitation rate were found for State of Maryland from the National Weather Service, physical properties of the pavement layers and underlying soils were used from Li et al. (2007), leaching characteristics of the byproducts derived from column leaching tests and transport parameters for the subsurface layers were used from Li et al. (2007). The parameters that were used in the current study, are summarized in Table 3.8 and Table 3.9.

Figure 3.9 shows that schematic diagram of a typical highway structure including asphalt layer along with the pavement and shoulders, fly ash stabilized base layer and a subgrade. The depth of groundwater can be adjusted according to the properties of the region. All materials in the profile are assumed to be homogeneous and isotropic. In addition, in WiscLEACH it is assumed that all precipitation falling on the pavement surface, the shoulders and surrounding ground will infiltrate the soil (Li et al. 2007).

3.6.2 Model Formulation in Vadose Zone

WiscLEACH considers only steady 1D unit gradient flow in the pavement layers and the soil vadose zone and the rate of flow q_v is determined by the comparison of the least conductive layer in the profile and the annual precipitation rate. The lowest of these values are used as the rate of flow in the program. It is assumed that possible horizontal movement of the flow is ignored whereas the rate of vertical flow may change with depth, but the net infiltration rate is assumed to equal q_v. No water loss is assumed and the water infiltrates to the soil vadose zone toward groundwater without any loss on the pavement and ground surface. Surface runoff and evaporation from the pavement surface are ignored (Li et al. 2007). In the current study leaching pattern is first-flush leaching from the HCFA stabilized base layer. In WiscLEACH a first-flush leaching from the HCFA base layer is assumed to follow the ADRE with linear, instantaneous and reversible sorption (Li et al. 2007).

In WiscLEACH, transport in the vadose zone beneath the HCFA layer is assumed to follow the ADRE for 1D steady state vertical flow with 2D dispersion and linear, instantaneous and reversible sorption (Li et al. 2007).

Equation 1. $R\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} + D_Z\frac{\partial^2 C}{\partial z^2} - \vartheta_z\frac{\partial C}{\partial z}$

C: Metal concentration

T: Time

X: Horizontal distance from the centerline of the pavement

Z: Depth below ground surface

υ_z: Seepage velocity in vertical direction

D_x: Dispersion coefficient in x direction

D_z: Dispersion coefficient in z direction

R: Retardation factor

The analytical solution to Equation 1 is obtained by applying the following initial and boundary conditions (Li et al. 2007):

Equation 2.a $$C(x, z, t = 0) = \begin{cases} C_0 & at\ z_t \leq z \leq z_B \quad and - L \leq x \leq L \\ 0 & otherwise \end{cases}$$

Equation 2.b $$\vartheta_z C - D_z \frac{\partial C}{\partial z}\bigg|_{z=0} = 0$$

Equation 2.c $$\frac{\partial C}{\partial x}(\pm\infty, z, t) = 0$$

Equation 2.d $$\frac{\partial C}{\partial z} = (x, \infty, t) = 0$$

C_o: Initial metal concentration

Z_T: Depth of the top of the fly ash stabilized base layer

Z_B: Depth of the bottom of the fly ash stabilized base layer

L: Sum of the width of the shoulder and half of the pavement width

Equation 2a and 2b indicate that the fly ash stabilized base layer is the only source of trace elements and no trace elements leached from the pavements or ground surface that is above the fly ash stabilized base layer. Equations 2c and 2d imply that the effect of dispersion and diffusion in the soil vadose zone is insignificant with a distance from the pavement surface and the centerline of the pavement structure. The analytical solution to Equations 1 and 2 is (Li et al. 2007):

$$
\begin{aligned}
C(x,z,t) = \frac{C_0}{4}\Bigg\{ & e^{\left(\frac{\vartheta_z z}{D_z}\right)}\left[\left(\frac{1+\vartheta_z z}{D_z}\left(z+z_T+\frac{\vartheta_z t}{R}\right)\right) x erfc\left(\frac{R(z+z_T)+\vartheta_z t}{\sqrt{4RD_z t}}\right)\right] - exp\left(\frac{\vartheta_z z}{D_z}\right) \\
& x\left[\left(1+\frac{\vartheta_z}{D_z}\left(z+z_B+\frac{\vartheta_z t}{R}\right)\right) erfc\left(\frac{R(z+z_B)+\vartheta_z t}{\sqrt{4RD_z t}}\right)\right] + erfc\left(\frac{R(z-z_B)-\vartheta_z t}{\sqrt{4RD_z t}}\right) - \\
& erfc\left(\frac{R(z-z_T)-v_z t}{\sqrt{4RD_z t}}\right) \\
& + \sqrt{\frac{4v_z^2 t}{\pi R D_z}}\exp\left(\frac{v_z z}{D_z}\right)\left[exp\left(-\frac{[R(z-z_B)+v_z t]^2}{4RD_z t}\right) - exp\left(-\frac{[R(z+z_T)+\vartheta_z t]^2}{4RD_z t}\right)\right]\Bigg\} x \\
& \left[erfc\left(\frac{x-L}{\sqrt{\frac{4D_x t}{R}}}\right) - erfc\left(\frac{x+L}{\sqrt{\frac{4D_x t}{R}}}\right)\right]
\end{aligned}
$$

Equation 3. Analytical solutions to Equations 1 and 2

Equation 3 is applied from the surface of the pavement to the groundwater table (Fig. 9).

3.6.3 Model Formulation in Groundwater

The transportation of the trace metal elements that leach into the groundwater is at horizontal and vertical direction, although the direction of horizontal flow movement is dominant in the groundwater (Li et al. 2007). The groundwater flow is assumed to be saturated, and the transport of the trace elements is assumed to follow the ADRE with instantaneous, reversible and linear sorption as assumed in transportation in soil vadose zone (Li et al. 2007).

Equation 4. $R_w \frac{\partial C}{\partial t} = D_{xw}\frac{\partial^2 C}{\partial x^2} - \vartheta_h \frac{\partial C}{\partial x} + D_{zw}\frac{\partial^2 C}{\partial z^2} - \vartheta_z \frac{\partial C}{\partial z}$

C: Metal concentration

T: Time

υ_h: Groundwater seepage velocity in the horizontal direction

D_{xw}: Hydrodynamic dispersion coefficient in horizontal direction

D_{zw}: Hydrodynamic dispersion coefficient in vertical direction

R_w: Retardation factor in groundwater

.In Equation 4 the cross – dispersion terms are ignored due to the dominant horizontal flow in a uniform and isotropic medium (Li et al. 2007). An analytical solution to Equation 4 for the following initial and boundary conditions:

Equation 5.a $C(x, z, t = 0) = 0$

Equation 5.b $\left(\vartheta_z C - D_{zw}\frac{\partial C}{\partial z}\right)\Big|_{z=z_{GWT}} = f(x) = \begin{cases}\vartheta_z g(x, z_{GWT}, t), & x_1 \leq x \leq x_2 \\ 0, & otherwise\end{cases}$

Equation 5.c $\frac{\partial C}{\partial x}(\pm\infty, z, t) = 0$

Equation 5.d $\frac{\partial C}{\partial z}(x, \infty, t) = 0$

z_{gwt}: Depth of groundwater table

$g(t)$: Metal concentration at the groundwater table

x_1, x_2: Lateral extent over $g(t)$ applies

It is assumed that initially groundwater is not contaminated with any trace elements or any other elements that can effect to the sorption of the trace elements which is suggested by Equation 5a.

Equation 5b indicates that the amount of trace elements in the vadose zone of the soil directly above the groundwater table is equal to the amount in the groundwater. Equations 5c and 5d indicate that the effect of diffusion and dispersion in groundwater are ignorable at the locations that are very far from the centerline of the pavement and the groundwater table. The solution to Equations 4 and 5 for a condition if Z is larger than Z_{GWT} is (Li et al. 2007):

$$C(x,z,t) = \int_0^t \frac{\vartheta_z g(t-\tau)}{2R_w}\left[erfc\left(\frac{R_w(x-x_2)-\vartheta_h\tau}{\sqrt{4R_w D_{xw}\tau}}\right) - erfc\left(\frac{R_w(x-x_1)-\vartheta_h\tau}{\sqrt{4R_w D_{xw}\tau}}\right)\right] x$$
$$\left[\sqrt{\frac{R_w}{\pi D_{zw}\tau}}\,exp\left(-\frac{(R_w(z-z_{GWT})-\vartheta_z\tau)^2}{4R_w D_{zw}\tau}\right) - \frac{\vartheta_z}{2D_{zw}}\,exp\left(\frac{v_z(z-z_{GWT})}{D_{zw}}\right) x\,erfc\left(\frac{R_w(z-z_{GWT})+\vartheta_z\tau}{\sqrt{4R_w D_{zw}\tau}}\right)\right]$$

Equation 6. Analytical solution of the Equation 4 and 5

Equation 6 estimates the metal concentrations that leached from a line source at the groundwater table between X_1 and X_2.

3.6.4 WiscLEACH Results

WiscLEACH was used to predict the metal concentrations in contour graphs at different years and determine the location of maximum concentrations of the trace metals in the groundwater in 100 years. The input data in Table 3.8 used for all the soil mixture same to be consistent. The hydraulic conductivities and transport parameters of the pavement layers and soil mixtures were summarized in Table 3.9. Layer thicknesses for each different specimen were obtained from Cetin et al. (2010). The transport parameters were determined from laboratory tracer tests. The pavement properties and subgrade properties were used from Li et al. (2007). The retardation factors for all soil mixtures and different metals were shown in Table 3.10.

The pavement structural variables that were needed to be input into the program were provided by Cetin et al. (2010). The annual precipitation rate selected in this study was 2.19 m/year which is the average annual rainfall in the State of Maryland according to the U.S. Geological Survey. The leaching behavior of the four metals for all soil mixtures is shown in The Trace metals concentrations in the column leach tests (CLT) effluents are summarized in Table 3.9. The retardation factor for the specimens and the metals were determined from laboratory tracer tests and shown in Table 3.10.

Figures 3.10 and 3.11 show the contour plots of the predicted concentrations of Cr, Al, in the soil vadose zone as well as the groundwater, respectively. Other contour plots for Cr, Al, Zn and Cu are in Appendix A. The contour plots provide the predictions of the metal concentrations after 1, 2, 4 and 8 years of construction. As expected, metal concentrations in the vadose zone decrease significantly with time. Previous studies show that the leaching of metals from the fly ash amended soil exhibits a first-flush pattern, meaning initially the release of metals in the vadose zone is very high, then with time the leached metal concentrations decreases significantly (Bin- Shafique et al.2006, Goswami and Mahanta 2007). Except Al, the other metals were not observed in the groundwater even after 10 years, according to the WiscLEACH model.

As shown in Figures 3.10 and 3.11 the metal concentrations decreases with distance from HCFA stabilized layer surface and groundwater surface which is most probably due to the dispersion of the metals in the soil vadose zone. High annual precipitation rate may also have caused an increase in the leaching rate of the metals from HCFA stabilized base layer and absorbing the metals before reaching to the groundwater.

3.7CONCLUSIONS

A laboratory study was conducted to investigate the environmental feasibility of reusing chemically stabilized road surface material in construction of highway bases. Non-cementitious off-spec high carbon fly ash was activated with lime kiln dust and used to stabilize an unpaved road material (URM) collected from within the state of Maryland. The effects of both fly ash and lime kiln dust addition on environmental suitability of highway base layers were studied. A series of column leach and water leach tests were performed to evaluate leaching potential of heavy metals from high carbon fly ash. The observations from the current study are as follows:

1. The initial pH values from column leach tests (CLT) were relatively higher than those measured in water leach tests (WLT) most likely due to difference between the liquid-to-solid-ratio in two tests (a ratio of 20:1 in WLTs versus 0.1:1 in the initial PVFs in CLTs).
2. The metal concentrations increased with increasing fly ash content in WLTs which can be a result of the increased total metal amount in the soil compound. The addition of fly ash, on the other hand, caused an increase in pH values and in concentrations of Cu, Sb, V and Mn. However, the increase in the metal source (fly ash addition) seemed to be more dominant compared the effect of pH increase on metal solubility.
3. The addition of lime kiln dust (LKD) had different effects on the leaching of metal into the porous medium. Since the addition of LKD is directly correlated to a change in pH of the effluent solutions, it is an important variable to consider in the control of metal leaching. LKD addition caused a decrease in CLT concentrations of Cu, Sb, V and Mn due to an increase on the negative surface charge on the solid surface. However, Al and Cr concentrations increased with LKD addition due to an increase on the solubility of their anionic species.

4. The release of all metals from the soil mixtures in CLTs exhibited a first-flush pattern followed by a decrease in concentrations. Most of the metals were leached out at the beginning of the tests, and eventually reached an equilibrium concentration over time (at 50-60 pore volumes of flow). The higher initial pH values of the effluent solutions may have contributed to an increase in the solubility of anionic species, especially for Al and Cr.
5. An attempt was made to establish a correlation between the metal concentrations from CLTs and the metal concentrations from WLTs to provide a practical tool to field engineers. The concentrations of Al, Cu, Zn, V, Fe, Sb and Mn can be conservatively estimated from WLTs by multiplying the concentrations with 50, 40, 30, 11, 100, 50 and 20, respectively. However, caution should be exercised in using these correlation factors as the testing conditions are different for these two systems, due to different liquid-to-solid ratios, test durations, and agitation motion in the batch procedure as compared to the relatively smooth fluid movement inside the column set-up.
6. The concentrations of Cr, Sb, V, Zn, Cu, Mn, and Fe were below the EPA MCLs, WQLs and Maryland ATLs. Al was only the exception. It should be noted that Al is on the EPA list of secondary drinking water regulations, and there are no limits for Al specified in Maryland groundwater protection guidelines.
7. Numerical simulations showed that the metal concentrations decrease over time and distance and that all the metals are sufficiently dispersed in the vadose zone such that they do not reach the groundwater after approximately 8 years.

TABLES

Table 3.1**.** Index properties of the materials used in current study

Sample	C_u	Gs	w_{opt} (%)	γ_d (kN/m^3)	LL (%)	PI (%)	Gravel Content (%)	Fines Content (<75 µm) (%)	Fineness (>45 µm) (%)	Classification	
										USCS	AASHTO
URM	6.7	2.64	13.4	18.8	NP	NP	30	3	0	SP	A - 1 – b (0)
BS	0.43	2.17	–	–	NP	NP	–	80	60	ML	A - 2 – 4 (0)
PS	11	2.2	–	–	NP	NP	–	95	86	ML	A - 2 – 4 (0)
DP	3.6	2.37	–	–	NP	NP	–	85	77	ML	A - 2 – 4 (0)

.

Table 3.2. Chemical composition of the fly ashes. Concentrations of major minerals were determined by X-ray fluorescence spectroscopy analysis. All concentrations are in percentage by weight.

		Chemical Composition													
Fly ash	pH	LOI (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	K_2O (%)	TiO_2 (%)	MgO (%)	Na_2O (%)	Cr_2O_3 (%)	P_2O_5 (%)	SrO (%)	BaO (%)
BS	9.6	13.4	45.1	23.1	3.16	7.8	1.7	1.4	0.8	0.3	0.02	0.09	0.06	0.06
PS	7.55	10.7	50.8	26.9	5.5	0.7	2.2	1.5	0.6	0.2	0.02	0.2	0.03	0.05
DP	8.8	20.5	34.9	24.4	12.6	3.2	1.1	1.3	0.5	0.3	0.03	1.0	0.2	0.11

URM: Unpaved road material, PS: Paul Smith fly ash, DP: Dickerson Precipitator fly ash, BS: Brandon Shores fly ash, LOI: Loss on ignition. Gs: Specific gravity, C_u: coefficient of uniformity, C_c: coefficient of curvature, w_{optm}: optimum water content, γ_{dmax}: maximum dry unit weight, LL: liquid Limit, PL: plastic limit, NP: Nonplastic.

Table 3.3Total metal content of the fly ashes and unpaved road material from the total elemental analysis.

Sample	Al (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Sb (ppm)	V (ppm)	Zn (ppm)
URM	2367	15.5	1.28	6,313	26.5	0.02	16.5	82.3
BS	28637	65.7	74.7	34,619	114.9	0.01	164.3	58.2
PS	10060	24.3	25.3	10,757	38.2	0.02	53.7	28.5
DP	19257	47.1	58.7	12,770	38.3	0.02	82.4	45.6

Table 3.4. Legend and compositions of the mixtures.

Legend of Mixtures	Fly Ash Content (%)	LKD Content (%)	Optimum Water Content (%)	Maximum Dry Unit Weight (kN/m^3)
URM	0	0	13.4	18.8
URM+10 BS + 2.5 LKD	10	2.5	10	19.2
URM+10 BS + 5 LKD	10	5	9.5	19.2
URM+20 BS + 2.5 LKD	20	2.5	10	18.5
URM+20 BS + 5 LKD	20	5	13	17.4
URM+10 PS + 2.5 LKD	10	2.5	9.0	18.8
URM+10 PS + 5 LKD	10	5	10	18.8
URM+20 PS + 2.5 LKD	20	2.5	12	17.3
URM+20 PS + 5 LKD	20	5	13	17.0
URM+10 DP + 2.5 LKD	10	2.5	9.0	19.1
URM+10 DP + 5 LKD	10	5	10	19.4
URM+20 DP +2.5 LKD	20	2.5	10	18.1
URM+20 DP + 5 LKD	20	5	12	18.0

Note: BS: Brandon Shores fly ash, PS: Paul Smith fly ash, DP: Dickerson Precipitator fly ash, LKD: Lime kiln dust, URM: Unpaved road material. The numbers that follow the fly ashes and LKD indicate the percentages by weight of admixtures added to the soil.

Table 3.5. pH and electrical conductivity values from batch water leach tests

Specimen Name	Fly Ash Content (%)	LKD Content (%)	pH^{NaBr}	EC^{NaBr} (mmho)
100 BS	100	-	7.91	8.36
10 BS + 2.5 LKD	10	2.5	11.54	8.43
10 BS + 5 LKD	10	5	11.82	8.96
20 BS + 5 LKD	20	5	11.87	9.19
100 PS	100	-	7.53	8.36
10 PS + 2.5 LKD	10	2.5	11.67	9.07
10 PS + 5 LKD	10	5	12.02	9.91
20 PS + 5 LKD	20	5	12.04	10.06
100 DP	100	-	8.55	8.41
10 DP + 2.5 LKD	10	2.5	11.77	9.34
10 DP + 5 LKD	10	5	12.03	9.90
20 DP + 5 LKD	20	5	12.1	10.14
LKD	-	100	12.52	12.44
URM	100	-	4.81	8.08

Note: pH^{NaBr} = pH measured in WLTs with 0.1 M NaBr solution, EC^{NaBr} =electrical conductivity measured in WLTs with 0.1 M NaBr solution. 10 BS, 20 BS designate the specimens with 10 % and 20 % Brandon Shores fly ash respectively, 10 PS, 20 PSdesignate the specimens with 10 % and 20 % Paul Smith fly ash respectively, 10 DP, 20 DP designate the specimens with 10 % and 20 % Dickerson Precipitator fly ash respectively, LKD: Lime Kiln Dust).

Table 3.6. Aqueous concentrations of metals from WLTs

<table>
<tr><th rowspan="2">Specimen Name</th><th colspan="2">Aluminum (mg/L)</th><th colspan="2">Antimony (µg/L)</th><th colspan="2">Chromium(µg/L)</th><th colspan="2">Copper (µg/L)</th><th colspan="2">Iron (mg/L)</th><th colspan="2">Manganese (µg/L)</th><th colspan="2">Vanadium (µg/L)</th><th colspan="2">Zinc (µg/L)</th></tr>
<tr><th colspan="2">C_{aq}^{NaBr}</th><th colspan="2">C_{aq}^{NaBr}</th><th colspan="2">C_{aq}^{NaBr}</th><th colspan="2">C_{aq}^{NaBr}</th><th colspan="2">C_{aq}^{NaBr}</th><th colspan="2">C_{aq}^{NaBr}</th><th colspan="2">C_{aq}^{NaBr}</th><th colspan="2">C_{aq}^{NaBr}</th></tr>
<tr><td>100 BS</td><td colspan="2">557</td><td colspan="2">26</td><td colspan="2">9</td><td colspan="2">5.7</td><td colspan="2">12</td><td colspan="2">29.0</td><td colspan="2">156</td><td colspan="2">11.0</td></tr>
<tr><td>10 BS + 2.5 LKD</td><td colspan="2">6158</td><td colspan="2">6</td><td colspan="2">6.3</td><td colspan="2">2.3</td><td colspan="2">4.7</td><td colspan="2">2.0</td><td colspan="2">47.3</td><td colspan="2">4.0</td></tr>
<tr><td>10 BS + 5 LKD</td><td colspan="2">8797</td><td colspan="2">5.7</td><td colspan="2">6.6</td><td colspan="2">2.0</td><td colspan="2">4.31</td><td colspan="2">0.1</td><td colspan="2">26.4</td><td colspan="2">25.8</td></tr>
<tr><td>20 BS + 5 LKD</td><td colspan="2">17886</td><td colspan="2">6</td><td colspan="2">8.7</td><td colspan="2">2.2</td><td colspan="2">3.46</td><td colspan="2">0.2</td><td colspan="2">48.4</td><td colspan="2">21.5</td></tr>
<tr><td>100 PS</td><td colspan="2">1866</td><td colspan="2">14</td><td colspan="2">4.9</td><td colspan="2">3.2</td><td colspan="2">14.35</td><td colspan="2">11.7</td><td colspan="2">121.7</td><td colspan="2">9.1</td></tr>
<tr><td>10 PS + 2.5 LKD</td><td colspan="2">2692</td><td colspan="2">5</td><td colspan="2">3.8</td><td colspan="2">2.7</td><td colspan="2">6.9</td><td colspan="2">0.2</td><td colspan="2">37.5</td><td colspan="2">23.5</td></tr>
<tr><td>10 PS + 5 LKD</td><td colspan="2">2766</td><td colspan="2">3.6</td><td colspan="2">3.9</td><td colspan="2">2.1</td><td colspan="2">5.5</td><td colspan="2">0.1</td><td colspan="2">25.5</td><td colspan="2">51.5</td></tr>
<tr><td>20 PS + 5 LKD</td><td colspan="2">15513</td><td colspan="2">4.3</td><td colspan="2">4.2</td><td colspan="2">2.3</td><td colspan="2">3.67</td><td colspan="2">0.3</td><td colspan="2">34.8</td><td colspan="2">42.2</td></tr>
<tr><td>100 DP</td><td colspan="2">1278</td><td colspan="2">10</td><td colspan="2">7.7</td><td colspan="2">3.2</td><td colspan="2">16.76</td><td colspan="2">0.67</td><td colspan="2">135.6</td><td colspan="2">3</td></tr>
<tr><td>10 DP + 2.5 LKD</td><td colspan="2">2955</td><td colspan="2">5</td><td colspan="2">4.4</td><td colspan="2">2.7</td><td colspan="2">12.60</td><td colspan="2">0.8</td><td colspan="2">49</td><td colspan="2">14.8</td></tr>
<tr><td>10 DP + 5 LKD</td><td colspan="2">3075</td><td colspan="2">4.5</td><td colspan="2">4.5</td><td colspan="2">2.1</td><td colspan="2">7.55</td><td colspan="2">0.3</td><td colspan="2">30.5</td><td colspan="2">51.6</td></tr>
<tr><td>20 DP + 5 LKD</td><td colspan="2">6055</td><td colspan="2">5.3</td><td colspan="2">6</td><td colspan="2">2.5</td><td colspan="2">4.43</td><td colspan="2">0.4</td><td colspan="2">41</td><td colspan="2">32.8</td></tr>
<tr><td>URM</td><td colspan="2">44</td><td colspan="2"><3</td><td colspan="2">0.6</td><td colspan="2">1.26</td><td colspan="2">3.2</td><td colspan="2"><0.05</td><td colspan="2"><0.1</td><td colspan="2">58</td></tr>
<tr><td>U.S. EPA MCL (µg / L)</td><td colspan="2">200</td><td colspan="2">6</td><td colspan="2">100</td><td colspan="2">1300</td><td colspan="2">300</td><td colspan="2">50</td><td colspan="2">NA</td><td colspan="2">5000</td></tr>
<tr><td>U.S. EPA WQL (µg / L)</td><td colspan="2">750</td><td colspan="2">NA</td><td colspan="2">570</td><td colspan="2">340</td><td colspan="2">NA</td><td colspan="2">NA</td><td colspan="2">NA</td><td colspan="2">NA</td></tr>
<tr><td rowspan="2">MD ATL (µg / L)</td><td>Chronic</td><td>Acute</td><td>Chronic</td><td>Acute</td><td>Chronic</td><td>Acute</td><td>Chronic</td><td>Acute</td><td>Chronic</td><td>Acute</td><td>Chronic</td><td>Acute</td><td>Chronic</td><td>Acute</td><td>Chronic</td><td>Acute</td></tr>
<tr><td>NA</td><td>NA</td><td>NA</td><td>NA</td><td>74</td><td>570</td><td>9</td><td>13000</td><td>NA</td><td>NA</td><td>NA</td><td>NA</td><td>NA</td><td>NA</td><td>120</td><td>120</td></tr>
</table>

Notes: C_{aq}^{NaBr} = aqueous concentrations measured in WLTs with 0.1 M NaBr solution and; MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. ATL = aquatic toxicity limits for fresh water.

Table 3.7. Stabilized pH and peak effluent concentrations in CLTs.

Specimen Name	Fly Ash Content (%)	LKD Content (%)	pH	Al (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Mn (µg/L)	Sb (µg/L)	V (µg/L)	Zn (µg/L)
100 BS	100	-	8.63	1588	43	25	223	76	304	1533	128
10 BS + 2.5 LKD	10	2.5	12.1	4870	28	25	216	2	17	100	92
10 BS + 5 LKD	10	5	12.48	6850	40	15	197	0.5	9	72	113
20 BS + 5 LKD	20	5	12.53	7572	44	57	64	0.6	49	649	51
100 PS	100	-	7.56	262	76	43	174	1654	156	891	129
10 PS + 2.5 LKD	10	2.5	12.3	6028	11	15	18	1	19	89	141
10 PS + 5 LKD	10	5	12.49	6662	12	9	15.2	0.3	8	53	151
20 PS + 5 LKD	20	5	12.52	7227	15	40	13	0.4	24	487	88
100 DP	100	-	7.9	954	252	181	162	257	48	1093	78
10 DP + 2.5 LKD	10	2.5	12.1	5810	16	18	30	0.5	10	170	64
10 DP + 5 LKD	10	5	12.4	6250	26	17	21	0.3	7	78	94
20 DP + 5 LKD	20	5	12.6	8644	31	24	16	1	8.7	195	60
Field Material	100	-	6.5	122	0.8	49	91	3.5	33	32	258
U.S. EPA MCL (µg / L)				200	100	1300	300	50	6	NA	5000
U.S. EPA WQL (µg / L)				750	570	340	NA	NA	NA	NA	NA
MD ATL (µg / L)				NA	NA	13000	NA	NA	NA	NA	12000

Note: 10 BS, 20 BS designate the specimens with 10 % and 20 % Brandon Shores fly ash respectively, 10 PS, 20 PS designate the specimens with 10 % and 20 % Paul Smith fly ash respectively, 10 DP, 20 DP designate the specimens with 10 % and 20 % Dickerson Precipitator fly ash respectively. LKD: Lime kiln dust

Table 3.8. Input Site Parameters for conceptual model

	Point of compliance (W_{poc}), m	Pavement Width (W_p), m	Shoulder Width (W_s), m	Depth to the ground water table (Z_{GWT}), m	Annual precipitation (Prcpt), m/year	Maximum simulation time (T_{max}), years
Constant values for all specimens	20	10.4	1.5	6	2.19	60

Table 3.9 Hydraulic Properties and transport for pavement layers and aquifer input to WiscLeach

Specimen	Layer Thickness (m)	Hydraulic Conductivity, K_s,(m/s)	θ_r	Effective Porosity, n_e	Hydraulic Gradient	α_L (m)	α_T (m)	
10 BS + 5 LKD	0.407	1.34×10^{-7}	0.0	0.23	1.0	0.04	0.004	
20 BS + 5 LKD	0.356	1.04×10^{-7}	0.0	0.31	1.0	0.07	0.007	
10 PS + 5 LKD	0.375	2.22×10^{-7}	0.0	0.26	1.0	0.06	0.006	
20 PS + 5 LKD	0.396	2.5×10^{-7}	0.0	0.33	1.0	0.03	0.003	
10 DP + 5 LKD	0.375	2.86×10^{-7}	0.0	0.24	1.0	0.01	0.001	
20 DP + 5 LKD	0.396	1.87×10^{-7}	0.0	0.29	1.0	0.02	0.002	
URM	0.791	8.2×10^{-5}	0.0	0.32	1.0	0.085	0.0085	
Pavement	0.125	5.8×10^{-7}	0.0	0.35	1.0	0.1	0.01	
Subgrade	NA	3.2×10^{-8}	0.0	0.35	1.0	0.1	0.01	
Aquifer	NA	1.2×10^{-4}	0.0	0.30	1.0	0.1	0.01	

Notes;α_L : Longitudinal dispersivity, α_T : Transeverse dispersivity, the parameters for soil – water characteristics such as parameter alpha in soil water retention function is from HYDRUS 2D Database, hydraulic gradients is assumed as 1 to simulate the natural conditions,

Table 3.10. Retardation factors of the soil mixtures for different metals

Specimen	Retardation Factor, R_d			
	Aluminum	Chromium	Copper	Zinc
10 BS + 5 LKD	2.5	4.7	5.8	3.4
20 BS + 5 LKD	1.8	7	1.2	2.8
10 PS + 5 LKD	4.8	5.2	3.5	2.8
20 PS + 5 LKD	1.2	5.3	1.2	1.8
10 DP + 5 LKD	1.2	3.7	1.7	2.3
20 DP + 5 LKD	1.75	4.7	1.2	1.8
URM	2.1	1.87	2.22	2.04
Pavement	1	1	1	1
Subgrade	3.5	3.5	3.5	3.5
Aquifer	2	2	2	2

FIGURES

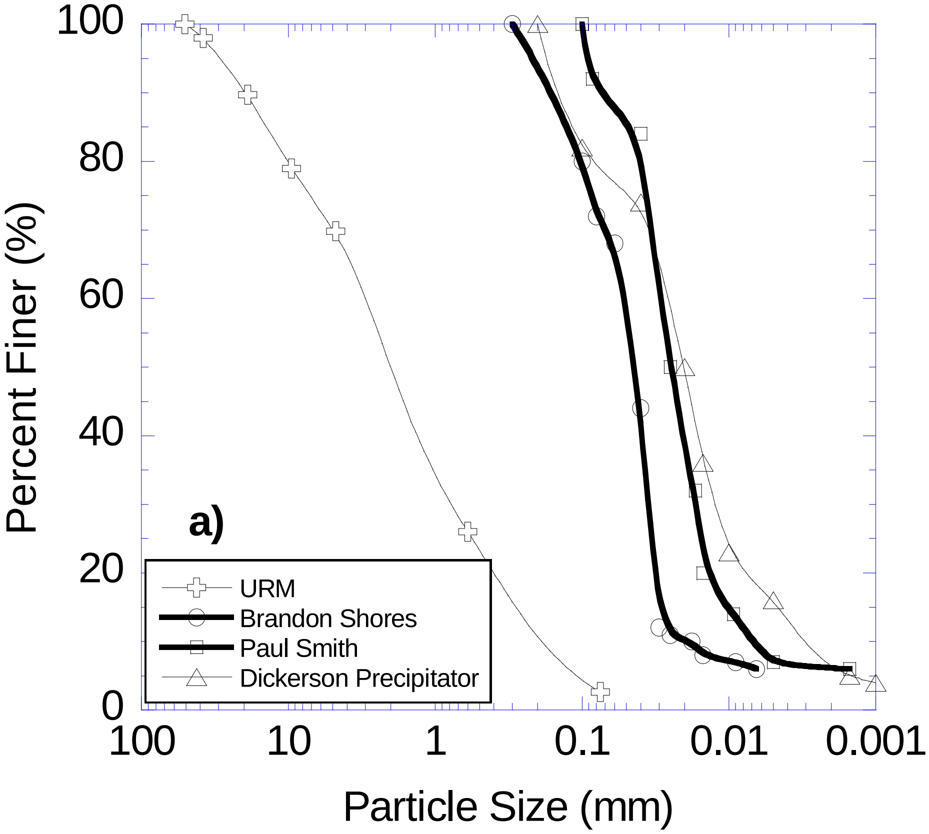


Figure 3.1**.**Particle size distribution of unpaved road material (URM) and fly ashes

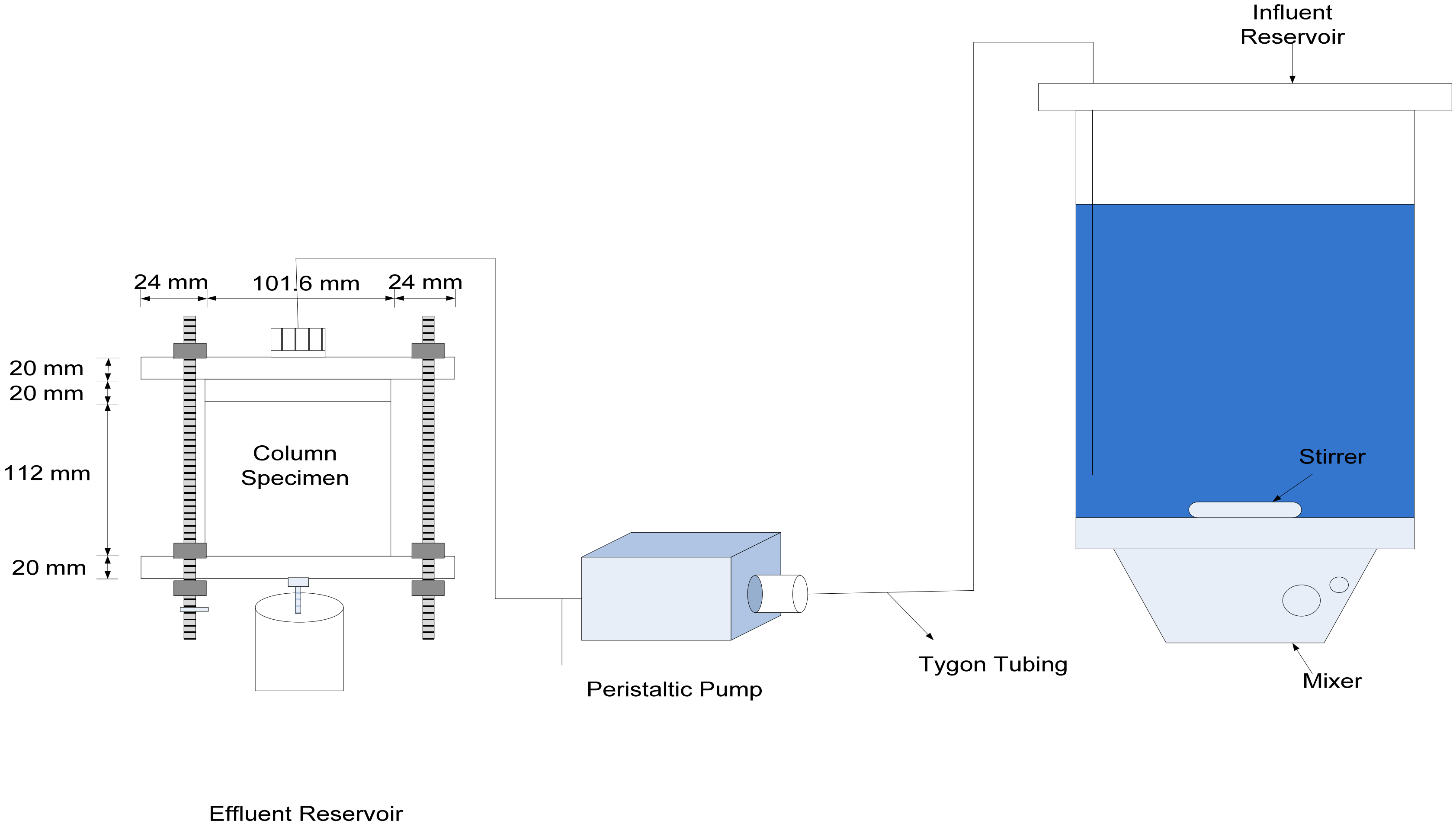


Figure 3.2. Schematic diagram of the column leach test set-up

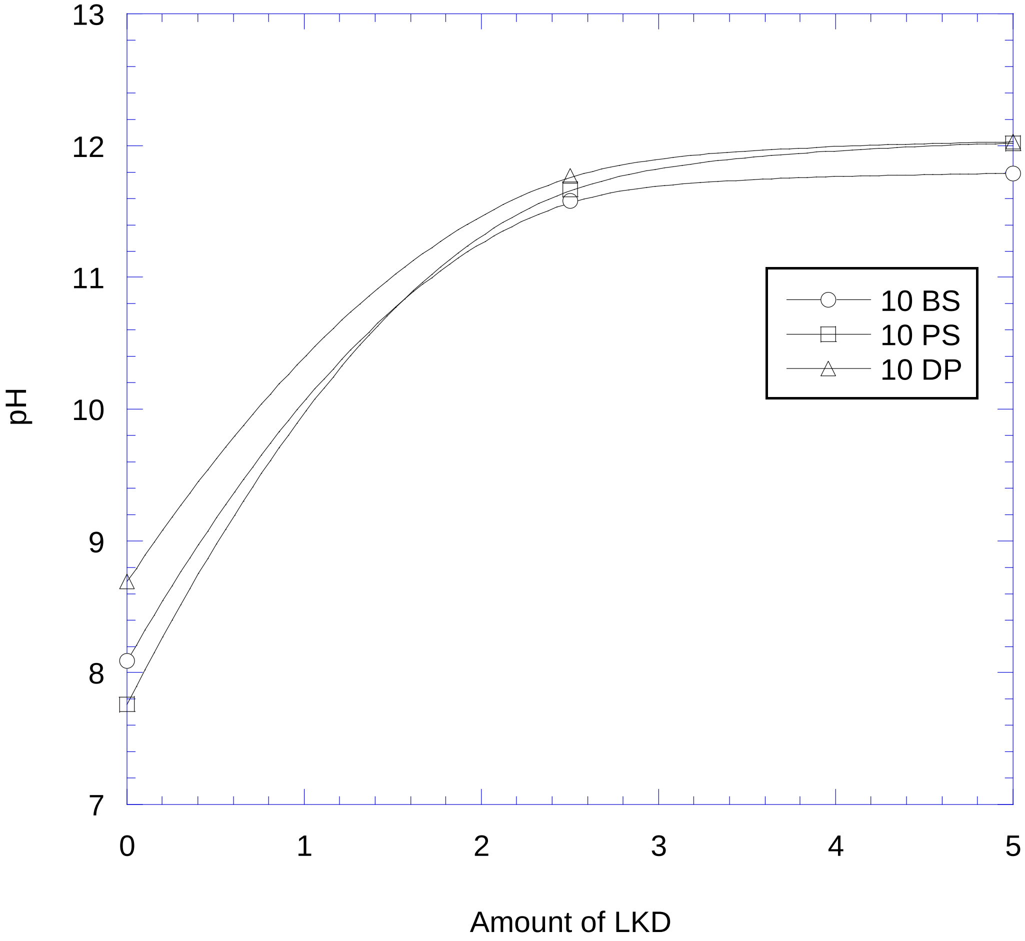
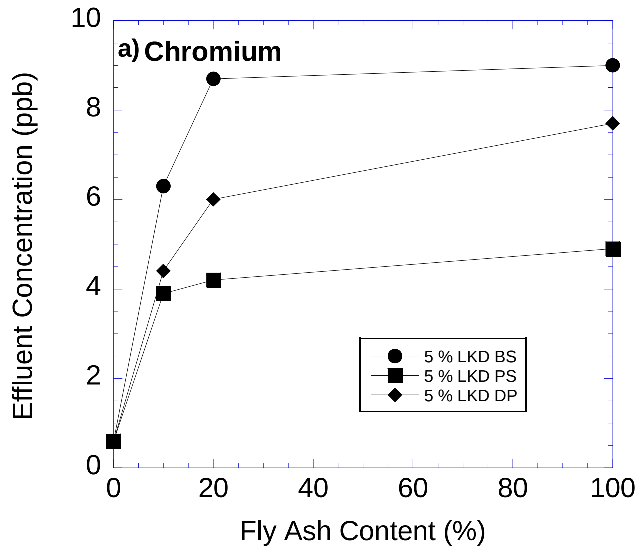
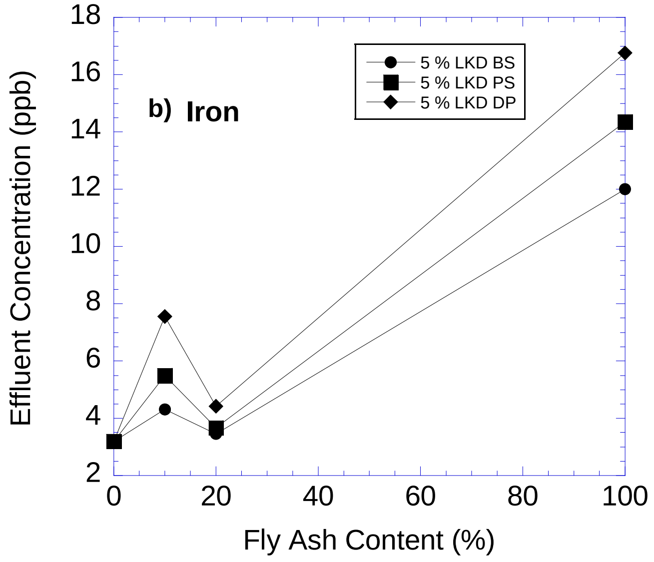


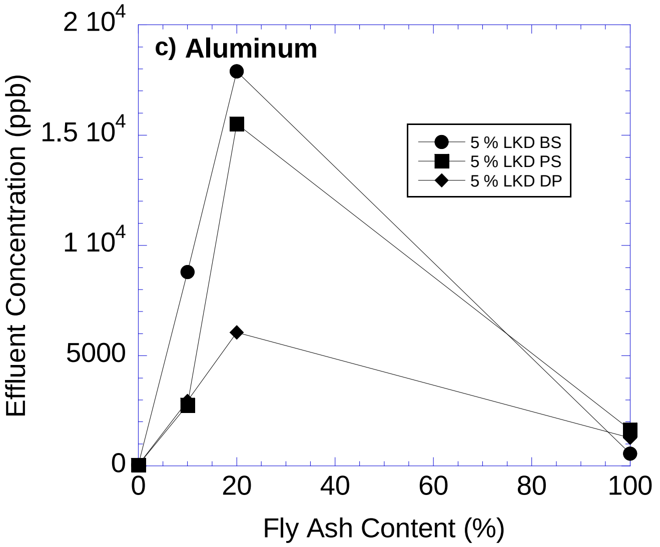
Figure 3.3 Effect of LKD content on pH of the soil mixtures
(Note: 10 BS, 10 PS, 10 DP designate the specimens with 10% Brandon Shores, Paul Smith, and Dickerson Precipitator fly ash respectively. LKD: Lime Kiln Dust).



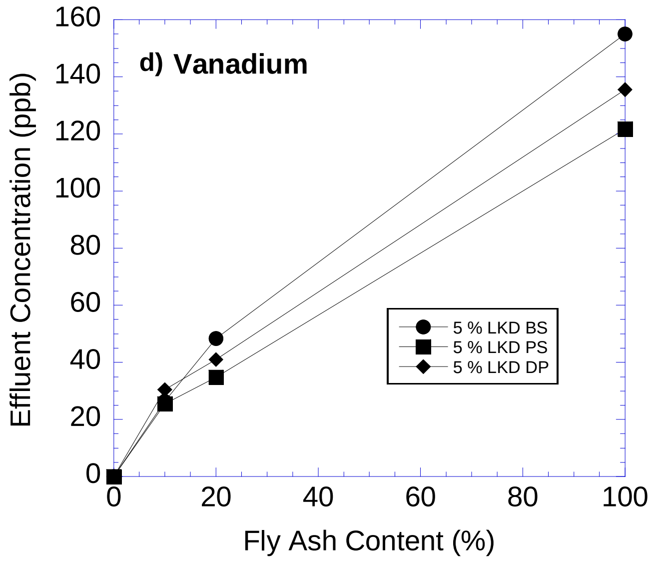
a) Chromium
Effluent Concentration (ppb)
0
2
4
6
8
10
Fly Ash Content (%)
0
20
40
60
80
100
● 5 % LKD BS
■ 5 % LKD PS
◆ 5 % LKD DP



b) Iron
Effluent Concentration (ppb)
2
4
6
8
10
12
14
16
18
Fly Ash Content (%)
0
20
40
60
80
100
● 5 % LKD BS
■ 5 % LKD PS
◆ 5 % LKD DP



c) Aluminum
Effluent Concentration (ppb)
0
5000
1 10^4
1.5 10^4
2 10^4
Fly Ash Content (%)
0
20
40
60
80
100
● 5 % LKD BS
■ 5 % LKD PS
◆ 5 % LKD DP



d) Vanadium
Effluent Concentration (ppb)
0
20
40
60
80
100
120
140
160
Fly Ash Content (%)
0
20
40
60
80
100
● 5 % LKD BS
■ 5 % LKD PS
◆ 5 % LKD DP

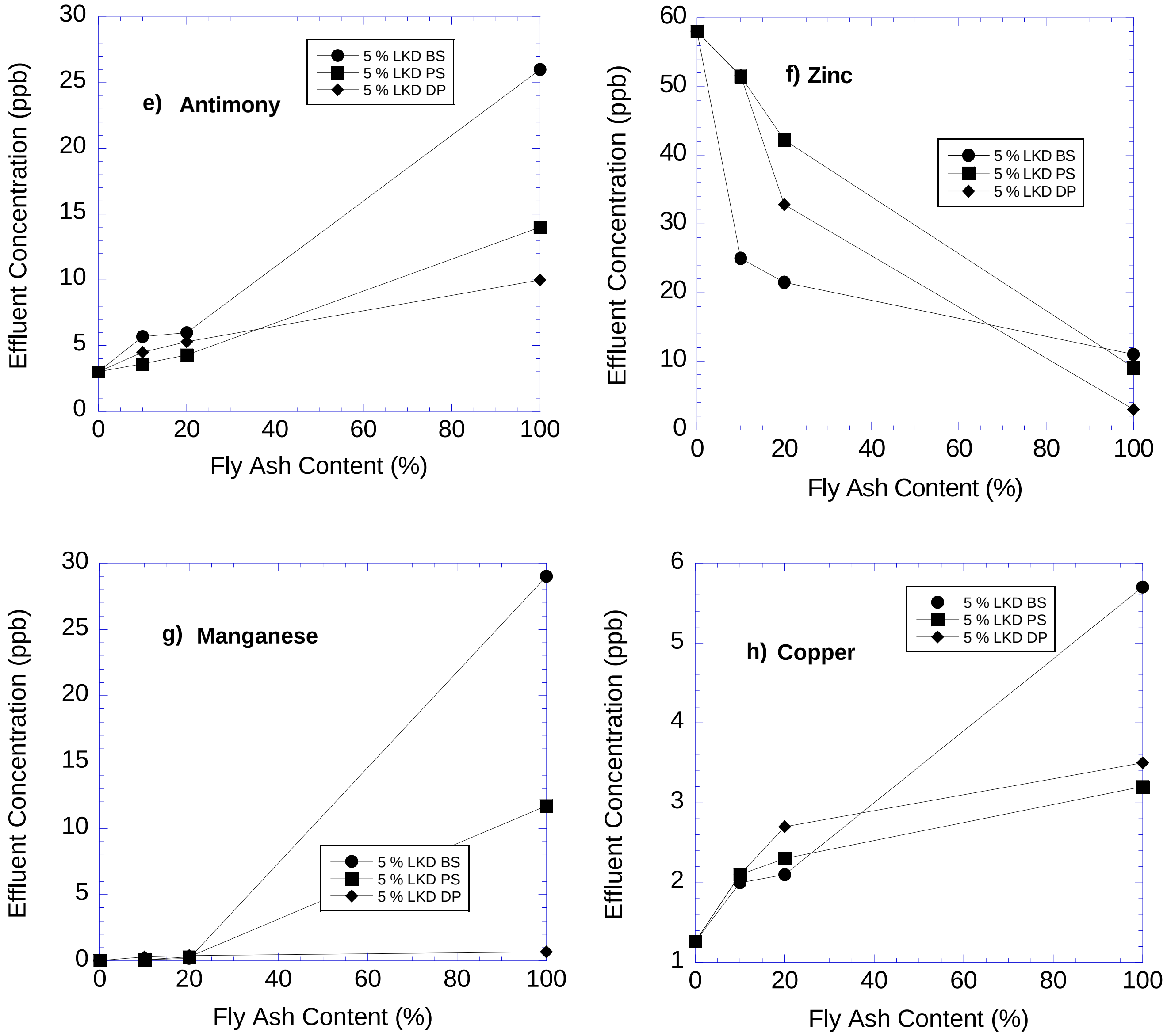


Figure 3.4 Concentrations of eight metals in effluent from WLTs
(Note: BS= Brandon Shores, PS= Paul Smith, DP= Dickerson Precipitator fly ash respectively. LKD: Lime Kiln Dust).

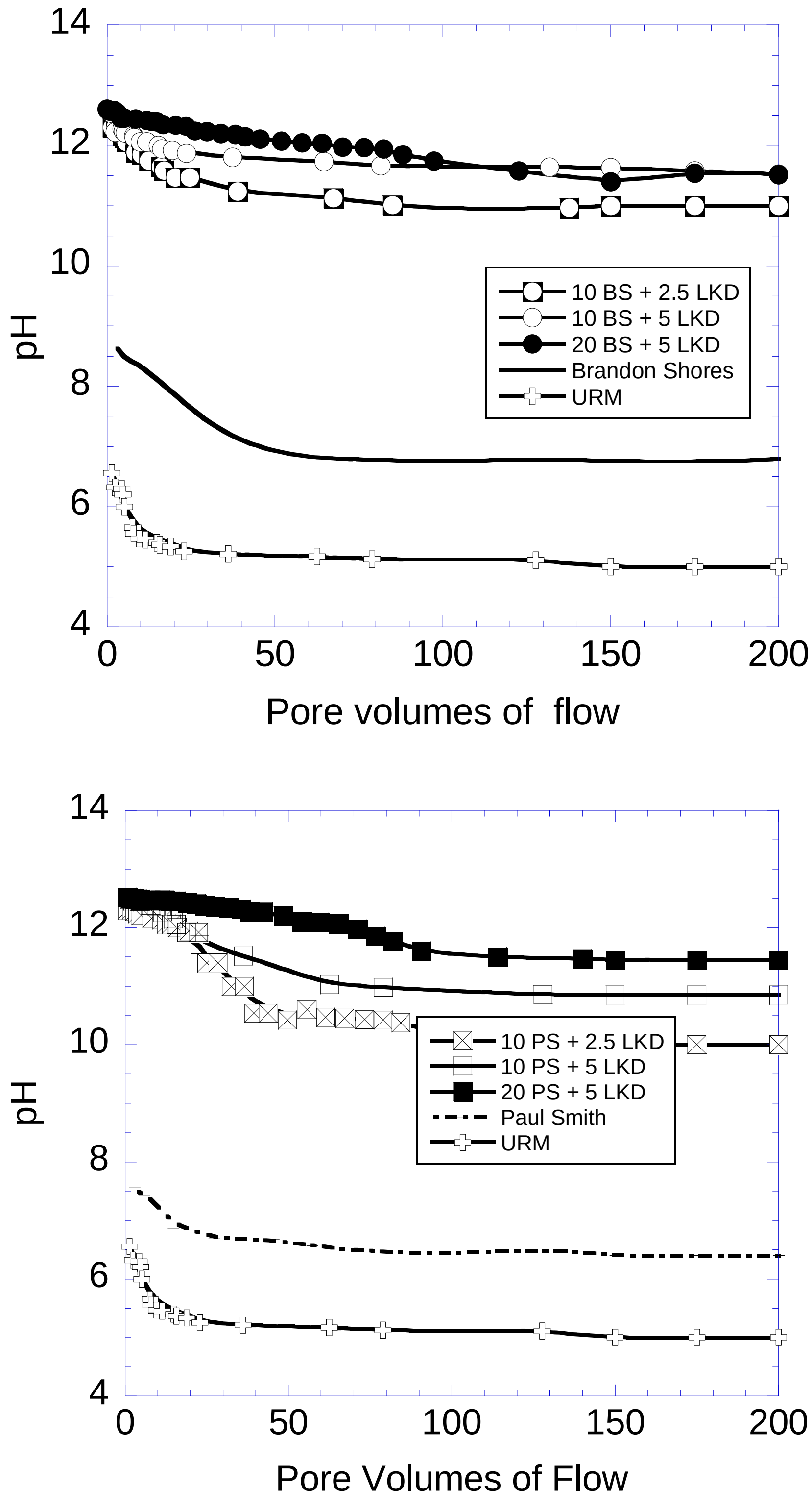


Figure 3.5 pH of the effluent from CLT conducted with soil mixtures
(Note: 10 BS, 20 BS, 10 PS, 20 PS designate the specimens with 10% and 20% Brandon Shores, and Paul Smith fly ash respectively. LKD: Lime Kiln Dust).

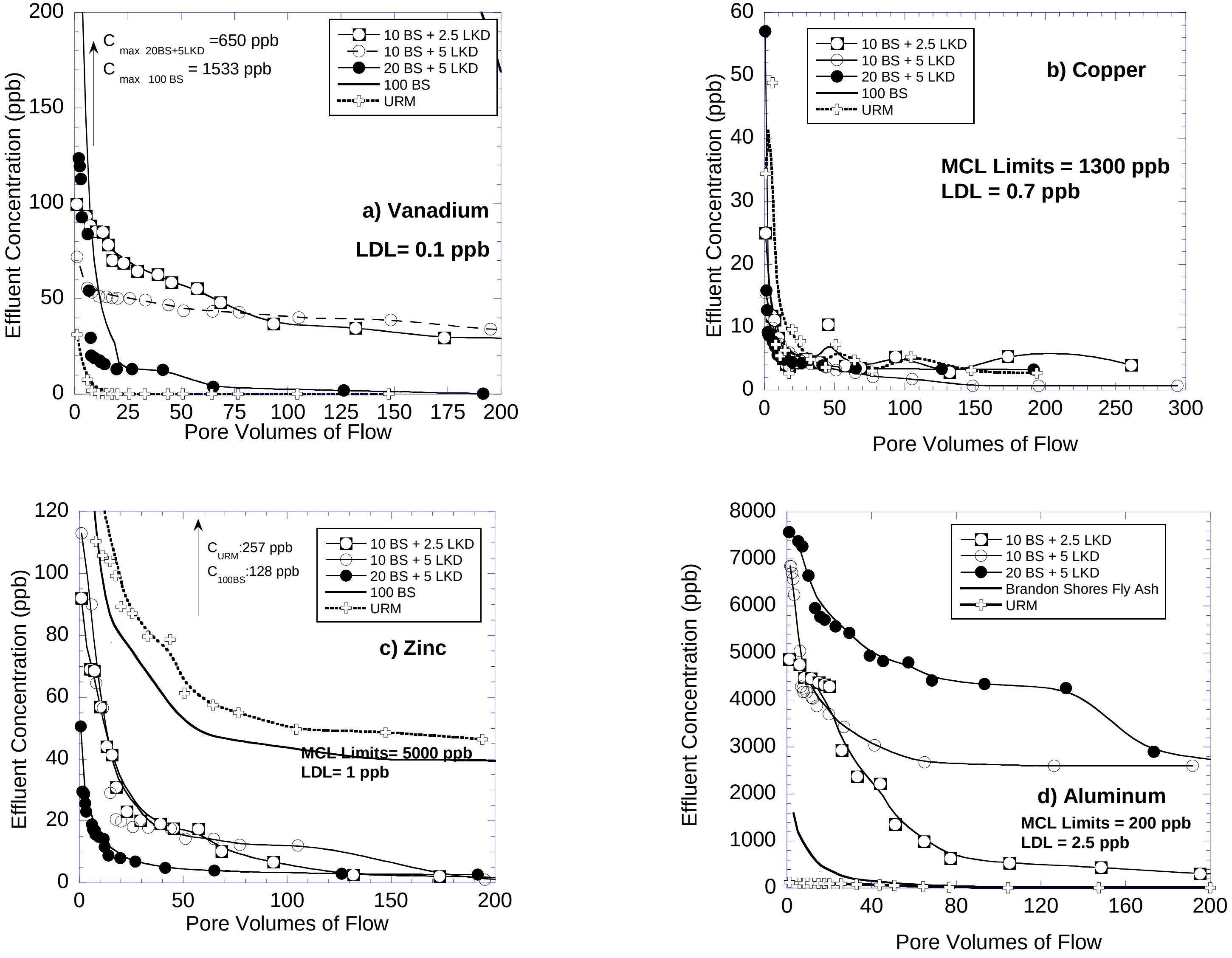


Figure 3.6. Elution curves (a) for Vanadium, (b) for Copper, (c) for Zinc (d) and for Al
(Note: 10 BS, 20 BS, designate the specimens with 10% and 20% Brandon Shores fly ash. LKD: Lime Kiln Dust. LDL: Lowest Detection Limits, MCL: Maximum contaminant level for drinking water).

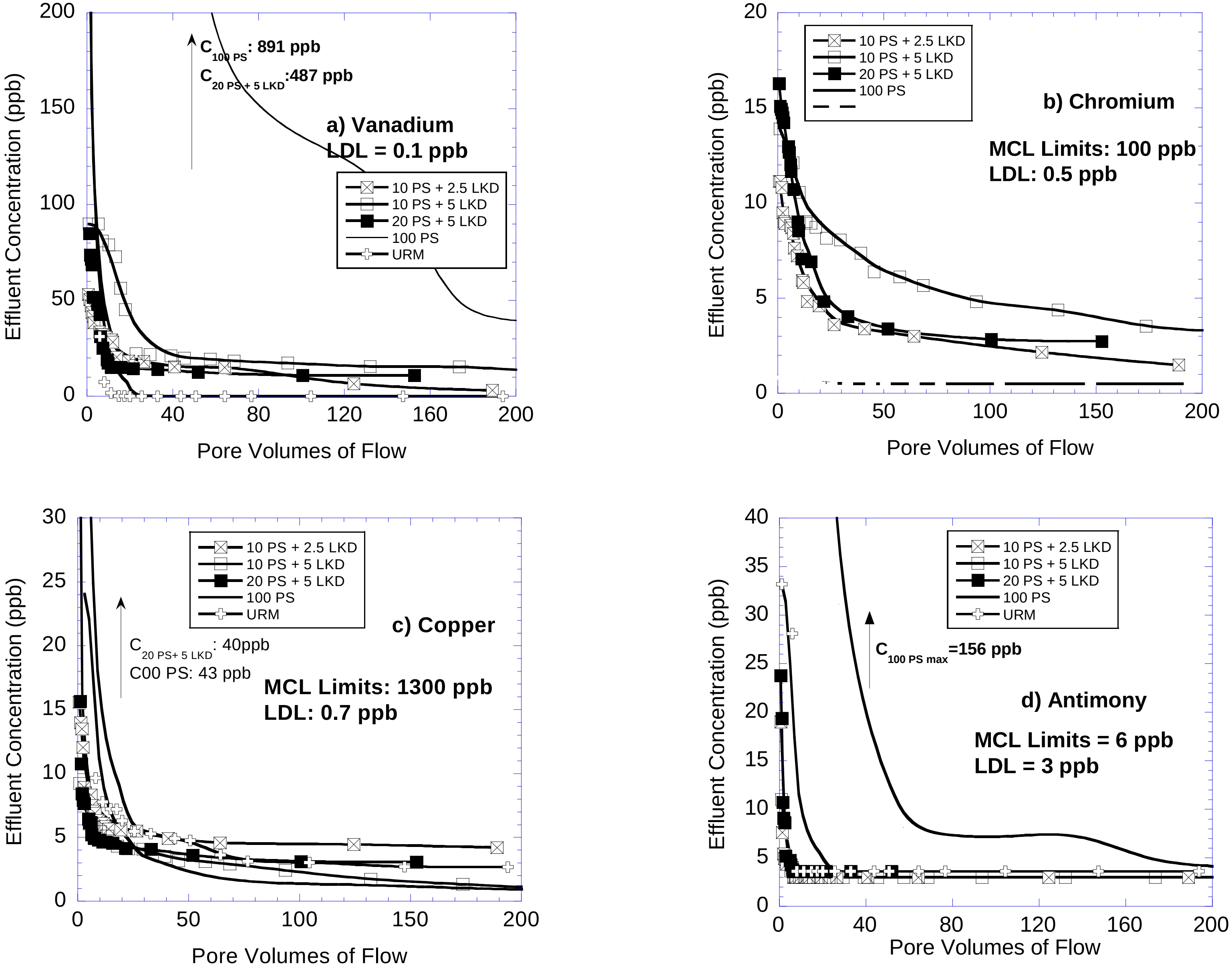
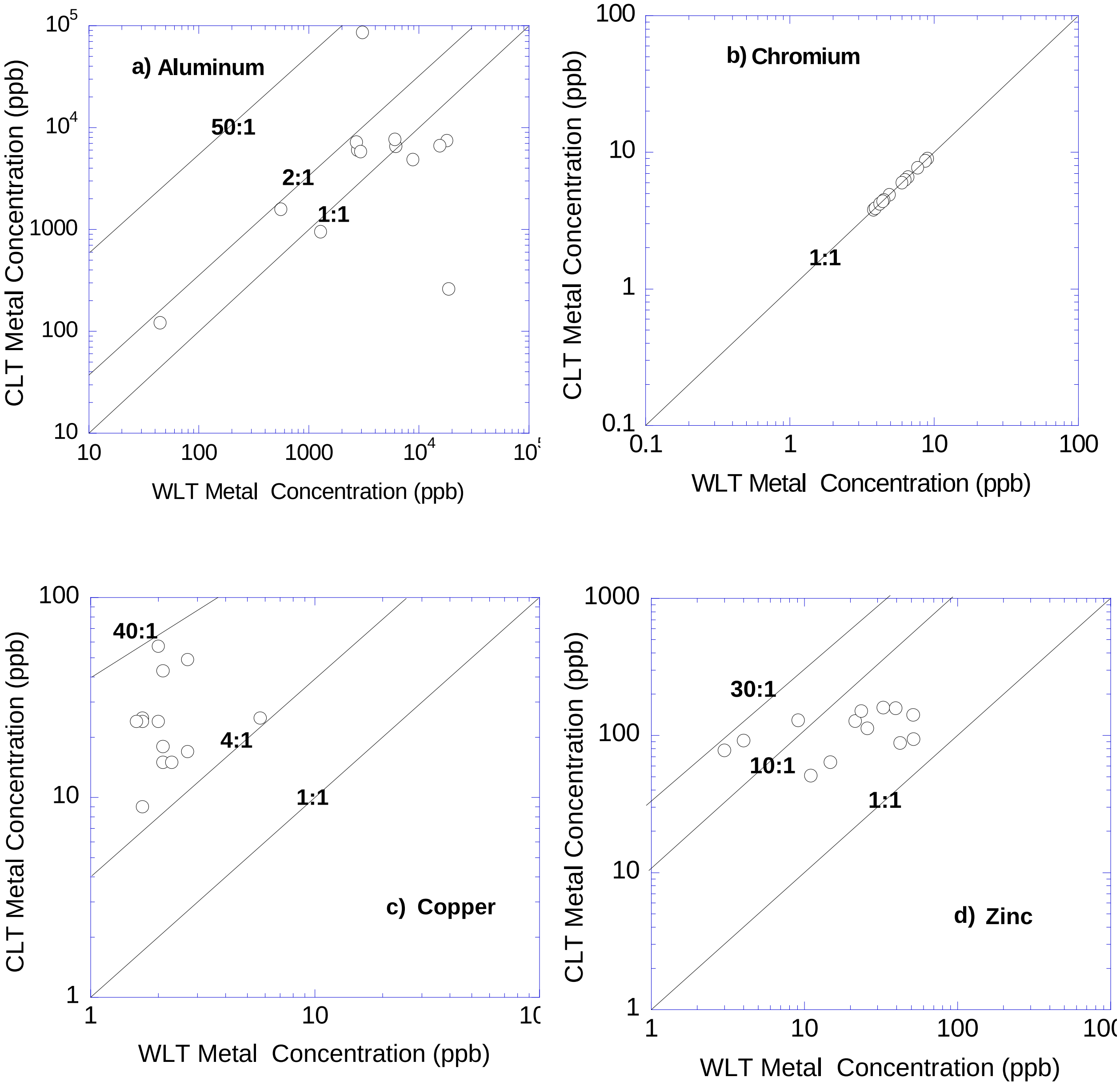


Figure 3.7 Elution curves (a) for Antimony, (b) for Chromium, (c) for Iron.
(Note: 10 PS, 20 PS, designate the specimens with 10% and 20% Paul Smith fly ash. LKD: Lime Kiln Dust. LDL: Lowest Detection Limits, MCL: Maximum contaminant level for drinking water).


a) Aluminum
50:1
2:1
1:1
CLT Metal Concentration (ppb)
WLT Metal Concentration (ppb)
10^5
10^4
1000
100
10
100
1000
10^4
b) Chromium
1:1
100
10
1
0.1
0.1
1
10
100
40:1
4:1
1:1
c) Copper
1
10
100
30:1
10:1
1:1
d) Zinc
1000
100
10
1
1
10
100

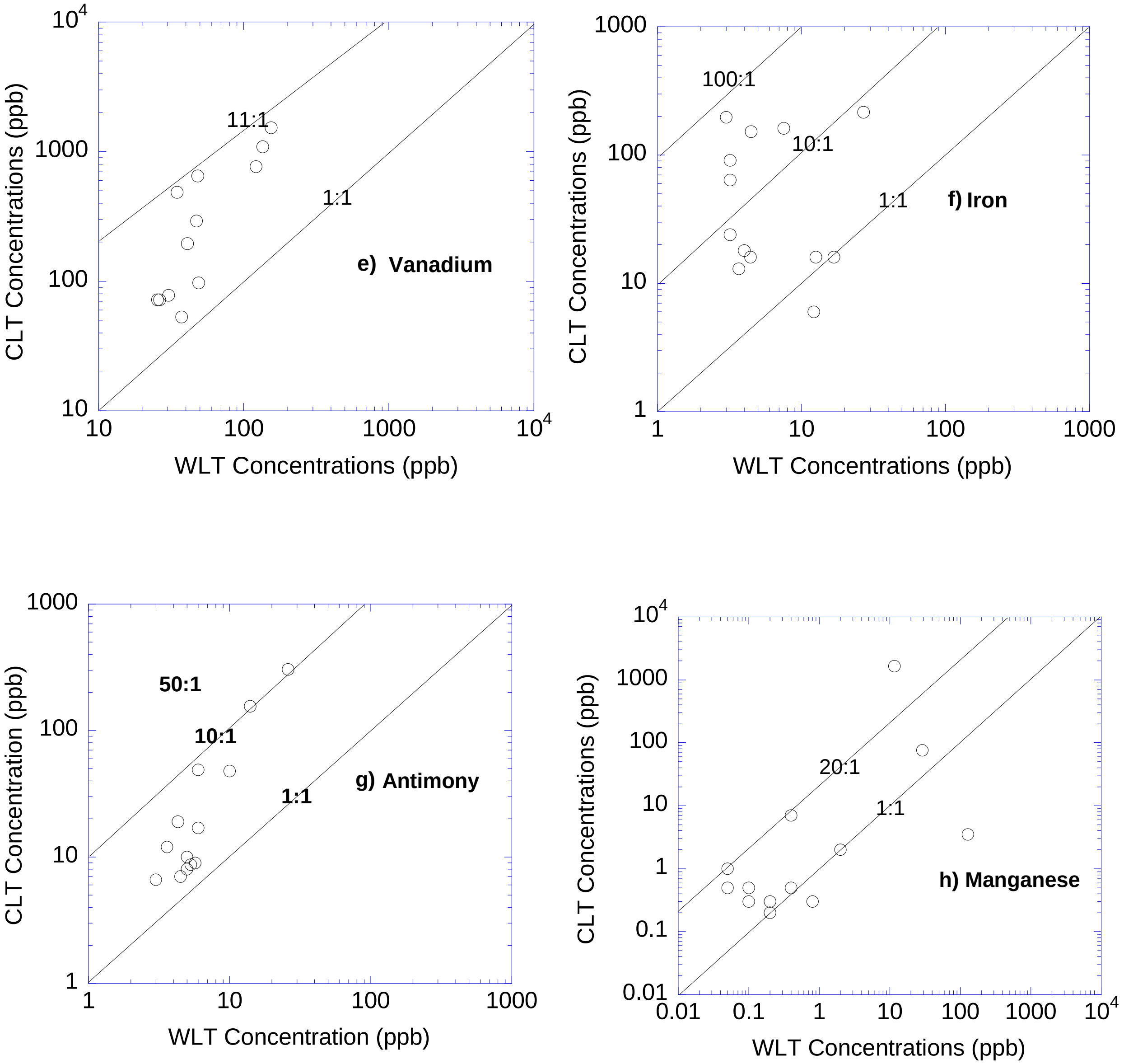


Figure 3.8 Comparison of peak effluent concentrations of eight metals from the CLTs and the WLTs

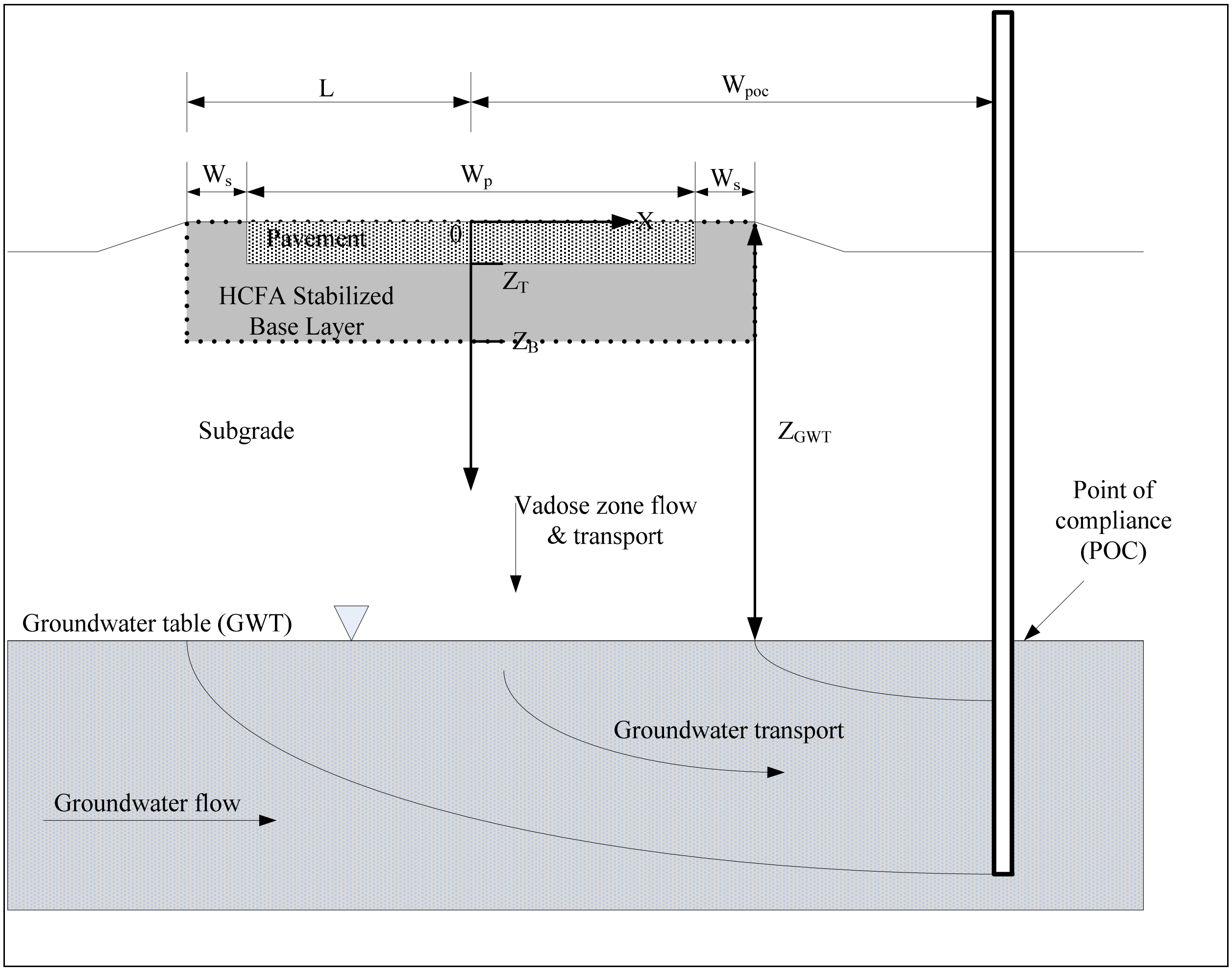


Figure 3.9 Conceptual model in WiscLeach for predicting impacts to the vadose zone and groundwater from HCFA stabilized highway base layer

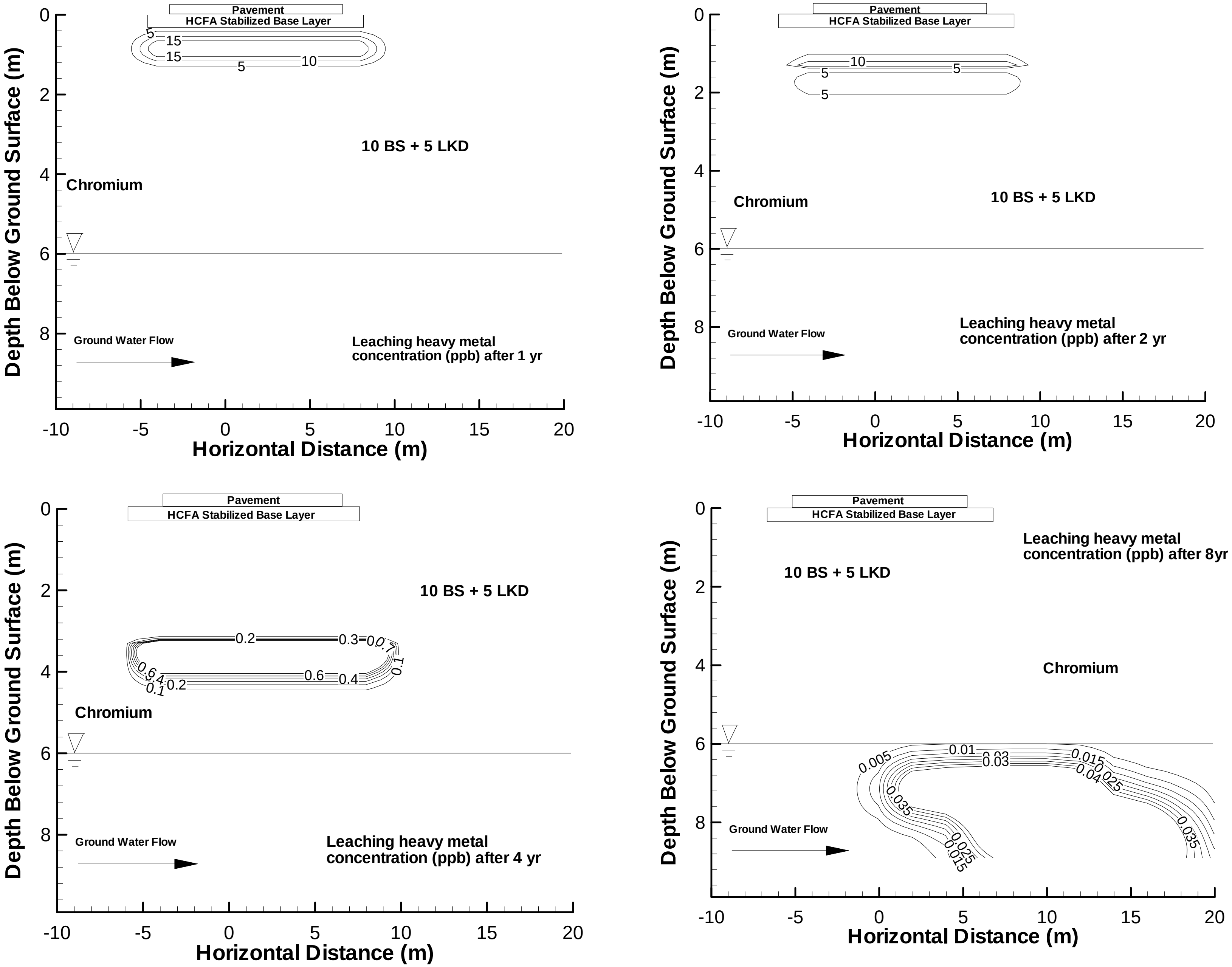


Figure 3.10 Predicted Cr concentrations in vadose zone and ground water (Note: 10 BS designate the specimens with 10 % Brandon Shores fly ash, LKD: Lime Kiln Dust

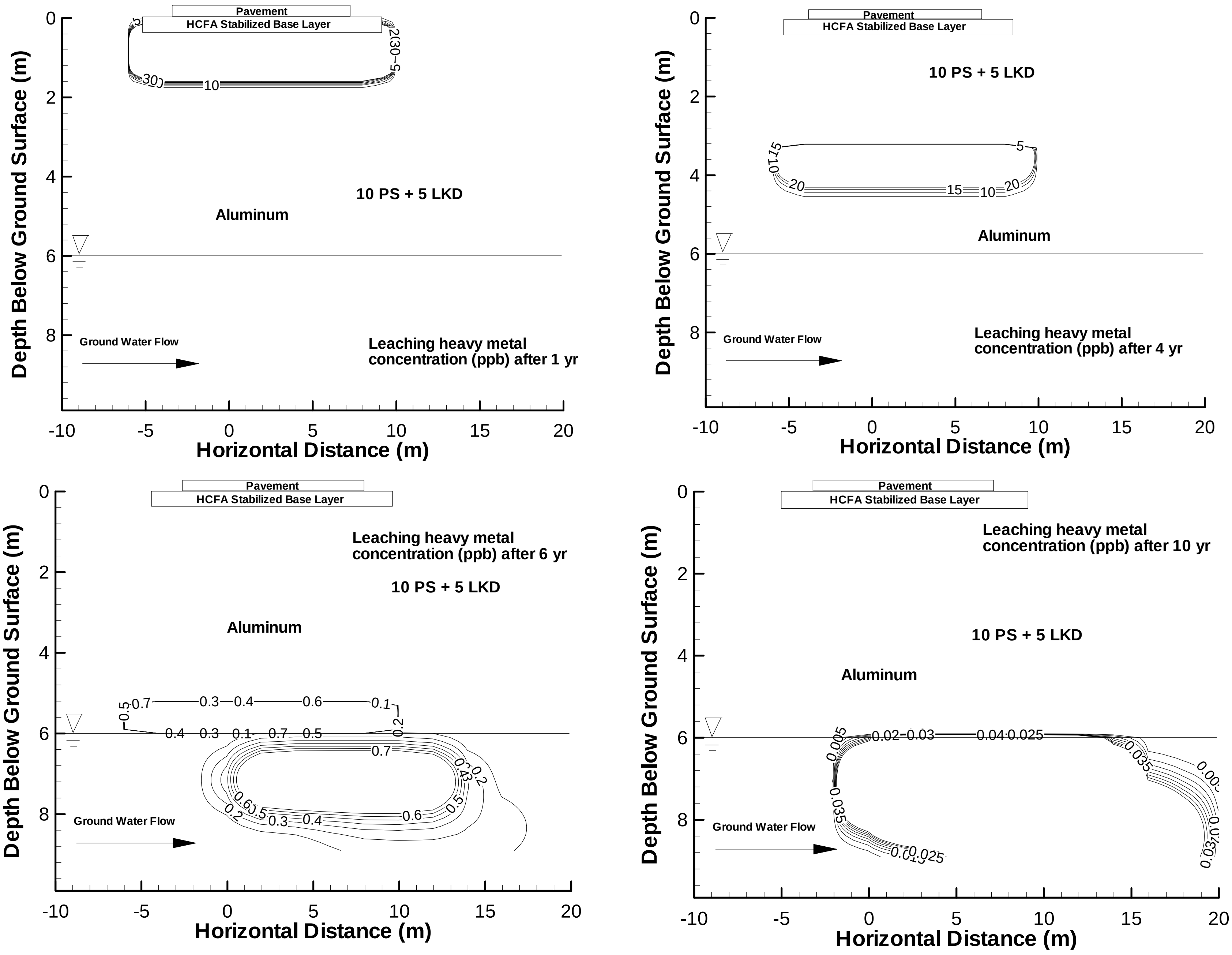


Figure 3.11. Predicted Al concentrations in vadose zone and ground water (Note: 10 PS designate the specimens with 10 % Paul Smith fly ash, LKD: Lime Kiln Dust

4 LEACHING OF METALS FROM HCFA AMENDED STRUCTURAL FILLS

4.1 INTRODUCTION

The objective of the current study in this section is to evaluate the leaching potential of embankment construction materials mixed with fly ash relative to those stabilized with conventional materials, and to evaluate the potential groundwater and surface water impacts. The beneficial reuse of fly ash in embankments construction not only helps ease one of the most pressing environmental problems (safe disposal), but may result in significant cost savings as well.

American Society of Civil Engineers estimates that $1.6 trillion is needed over a five-year period to bring the nation's infrastructure to a good condition. A large portion of the earthen materials needed for these transportation infrastructure projects have the potential to use recycled materials to aid in their stabilization; however, these materials must be also be safe for the environment in which they are placed. This issue becomes more critical if recycled materials are used in applications such as embankment repair and construction, where surface waters may be affected.

Utilization of fly ash in embankment construction has been documented in earlier studies (Baykal et al. 2004, Zhang and Solis 2008, Yoon et al. 2009). However, previous studies, in general, focused on the mechanical improvement of fly ash-amended embankments and no information was available for leached concentrations of metals and other inorganic under field conditions. Even though, mechanical properties of the fly ash-amended embankments deemed satisfactory, one key issue that precludes embankment stabilization with fly ash is the potential for surface and groundwater impacts caused by metals in the fly ash. Public perception on fly ash use was also affected by the failure of a dike in Tennessee. The failure of a dike built with 100% fly ash at the Kingston Fossil Plant, Tennessee in 2008 led to the release of approximately 5.4 million cubic yards of impounded fly ash onto surrounding land and into the adjacent Emory River. This event most directly affected citizens living in close proximity to the plant and indirectly impacted all coal burning utilities and other large coal users. For example, as a result of this event, the U.S. Environmental Protection Agency (EPA) directed plant operators and power companies to conduct on-site assessments to determine the structural integrity and vulnerabilities of all ash management facilities and to order repairs where needed. EPA determined in 1993 and in 2000 that waste from the combustion of coal and other fossil fuels is to be regulated as nonhazardous; however, many organizations, including Congress, are urging EPA to propose new rules regulating coal combustion waste under the Resource Conservation and Recovery Act (RCRA).

The Kingston release has focused new attention on all aspects of CCP management. Even though it was quickly recognized that the dike material was pure fly ash, additional research was warranted to ensure the environmental suitability of future soil-fly ash embankments. Moreover, high carbon fly ashes (HCFAs) may have different behavior than conventional Class F or C fly ashes and such behavior needs to be studied. In order to study the water quality impacts of fly ash amendment into embankments in Maryland, a research program was initiated. The objectives of this chapter of the current study are to determine the leaching pattern of the heavy metals and determine the effect of fly ash content and fly ash type on the leaching behavior of the trace metals from the embankments constructed with HCFA.

4.2MATERIALS

Sandy soil (borrow material) that is commonly used in embankment construction by the Maryland State Highway Administration was utilized in preparing the soil-fly ash mixtures. Soil was collected from a pit in Denton, Maryland, and was sieved through No 4 sieve (4. 75 mm) upon transporting to the laboratory. The soil was classified as poorly graded sand with silt (SP-SM) according to the Unified Soil Classification System, and A-3 (fine sand) according to the American Association of State Highway and Transportation Officials (AASHTO) Classification System. , and showed no plasticity. The physical properties of the soil along with the fly ashes are summarized in Table 4.1.

The fly ashes used in this study were collected from Brandon Shores (BS), Paul Smith Precipitator (PSP), Dickerson Precipitator (DP), Morgan Town (MT) and Columbia power plants. All fly ashes, except Columbia, were obtained from the power plants in Maryland were classified as off-spec fly ashes according to ASTM 618C. The Columbia ash, a Class C fly ash, was collected from a power plant in Wisconsin and was included in the testing program due its high CaO content and low loss on ignition value. All of the fly ashes consisted primarily of silt-size particles and contained 80 to 90% fines (passing the 75-mm sieve). Specific gravity of fly ashes ranged between 2.1 and 2.5 (ASTM D 854), and the pHs ranged between 4.5 and 9.5 (EPA Method SW- 846 Method 945), respectively. The physical properties and chemical compositions of the materials are summarized in Tables 11 and 12, respectively. Total elemental analyses of the 5 fly ashes and sandy soil were conducted following the procedures outlined in EPA SW-846 Method 6800 and summarized in Table 4.3.

Fly ash addition to the soil was 10, 20, and 40% by weight. The lower percentages were selected to cover the typical range used in soil stabilization by fly ash while 40% was chosen to study the effect of ash content on the leaching behavior. All column leach test specimens were compacted at their 2% dry of optimum moisture contents (OMCs) in an acrylic tube having a 101.6 mm inside diameter and 305 mm height. By compacting to the dry of OMC, higher hydraulic conductivities could be achieved that allow enough sample to be collected in a reasonable amount of time. Standard Proctor effort (ASTM D 698) was used during compaction consisting of 8 layers with 29 blows per layer to achieve a target dry unit weight of 19.2 kN/m^3, which is a minimum value for highway embankments specified by the Maryland State Highway Administration. The mixtures prepared with Maryland fly ashes were used directly after compaction. However, due to their high calcium content, Columbia fly ash mixtures were then cured for 7 days at 95% relative humidity and 23 C^o. Table 4.4 provides the list of soil mixtures that are used in the current study along with their maximum dry unit weights and optimum moisture contents.

4.3 METHODS

The testing procedures for WLT and CLT were same of those summarized in Section 3 tests. A series of toxicity leaching characteristic procedure (TCLP) tests were also conducted on fly ash amended borrow materials..

The soils, fly ashes their mixtures prepared for TCLP tests were the same materials prepared for WLTs. The TCLP test is designed to determine the mobility of organic and inorganic compounds present in liquid, solid and multiphase wastes. EPA Method 1311 was followed during TCLP tests. The soil mixtures were sieved through U.S. No. 3/8 inches sieve. Liquid to Solid (L:S) ratio of 20:1 was used for all soil-fly ash mixtures as used in WLTs. For all soil-fly ash mixtures, acetic acid solution with pH 5 were used as an extraction fluid. The acetate buffer is added only once, at the start of the extraction. pH and electrical conductivity measurements were recorded immediately after the sample collection. The protocol for sample preparation and preservation followed those employed in WLTs except the filtration procedure. The samples were vacuum filtered through TCLP glass fiber filters. Then filtered leachates were acidified to pH<2 with 2% HNO_3 acid solution and preserved in 4 C° for chemical analysis.

4.4 RESULTS

4.4.1 Water Leach Tests

Duplicate batch water leach test were conducted on fly ash alone, soil alone and soil – fly ash mixtures. The pH values for each specimen were measured and summarized in Table 4.5. Table 4.2 shows the chemical compositions of the fly ashes. Brandon Shores (BS) fly ash has the least CaO content in all fly ashes which could be a good explanation for the relatively lower pH obtained for this ash in the batch water leach test. Table 4.5 shows the variation of pH values and suggests a modest increase in pH with increasing fly ash content. This can be explained by the release of CaO, portlandite ($Ca(OH)_2$) and MgO minerals into the aqueous solutions (Cornelis et al. 2008). The pHs of the effluent solutions are between 5.5 and 9.8. Table 4.2 shows that there is a strong correlation between CaO contents and the pH of the effluent solutions. Morgan Town (MT) fly ash has the highest CaO content therefore the pH of the effluent solutions of the mixtures prepared with fly ash is relatively higher than others.

Table 4.5 shows that, expect the 100% fly ash specimens, the concentrations of six metals that leached from the soil mixtures are below the U.S EPA maximum concentration limits for drinking water (MCLs), EPA water quality limits (WQLs) for the protection of aquatic life and human health, and Maryland aquatic toxicity limits (ATLs) for fresh water. Arsenic, Chromium and Selenium concentrations were below the detection limits in soil mixtures, except the 100% MT and 100% PSP fly ash specimens due to the fact that As, Se and Cr show amphoteric leaching pattern (Langmuir 1997, Dutta et al. 2009, Komonweeraket et al. 2010). They dissolve lowest at the neutral pH but highest at the extreme pH conditions.

The Manganese and Boron concentrations increase with an increase in fly ash content in the soil-fly ash mixtures, except the ones prepared with MT fly ash (Table 4.5). The increase in B and Mn concentrations is not linear with fly ash content, even though the mass of metals in soil mixtures increases approximately linearly with fly ash content. Therefore, the use of linear dilution calculations will underestimate the resulting concentrations of these two metals from soil-fly ash mixtures.

Mn concentrations decrease with increasing fly ash content in soils amended with MT ashes. The leaching pattern of the Mn is generally dominated by the pH of the effluent solutions (Goswami and Mahanta 2007). Since the pH of the effluent vary between 7.2 and 10 for the soil-MT fly as mixtures, precipitation of Mn with Al-oxides and Fe-oxides occur and generates a decrease in Mn concentrations in the aqueous solutions even though the main source of metals was increased (McBride 1994, Goswami and Mahanta 2007, Jegadeesan et al. 2008).

There is no consistent relationship between the fly ash content of the soil mixtures and aluminum concentrations in the leachate solutions, except the ones prepared with MT fly ash (Table 4.5). This is somewhat expected as aluminum leaching is highly dependent on the pH of the solution, and a pH of 7 or above is usually required to see a pH effect on Al concentrations (Spark 2003). Furthermore, Al exhibits an amphoteric leaching behavior similar to As, Cr, Se (Komonweeraket et al. 2010).

4.4.2 Column Leach Tests

Figure 4.1 shows the variation of the effluent pHs as a function of pore volumes (PV) of flow. All tests were continued until a minimum of 50 pore volumes of flow was obtained to examine the behavior and persistency of the pH of the soil mixtures as discussed in Section 3. The pHs of the effluent solutions fluctuate for all specimens until 20 PV of flow then the pHs begins to remain constant. As observed in batch water leach tests, there is a strong correlation between the CaO content of the fly ashes and pH of the leachate solutions in column leach test. The pHs of the specimens prepared with Morgan Town (MT) fly ashes has the highest pH values. An increase in fly ash causes an increase in the effluent pHs of the all specimens as observed in water leach tests. Pure sandy soil has the lowest pH values.

Table 4.6 summarizes the variation of the six metal concentrations along with the pH of the aqueous solutions. Except Mn, the concentrations of Al, As, Cr, B and Se increase with an increase in fly ash content regardless of the ash type. The leaching of some of the metals exceeds the EPA MCLs, EPA WQLs and Maryland ATLs. Considering this, the design of the embankment construction should be analyzed carefully to ensure that the metal concentrations in the leachate of the solution do not exceed the quality limits mentioned above. However, column leach tests provide relatively high metal concentrations that are typically unrepresentative of field conditions (Bin-Shafique et al. 2006, Li et al. 2007). Thus, computer models, such as WisLEACH, become useful in predicting concentration profiles in the field.

As, Cr, Al and Se are the metals that generally show an amphoteric leaching behaviors. (Komonweeraket 2010). An increase in fly ash content causes an increase in the amount of main metal source and an increase in the pH of the effluent solution due to the dissolution of CaO and MgO minerals (Figure 4.2). Considering the observed pH range in the effluent of the column leach tests (pH= 5.75 – 10.0), As, Cr, Al, and Se are likely to be available in their anionic species. In this pH range the dominating Se species are SeO_4^{2-} and SeO_3^{2-} (Doina 2007), the dominant Cr species are $HCrO_4^-$ and CrO_7^{-2}, CrO_4^{-2}. It should be recognized that Cr (VI) is a toxic Cr species and an acute irritant for living cells and can be carcinogenic to humans via inhalation (Whalley et al. 1999).

Boron concentrations also increase with increasing fly ash content. However, B has cationic species and these species are adsorbed by the soil and fly ash particles in the aqueous solution or precipitated with Al-oxides and iron oxides at pH > 6.5 (Pagenkof and Connolly 1982). Therefore, the B concentrations are expected to decrease with an increase in pH of the effluent solution. However, an opposite trend is observed for the specimens tested in the current study. Figure 3.3 and Table 6 show that an increase in fly ash content increases the B concentrations in the effluent solution. It is speculated that the large amounts of boron in the fly ash is the main cause for the observed pattern (Table 4.3).

Table 4.6 and Figure 4.2 show that the leaching patterns of the Mn are strongly dominated by the pH of the effluent solutions. Mn tends to decrease with pH. In addition, Mn metals precipitate by complexing with cationic metals that exist in the aqueous solutions such as, Zn, Cu, Cd, Cr and Ca. Mn concentrations only increase with BS fly ash alone and PSP fly ash alone which have both pH around 7. However, the leaching of Mn is lower with MT fly ash alone compared to soil mixtures prepared with lower amount of MT fly ashes. This trend observed is due to the high pH of the leachate solution of the soil mixtures prepared with MT fly ash. No clear trends are evident for the mixtures amended with Columbia and Dickerson Precipitator fly ashes as these tests have not been completed yet.

Figure 4.3 to 4.9 show a series of column leach test elution curves for the specimens tested so far. The curves for all but As suggest a high initial leaching of metals followed by a sharp decrease to near constant concentrations after 5-15 pore volumes of flow. This is called first-flush of leaching and occurs due to the release of metals from the water soluble fraction as well as from the sites with low adsorption energies. The leaching curves for As metals showed a lagged flush response. The leaching of As metals keep increasing until 10-20 pore volumes of flow then start decreasing dramatically. The As concentrations that were leached out from the specimens prepared with 10% and 20% MT fly ashes were generally below the detection limit (0.01 ppm) and did not exhibit any clear leaching trend. The specimens prepared with 40% and 100% fly ashes showed lagged response type of leaching patterns. The As concentrations decreased significantly in the first 3-4 pore volumes of flow then increased up to 35 – 40 pore volumes of flow followed by a dramatic decrease. In general, the immobility of the metals causes a lagged response type leaching pattern in the aqueous solution (Sauer et al. 2005. Arsenic is very mobile at extreme acidic and extreme basic conditions (Komonweeraket et al. 2010, Dutta et al. 2009). The pHs of the effluent solutions of all specimens in the current study are either lower than 10 or higher than 6, which could be a reason for observing a lagged response leaching pattern for As.

4.4.3 Toxicity Leaching Procedure Tests

Duplicate Toxicity Leaching Procedure tests (TCLPs) were conducted on soil alone, fly ash alone and soil-fly ash mixtures. As expected, the effluent pH values of the specimens were stabilized at a pH of 4.8 to 4.9 except the specimens prepared with MT and Co fly ashes. The effluent solutions of these specimens were not buffered due to the high CaO content in these two fly ashes. Leaching of CaO to the aqueous solutions increased the pH values of the effluent solutions as seen in Table 4.7. Table 4.7 indicates that an increase in fly ash content generally caused an increase in the all six metals (Al, As, B, Cr, Mn, Se) concentrations regardless of fly ash types.

4.4.4 Comparison of the Leaching Results of Different Tests

Attempts were made to compare the water leach and column leach test data, column leach data and TCLP data, and TCLP data and WLT data obtained from sand alone, fly ash alone and soil- fly ash mixtures. The peak effluent concentrations from the CLTs are plotted against the concentrations from the WLTs in Figure 4.10. The maximum concentrations found in the leachate from the column leaching tests are consistently greater than the concentrations from the water leach tests. Differences in L:S ratio between the two leaching tests (a ratio of 20:1 in WLTs versus 0.1:1 in CLTs in the initial PVFs) could be responsible for the significant metal concentration differences measured in these two leaching tests. Figure 4.10 shows that the maximum concentrations of the Al, As, B, Cr, Mn and Se from CLTs is up to 16, 100, 100, 100, 35 and 50 times higher than the metal concentrations obtained from WLTs, respectively.

In addition, the maximum concentrations found in the leachate from the column leaching tests are consistently greater than the concentrations from the TCLP tests. Figure 4.11 shows that the maximum concentrations of the As, B, Cr, and Se from CLTs is several times higher than the metal concentrations obtained from TCLPs, respectively. No relations were found between CLT and TCLP results for Al and Mn metals concentrations. Furthermore, Figure 4.12 shows that the concentrations of the As, B, Cr, Mn and Se from TCLPs is up to 20, 20, 10, 33 and 16 times higher than the metal concentrations obtained from WLTs, respectively. No relation was found between TCLP and WLTs results for Al metal concentrations.

4.5 CHEMICAL TRANSPORT MODELING

4.5.1 Numerical Model

The flow and transport problem in fly ash mixed embankment construction was simulated using WiscLEACH. The input parameters that were used in the current study are summarized in Tables 4.8 and 4.9. Figure 4.10 shows that schematic diagram of a typical highway embankment structure including asphalt layer along with the pavement and shoulders, fly ash amended embankment and a subgrade.

4.5.2 WiscLEACH Results

WiscLEACH was used to predict the metal concentrations in contour graphs at different years and determine the location of maximum concentrations of the trace metals in the soil vadose zone and groundwater after a period of 50 years. The input data in Tables 4.8 and 4.9 were used for all soil mixtures. The hydraulic conductivities and transport parameters of the pavement layers and soil mixtures are summarized in Table 4.9. The transport parameters were determined from laboratory tracer tests. The pavement properties and subgrade properties are taken from Li et al. (2007). The retardation factors along with chromium concentrations for four different soil mixtures, S – 20 DP, S – 40 DP, S – 20 PSP, S – 40 PSP are shown in Table 4.9. (Note: 20 DP, 40 DP, 20 PSP, 40 PSP designate the specimens with 20% and 40% Dickerson Precipitator, 20% and 40% Paul Smith Precipitator fly ash respectively). The annual precipitation rate selected in this study was 1 m/year, the average annual rainfall in the State of Maryland according to the U.S. Geological Survey.

Figures 4.14-4.17 show the contour plots of the predicted concentrations of Cr in the soil vadose zone as well as the groundwater. The contour plots provide the predictions of the metal concentrations generally after 5, 10, 20 and 50 years of construction. WiscLEACH simulations indicate that Cr concentrations are below the EPA MCL Limits (100 ppb), except the S – 40 PSP specimen which is prepared with Paul Smith Precipitator fly ash at 40% by weight. The results indicate that the maximum Cr concentrations are reached in approximately 10 to 20 years. After it reaches its maximum concentration rate, Cr concentrations in the vadose zone decrease significantly with time. In addition, Cr concentrations are far below the EPA MCL limit when reaches to the ground water. Therefore, according to WiscLEACH results, using fly ash as a soil amendment in embankment construction is safe when it is used at reasonable percentages such as 10% to 20%.

As shown in Figures 4.14 through 4.17, the Cr metal concentrations decreases with away from the embankment surface which is most probably due to the dispersion of the metals in the soil vadose zone. High annual precipitation rate may also have caused an increase in the leaching rate of the metals from HCFA amended embankment and absorbing the metals before reaching groundwater.

4.6 CONCLUSIONS

The primary objective of this study was to investigate the leaching behavior and the controlling mechanisms of the heavy metals from fly ash-amended soils used in embankment constructions. A second objective was to estimate the potential contamination of the groundwater in an embankment construction through computer modeling. The effect of fly ash addition and its feasibility to use in geotechnical applications is studied. To achieve these objectives, a series of batch water leach test (WLTs) and column leach test (CLTs) to evaluate the leaching pattern of the metals from fly ash mixed soils. The conclusions from the current study are summarized as follows:

1. An increase in fly ash content increases the pH values of the soil – fly ash mixtures significantly due to the release of CaO, and MgO minerals regardless type of fly ashes. An increase in fly ash content from 0 to 40 % is by weight has greater influence on pH increase than an increase in fly ash content from 40 to 100 %.
2. Except the concentrations of manganese all other five metals (Arsenic, Aluminum, Chromium, Boron and Selenium) concentrations increases with fly ash amount. The solubility of Mn is highly dependent on the pH of the effluent solution and pH > 6 the Mn metals are likely to precipitate with Al – oxides and Fe – oxides.
3. The curves for all but As exhibit a first flush leaching pattern that occurs due to the release of metals from the water soluble fraction as well as from the sites with low adsorption energies. The concentrations of Al, B, Cr, Mn and Se metals begin to stabilize after 10 – 15 pore volumes of flows. Only the leaching curves for As metals showed lagged flush response. The leaching of As metals keep increasing until 10 – 20 pore volumes of flow then start decreasing dramatically.
4. The concentrations of the six metals are influenced by the pH of the effluent solution significantly which suggest that the leaching pattern is highly dependent on the pH of the aqueous solutions.
5. The concentrations of the metals exceeded the EPA MCLs beyond addition of 20% of fly ashes especially with the specimens prepared with MT fly ash, most probably due to

high pH of the MT fly ash. Increase in pH of the effluent solution increases metal concentrations, except B and Mn metals

6. The laboratory test results obtained in current study suggest that, in a real field application, aqueous samples should be collected especially during the construction phase since metal concentrations in leachates that come out of the mixtures are expected to be higher at the initial stages. The laboratory test results suggested that metal concentrations are expected to be very low after this first-flush period.
7. The WiscLeach results indicated that the maximum Cr concentrations are reached in approximately 10 to 20 years, after which Cr concentrations in the vadose zone decrease significantly with time. In addition, Cr concentrations are far below the EPA MCL limit upon reaching ground water. Therefore, according to WiscLEACH results, using fly ash as a soil amendment in embankment construction is safe when it is used at reasonable percentages.

TABLES

Table 4.1. Physical Properties of the soil and fly ashes

Sample	Gs	w_{opt} (%)	γ_d (kN/m^3)	LL (%)	PI (%)	Fines Content (<75 µm) (%)	Fineness (>45 µm) (%)
Sandy Soil	2.6	11	19.2	NP	NP	2	-
BS	2.28	16	11.87	NP	NP	84	13
PSP	2.17	22	9.96	NP	NP	87	20
DP	2.43	36	9.93	NP	NP	82	15
MT	2.4	25	13.8	NP	NP	80	16
Co	2.7	21	15.6	NP	NP	90	14.4

BS: Brandon Shores, PSP: Paul Smith Precipitator fly ash, DP: Dickerson Precipitator fly ash, BS: Morgan Town fly ash, Co: Columbia fly ash, Gs: Specific gravity, w_{optm}: optimum water content, γ_{dmax}: maximum dry unit weight, LL: liquid Limit, PL: plastic limit, NP: Nonplastic.

Table 4.2. Chemical composition of the fly ashes. Concentrations of major minerals were determined by X-ray fluorescence spectroscopy analysis. All concentrations are in percentage by weight.

Fly ash	Chemical Composition								
	pH	LOI (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	$SiO_2 + Al_2O_3 + Fe_2O_3$, min (%)	Moisture Content, (max)(%)
BS	6.1	6.2	45.1	27.1	3.16	1.07	0.6	75	0.007
PSP	6.6	6.8	52.8	21.4	6.7	0.4	1.2	81	0.004
DP	8.1	16	40.1	32.1	14.7	0.6	1.5	87	0.006
MT	9.5	8.1	49.2	25.5	13.7	2.5	1.9	88	0.011
Co	FW	0.4	31.1	18.3	6.1	19.41	3.7	56	0.004
Class C	NA	6	40	17	6	24	5	70	3
Class F	NA	6	55	26	7	9	2	50	3

BS: Brandon Shores PSP: Paul Smith Precipitator fly ash, DP: Dickerson Precipitator fly ash, BS: Morgan Town fly ash, Co: Columbia fly ash, LOI: Loss on ignition. FW: Future Work, NA : Not applicable

Table 4.3. Total metal content of the fly ashes and sandy soil material from the total elemental analysis.

Sample	Al (ppm)	As(ppm)	B (ppm)	Cr (ppm)	Mn (ppm)	Se (ppm)
Sandy Soil	28760	<3	2.86	15.5	38.16	<3
BS	21333	24.16	21.33	49.51	33.93	38.5
PSP	11770	39.68	30.43	30.08	215.64	21.4
DP	17638	41.63	78.73	42	61.58	9.47
MT	29123	52.08	240.77	68	207.73	46
Co	91848	15.01	600.4	64.6	91.58	54

Table 4.4 Legend and compositions of the mixtures.

Legend of Mixtures	Fly Ash Content (%)	Optimum Water Content (%)	Maximum Dry Unit Weight (kN/m^3)
100 Soil	0	11	19.2
S – 10 BS	10	9	19.33
S – 20 BS	20	11	18.79
S – 40 BS	40	13	16.7
100 BS	100	26	11.87
S – 10 PSP	10	11	19.11
S – 20 PSP	20	13	18.74
S – 40 PSP	40	17	16.00
100 PSP	100	22	9.96
S – 10 MT	10	10	19.24
S – 20 MT	20	11	19.03
S – 40 MT	40	12	18
100 MT	100	25	13.18
S – 10 DP	10	14	16.62
S – 20 DP	20	15	15.62
S – 40 DP	40	18	13.2
100 DP	100	36	9.93
S – 10 Co	10	11	18.94
S – 20 Co	20	13	18.79
S – 40 Co	40	16	16.4
100 Co	100	21	15.58

Note: BS: Brandon Shores fly ash, PSP: Paul Smith Precipitator fly ash, DP: Dickerson Precipitator fly ash, MT: Morgan Town fly ash, Co: Columbia fly ash. The numbers that follow the fly ashes indicate the percentages by weight of admixtures added to the soil.

Table 4.5 Stabilized pH and effluent concentrations in WLTs

Specimen Name	Fly Ash Content (%)	pH	Al (mg/L)	As (µg/L)	B (µg/L)	Cr (µg/L)	Mn (µg/L)	Se (µg/L)
S – 10 BS	10	6.3	0.08	<0.01	<0.02	<0.001	0.028	<0.03
S – 20 BS	20	6.4	0.001	<0.01	0.178	<0.001	0.034	<0.03
S – 40 BS	40	6.81	0.05	0.01	0.12	<0.001	0.075	<0.03
100 BS	100	5.5	0.146	<0.01	0.340	<0.001	0.031	<0.03
S – 10 PSP	10	6	0.215	<0.01	FW	<0.001	0.017	<0.03
S – 20 PSP	20	6.4	<0.05	<0.01	0.163	<0.001	0.027	<0.03
S – 40 PSP	40	7.02	<0.05	0.21	0.34	0.01	0.12	0.09
100 PSP	100	7.7	0.683	0.226	0.579	0.007	0.018	0.132
S – 10 MT	10	7.2	0.2	<0.01	0.747	0.011	<0.001	<0.03
S – 20 MT	20	8.7	0.345	<0.01	1.355	0.021	<0.001	0.076
S – 40 MT	40	9.64	2.44	0.08	2.23	0.06	<0.001	0.12
100 MT	100	9.8	6.736	0.058	6.562	0.126	<0.001	0.279
S – 10 DP	10	7.05	<0.05	<0.01	0.2	0.002	0.07	<0.03
S – 20 DP	20	7.11	<0.05	<0.01	0.33	0.008	0.03	0.04
S – 40 DP	40	7.78	<0.05	0.04	0.74	0.01	0.01	0.12
100 DP	100	7.96	0.07	0.05	1.45	0.015	0.03	0.17
S – 10 Co	10	11.88	45	<0.01	0.65	0.04	<0.001	<0.03
S – 20 Co	20	11.95	48	<0.01	0.22	0.06	<0.001	<0.03
S – 40 Co	40	12.07	57	<0.01	0.16	0.06	<0.001	<0.03
100 Co	100	12.15	55	<0.01	<0.02	0.04	<0.001	<0.03
Sandy Soil	-	6.74	<0.05	<0.01	<0.02	<0.001	<0.001	<0.03
MDL (mg/L)			0.05	0.01	0.02	0.001	0.001	0.03
U.S. EPA MCL (mg / L)			0.2	0.01	NA	0.1	0.05	0.05
U.S. EPA WQL (mg / L)			0.75	0.34	NA	0.57	NA	0.005
MD ATL (µg / L)			NA	NA	13000	0.57	NA	NA

Note: 10 BS, 20 BS, 40 BS designate the specimens with 10 %, 20 % and 40 % Brandon Shores fly ash respectively, 10 PSP, 20 PSP, 40 PSP designate the specimens with 10 %, 20 % and 40 % Paul Smith Precipitator fly ash respectively, 10 MT, 20 MT, 40 MT designate the specimens with 10 %, 20 % and 40 % Morgan Town fly ash respectively 10 DP, 20 DP, 40 DP designate the specimens with 10 %, 20 % and 40 % Dickerson Precipitator fly ash respectively, 10 Co, 20 Co, 40 Co designate the specimens with 10 %, 20 % and 40 % Columbia fly ash respectively, MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. ATL = aquatic toxicity limits for fresh water.

Table 4.6Stabilized pH and peak effluent concentrations in CLTs.

Specimen Name	Fly Ash Content (%)	pH	Al (mg/L)	As (mg/L)	B (mg/L)	Cr (mg/L)	Mn (mg/L)	Se (mg/L)
S – 10 BS	10	5.75	0.132	<0.01	1.46	<0.001	0.902	<0.03
S – 20 BS	20	6.25	0.162	0.04	1.63	<0.001	0.816	0.04
S – 40 BS	40	6.7	0.16	0.09	8.68	0.03	0.82	<0.03
100 BS	100	7.3	0.14	0.73	19.11	0.05	3.07	<0.03
S – 10 PSP	10	6.3	0.062	<0.01	1.05	<0.001	0.253	0.031
S – 20 PSP	20	6.6	0.1	0.09	2.78	0.003	0.332	0.09
S – 40 PSP	40	7	0.38	1.58	30.54	0.44	3.88	1.79
100 PSP	100	7.1	0.34	2.06	56	0.06	1.68	2.08
S – 10 MT	10	7.2	0.11	<0.01	13.8	0.318	0.023	0.063
S – 20 MT	20	8.3	0.296	0.075	26.4	1.59	0.006	0.202
S – 40 MT	40	9.8	2.7	0.34	115	3.48	0.005	1.74
100 MT	100	10	12.6	0.36	166	3.23	0.01	5.84
S – 10 DP	10	6.6	0.17	<0.01	11.6	0.002	1.28	0.11
S – 20 DP	20	6.72	0.07	0.34	23.8	0.003	0.6	0.37
S – 40 DP	40	7.2	0.32	0.5	42.12	0.01	0.39	1.12
100 DP	100	7.9	2.41	0.75	43.2	0.03	0.048	1.68
S – 10 Co	10	11.88	98.3	0.03	1.52	0.17	0.003	0.05
S – 20 Co	20	11.95	187.26	0.07	23.6	0.36	0.58	0.36
S – 40 Co	40	12.07	94.48	0.08	1.44	0.12	<0.001	0.08
100 Co	100	12.15	206.14	0.05	7.86	1.13	0.0025	0.94
Sandy Soil	-	5.2	<0.05	<0.01	0.7	<0.001	0.64	<0.03
MDL (mg/L)			0.05	0.01	0.02	0.001	0.001	0.03
U.S. EPA MCL (mg / L)			0.2	0.01	NA	0.1	0.05	0.05
U.S. EPA WQL (mg / L)			0.75	0.34	NA	0.57	NA	0.005
MD ATL (µg / L)			NA	NA	13000	NA	NA	NA

Note: 10 BS, 20 BS, 40 BS designate the specimens with 10 %, 20 % and 40 % Brandon Shores fly ash respectively, 10 PSP, 20 PSP, 40 PSP designate the specimens with 10 %, 20 % and 40 % Paul Smith Precipitator fly ash respectively, 10 MT, 20 MT, 40 MT designate the specimens with 10 %, 20 % and 40 % Morgan Town fly ash respectively 10 DP, 20 DP, 40 DP designate the specimens with 10 %, 20 % and 40 % Dickerson Precipitator fly ash respectively, 10 Co, 20 Co, 40 Co designate the specimens with 10 %, 20 % and 40 % Columbia fly ash respectively, MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. ATL = aquatic toxicity limits for fresh water.

Table 4.7. Effluent metal concentrations in TCLP tests.

Specimen Name	Fly Ash Content (%)	pH	Al (mg/L)	As (µg/L)	B (µg/L)	Cr (µg/L)	Mn (µg/L)	Se (µg/L)
S – 10 BS	10	4.82	<0.05	<0.01	0.1	0.01	0.21	<0.03
S – 20 BS	20	4.82	0.055	<0.01	0.08	0.01	0.105	<0.03
S – 40 BS	40	4.82	<0.05	<0.01	0.135	0.01	0.135	<0.03
100 BS	100	4.83	0.06	0.045	0.39	0.02	0.04	<0.03
S – 10 PSP	10	4.84	0.085	<0.01	0.105	<0.001	0.18	<0.03
S – 20 PSP	20	4.85	<0.05	<0.01	0.15	<0.001	0.18	<0.03
S – 40 PSP	40	4.85	0.27	0.15	0.35	<0.004	0.3	0.075
100 PSP	100	4.86	0.58	0.465	1.025	0.0045	0.475	0.345
S – 10 MT	10	4.87	0.185	<0.01	0.91	0.02	0.15	<0.03
S – 20 MT	20	4.89	0.32	<0.01	1.37	0.03	0.16	<0.03
S – 40 MT	40	4.92	2.37	<0.01	2.435	0.085	0.29	<0.03
100 MT	100	5.12	5.425	0.03	7.3	0.11	0.43	0.085
S – 10 DP	10	7.05	4.83	0.605	0.01	0.25	0.01	0.23
S – 20 DP	20	7.11	4.87	1.25	0.145	0.38	0.02	0.24
S – 40 DP	40	7.78	4.87	2.07	0.455	0.525	0.03	0.235
100 DP	100	7.96	4.87	8.695	0.05	1.65	0.06	0.275
S – 10 Co	10	5.21	3.945	<0.01	1.115	0.02	0.18	<0.03
S – 20 Co	20	5.42	0.985	0.025	1.725	0.035	0.21	0.045
S – 40 Co	40	7.41	0.05	0.045	3.075	0.07	0.11	0.135
100 Co	100	10.86	14.445	0.06	4.315	0.225	0.04	0.345
Sandy Soil	-	6.74	<0.05	<0.01	<0.02	<0.001	<0.001	<0.03
MDL (mg/L)			0.05	0.01	0.02	0.001	0.001	0.03
U.S. EPA MCL (mg / L)			0.2	0.01	NA	0.1	0.05	0.05
U.S. EPA WQL (mg / L)			0.75	0.34	NA	0.57	NA	0.005
MD ATL (µg / L)			NA	NA	13000	0.57	NA	NA

Note: 10 BS, 20 BS, 40 BS designate the specimens with 10 %, 20 % and 40 % Brandon Shores fly ash respectively, 10 PSP, 20 PSP, 40 PSP designate the specimens with 10 %, 20 % and 40 % Paul Smith Precipitator fly ash respectively, 10 MT, 20 MT, 40 MT designate the specimens with 10 %, 20 % and 40 % Morgan Town fly ash respectively 10 DP, 20 DP, 40 DP designate the specimens with 10 %, 20 % and 40 % Dickerson Precipitator fly ash respectively, 10 Co, 20 Co, 40 Co designate the specimens with 10 %, 20 % and 40 % Columbia fly ash respectively, MDL: Minimum Detection Limits, MCL= maximum contaminant levels for drinking water; MCL for Al is based on a secondary non-enforceable drinking water regulation; WQL= water quality limits for protection of aquatic life and human health in fresh water. ATL = aquatic toxicity limits for fresh water.

Table 4.8 Input Site Parameters for conceptual model.

	Wpoc	Wp	Ws	ZGWT	Prcpt	Tmax	T (m)	Side Slope (H:V)
Constant values for all specimens	30	6	2	5	1.00	50	5	2:1

Notes: All measurements are in meter, W_{poc}: Point of compliance, W_p: Pavement width, W_s: Shoulder width, Z_{GWT}: Depth to groundwater table, Prcpt; Annual precipitation rate in m/year, T_{max}: 50 years, Thicknes of embankment structure,

Table 4.9 Hydraulic Properties and transport for pavement layers and aquifer input to WiscLeach

Specimen	Hydraulic Conductivity, K_s,(m/year)	n_e	Hydraulic Gradient	α_L (m)	α_T (m)	R_d for Cr
S – 20 PSP	8.67	0.302	0.001	0.193	0.0193	27
S – 40 PSP	6	0.395	0.001	0.485	0.0485	8
S – 20 DP	25.23	0.42	0.001	0.401	0.0401	1.1
S – 40 DP	20.08	0.489	0.001	0.671	0.0671	15
Pavement	18.29	0.35	0.001	0.1	0.01	1
Subgrade	1.01	0.35	0.001	0.1	0.01	3.5
Aquifer	3784	0.30	0.001	0.1	0.01	1

Notes;α_L : Longitudinal dispersivity, α_T : Transeverse dispersivity, hydraulic gradients is assumed as 0.001 to simulate the natural conditions, n_e : effective porosity, Cr: Chromium.

FIGURES

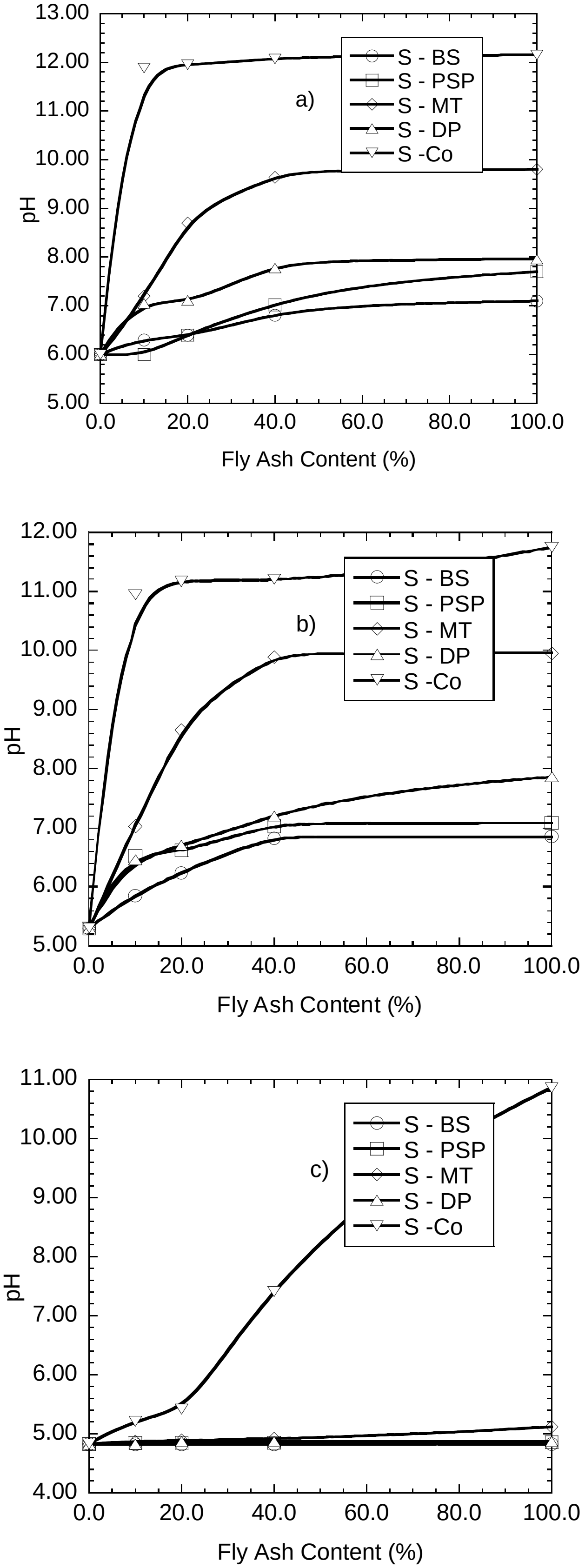


Figure 4.1. Effect of fly ash content on pH of the soil mixtures (Note: BS: Brandon Shores Fly Ash, PSP: Paul Smith Precipitator Fly ash, MT: Morgantown Fly ash)

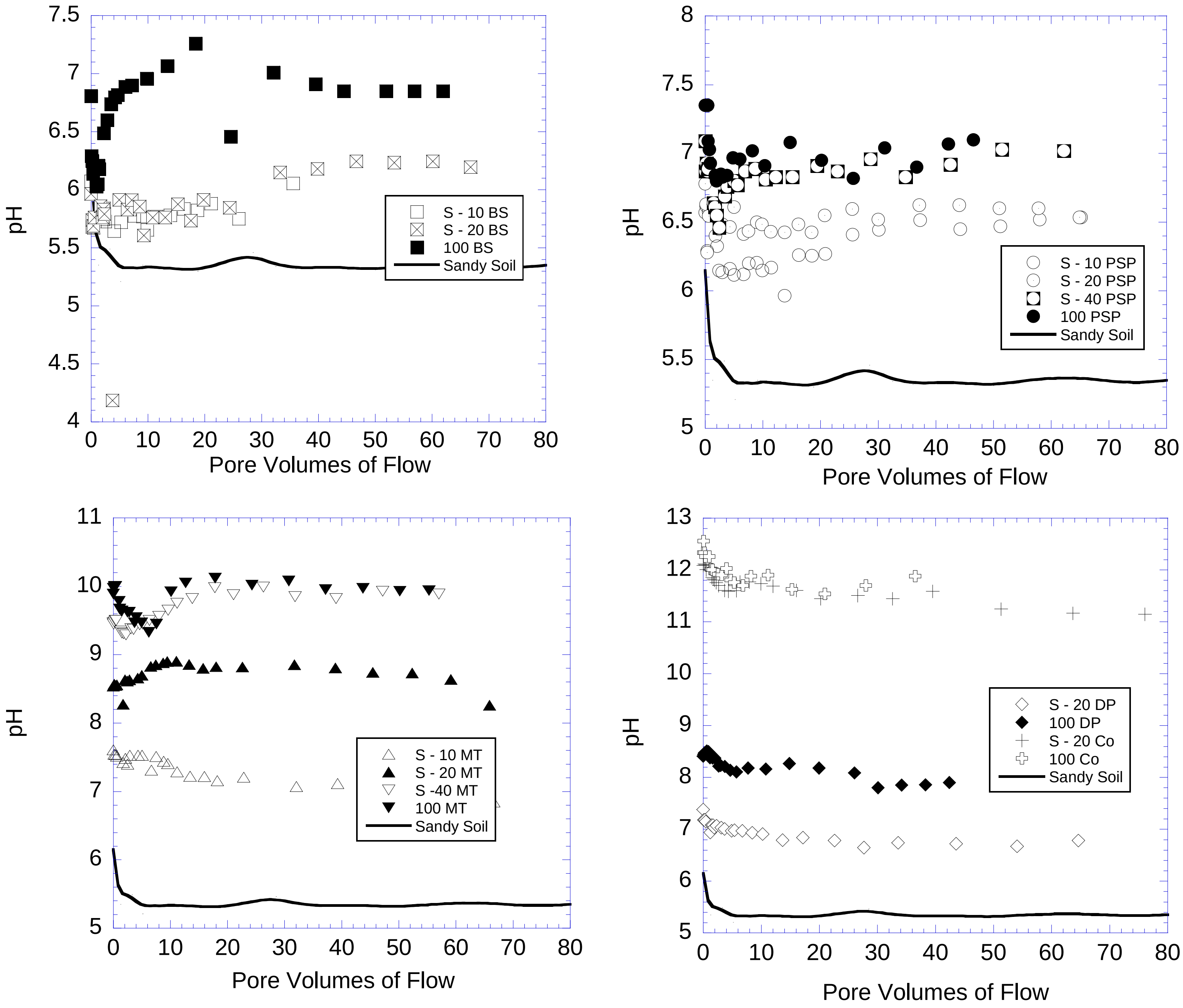


Figure 4.2 pH of the effluent from CLT conducted with soil mixtures

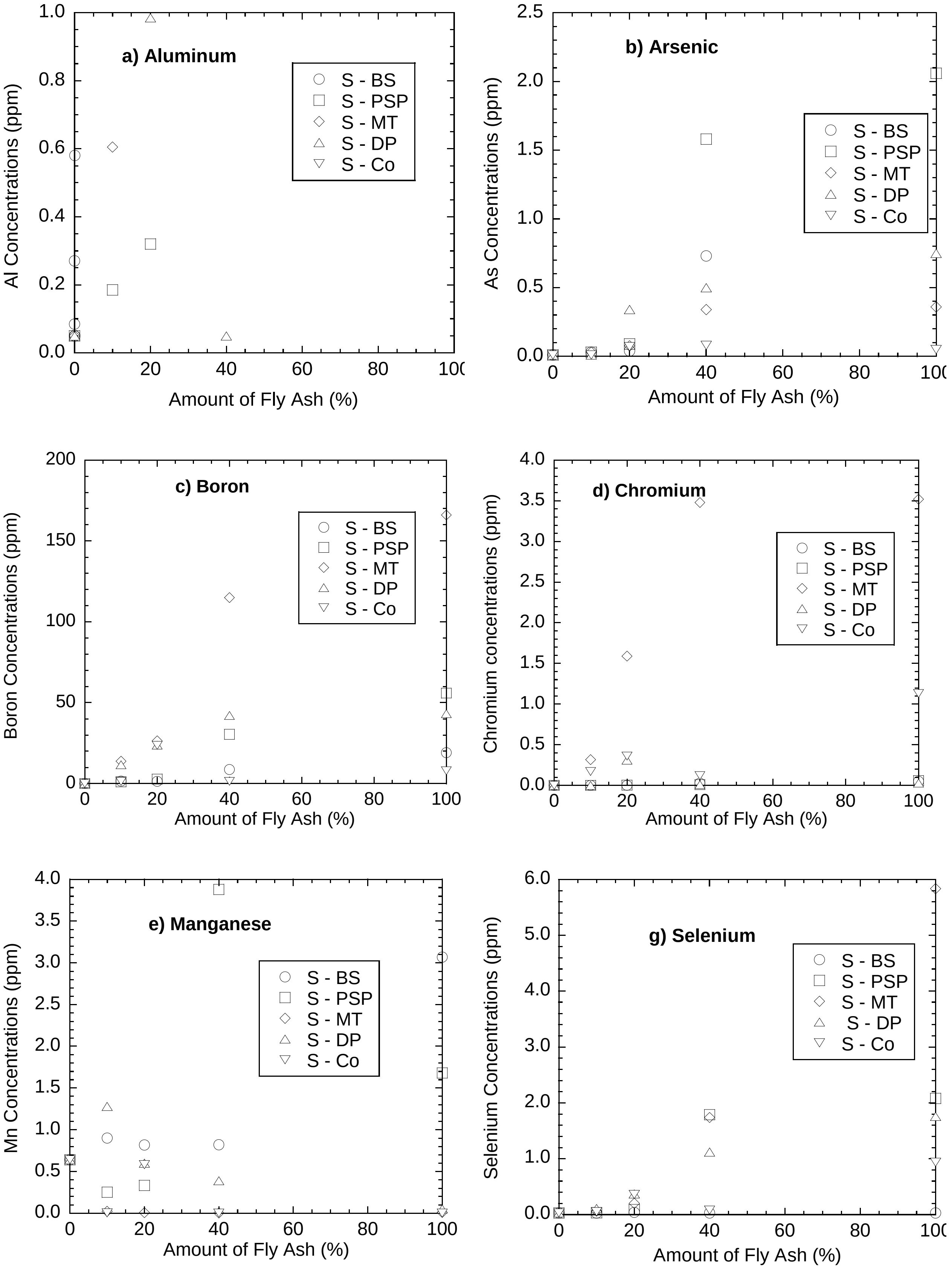


Figure 4.3 Concentrations of 6 metals in the effluent from CLTs(Note: BS: Brandon Shores, PSP: Paul Smith Precipitator, MT: Morgan Town)

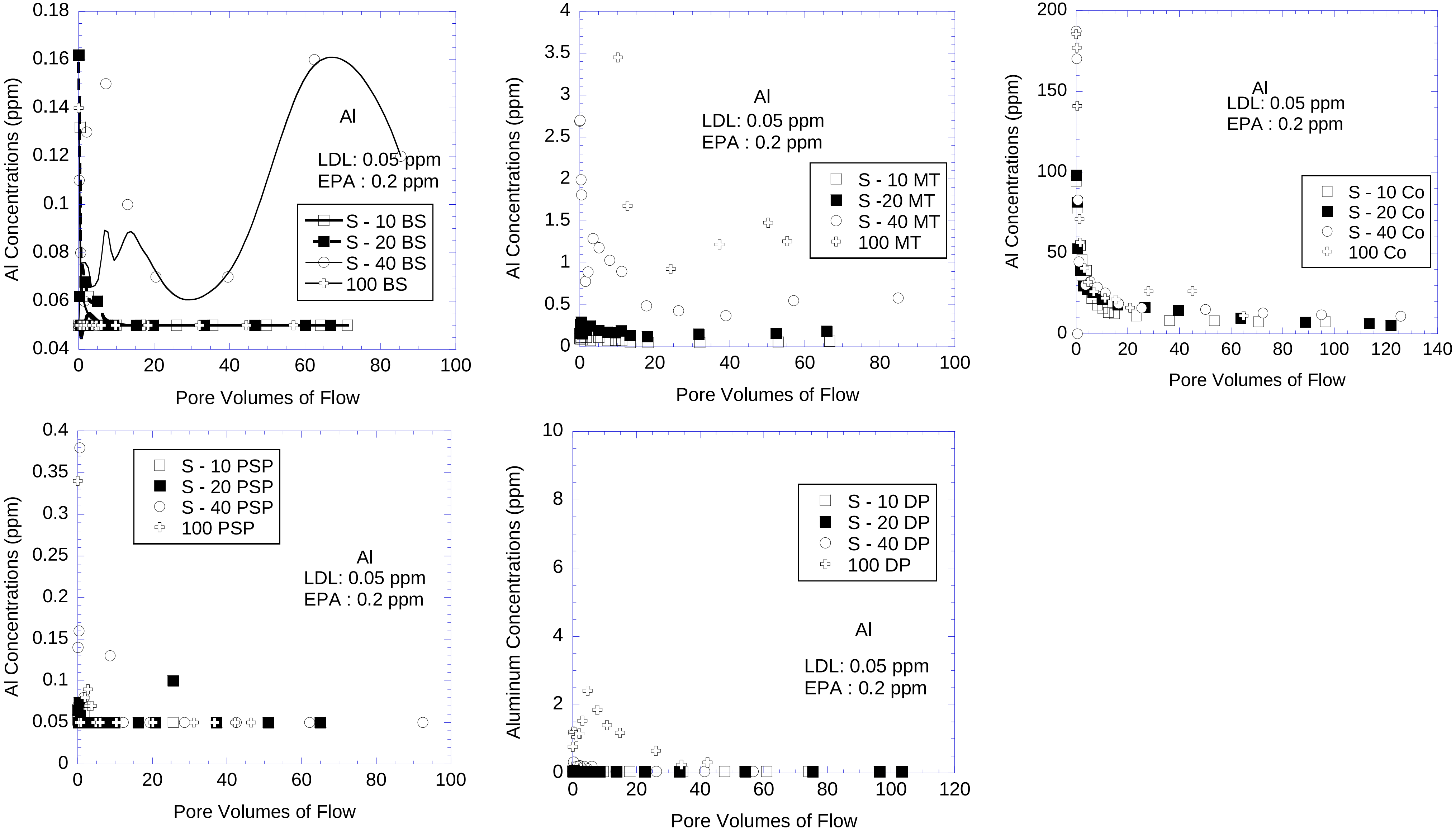


Figure 4.4 Elution curves for Aluminum Metal

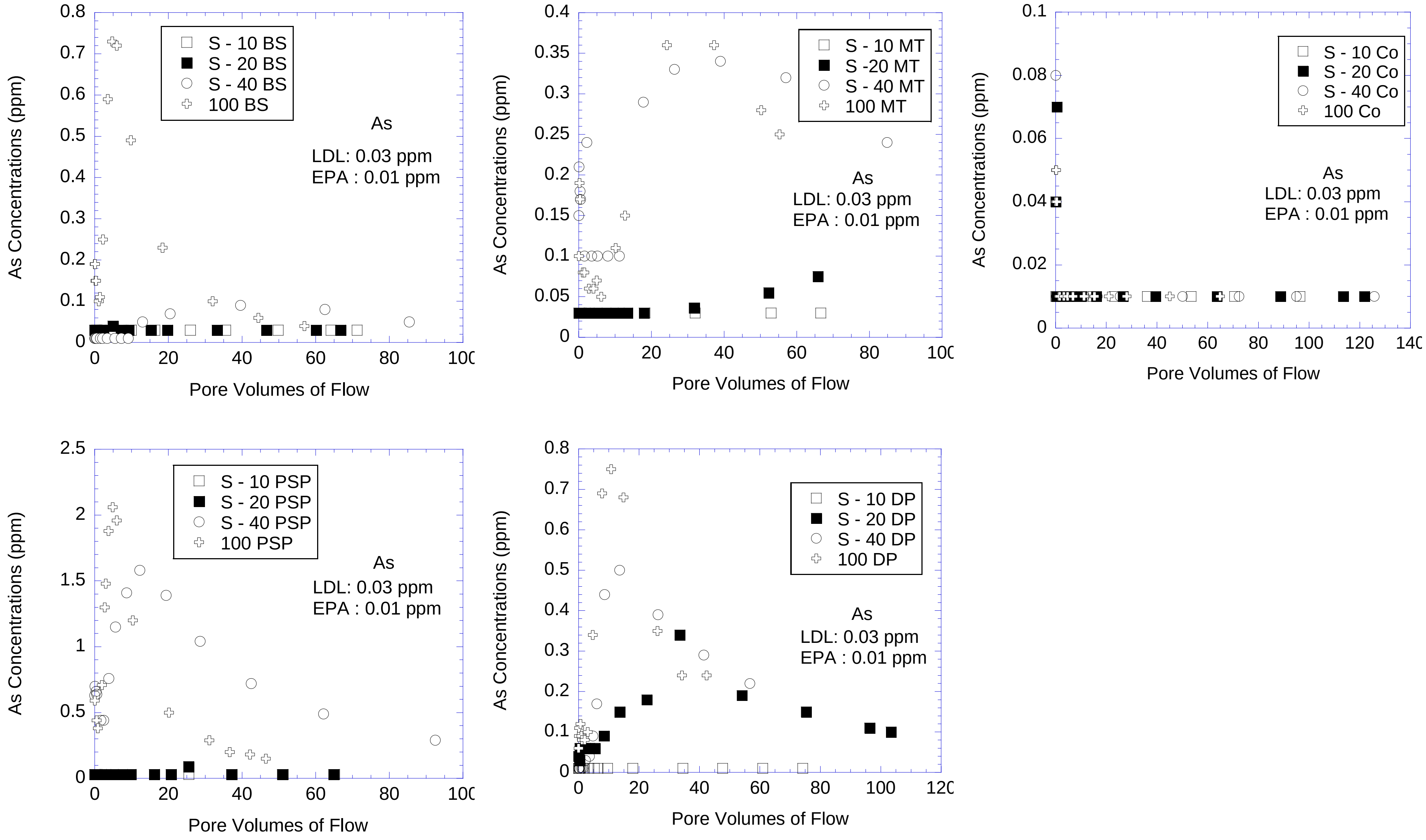


Figure 4.5 Elution curves for Arsenic Metal

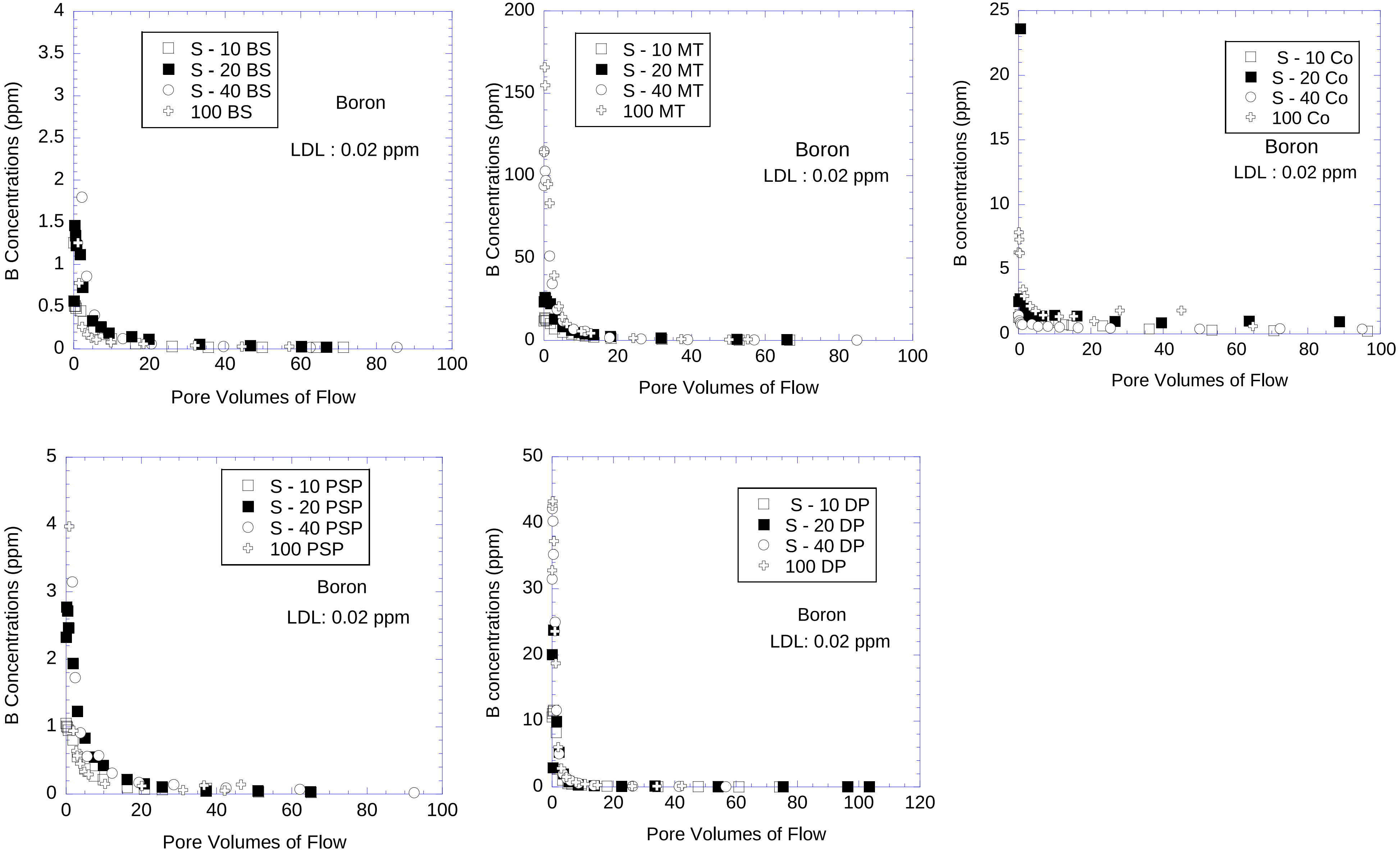


Figure 4.6 Elution Curves for Boron metal

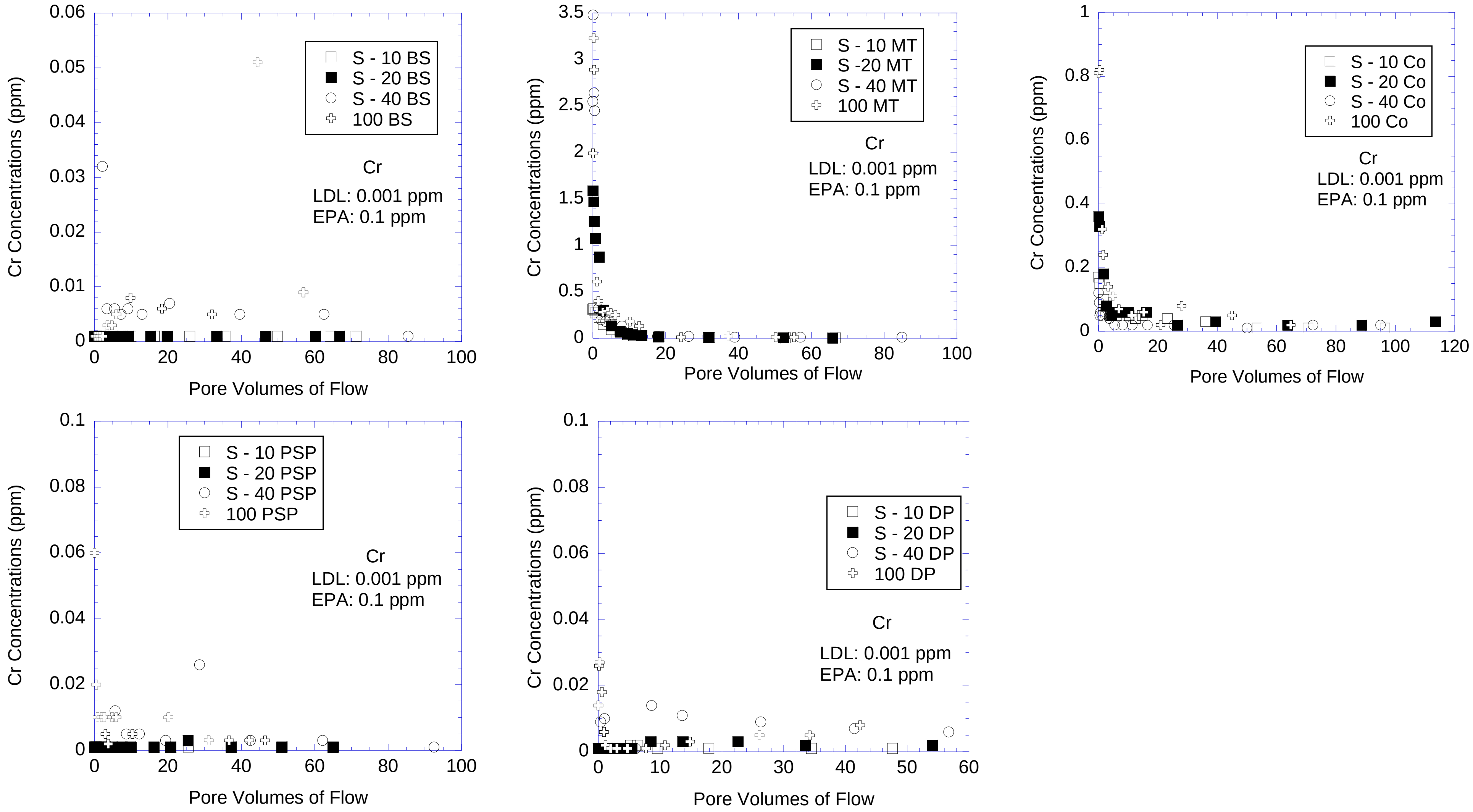


Figure 4.7 Elution curves for chromium metal

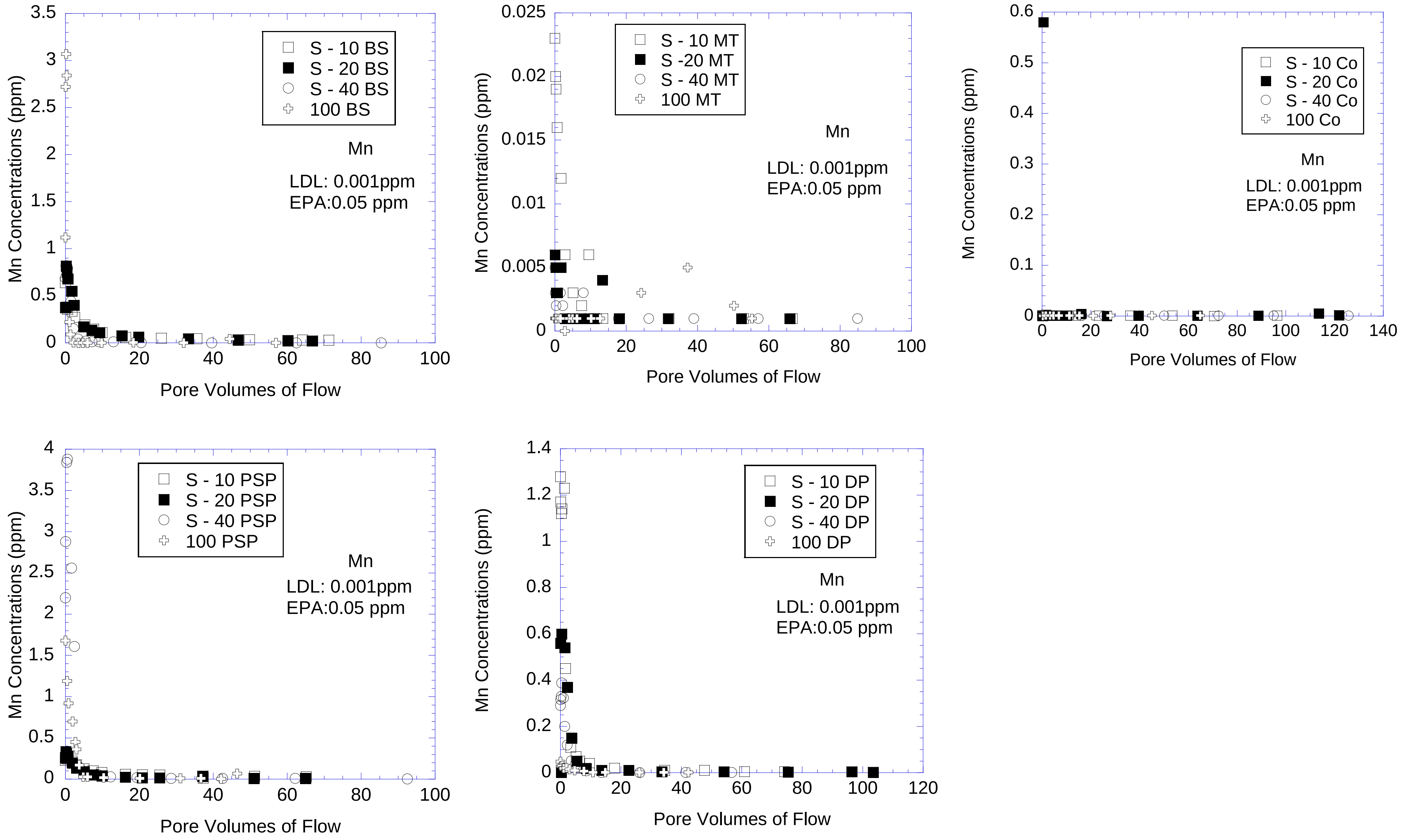


Figure 4.8 Elution curve for Manganese metal

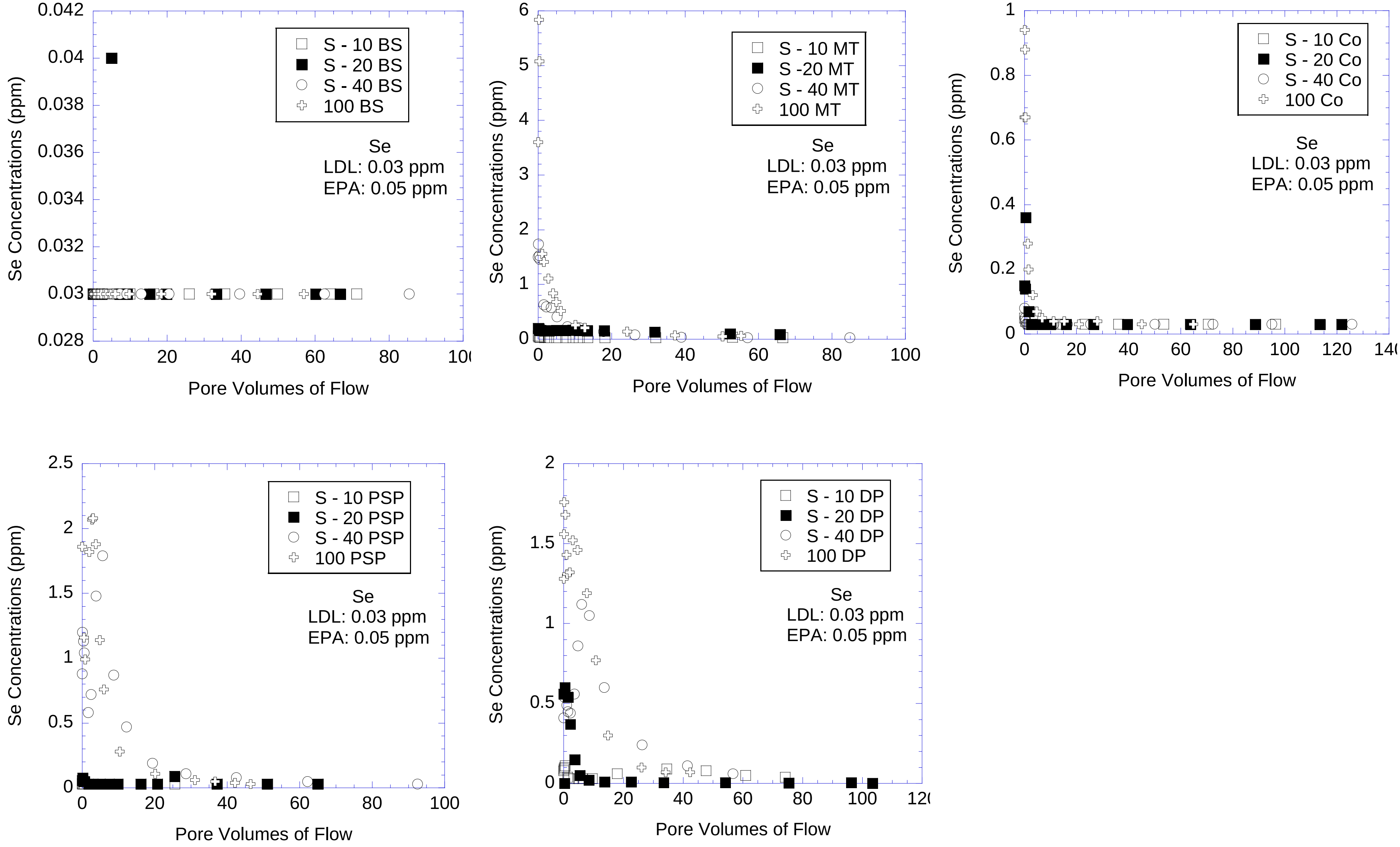


Figure 4.9 Elution curves for selenium metal

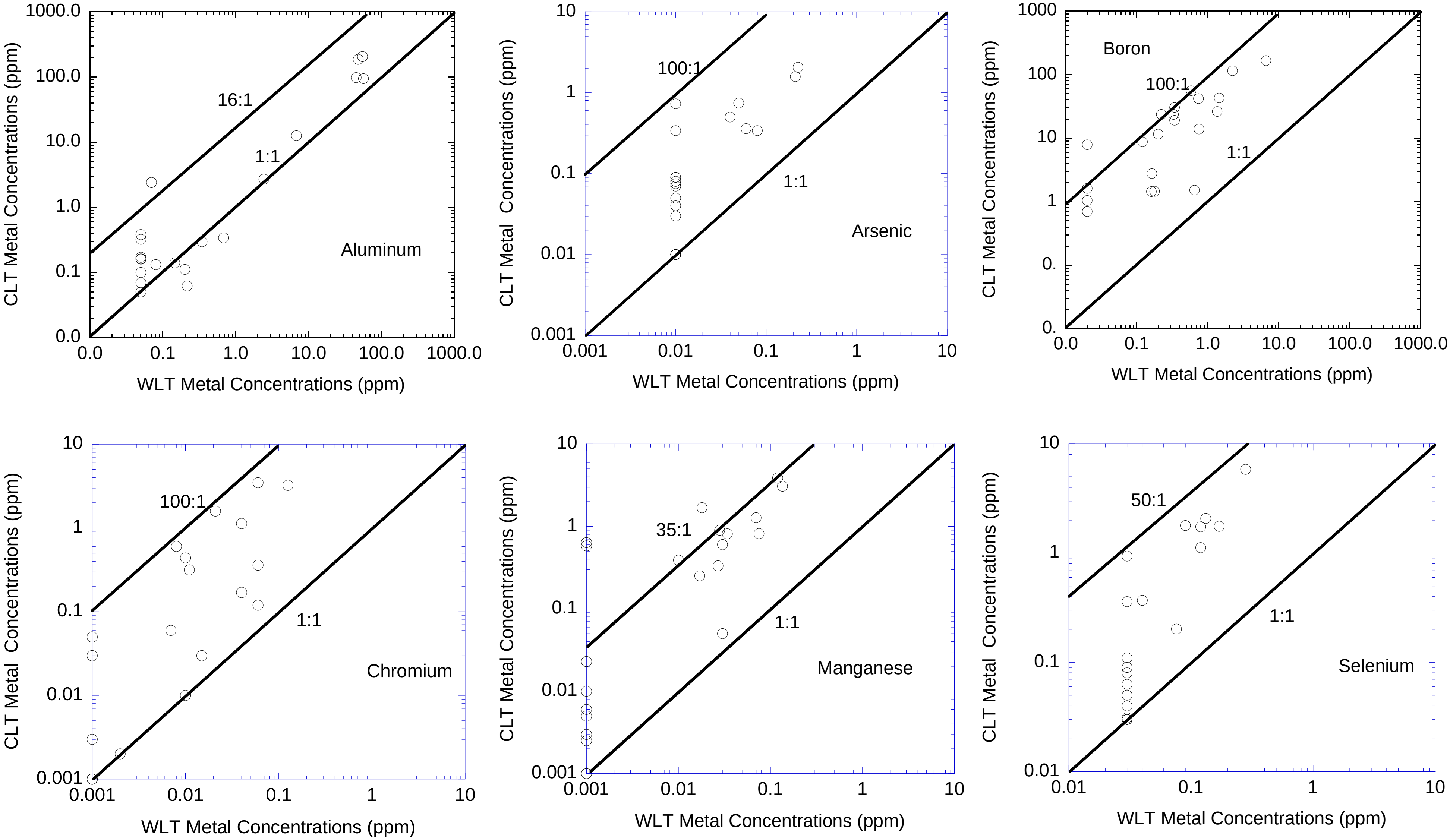


Figure 4.10. Comparison of peak effluent concentrations of six metals from the CLTs and the WLTs

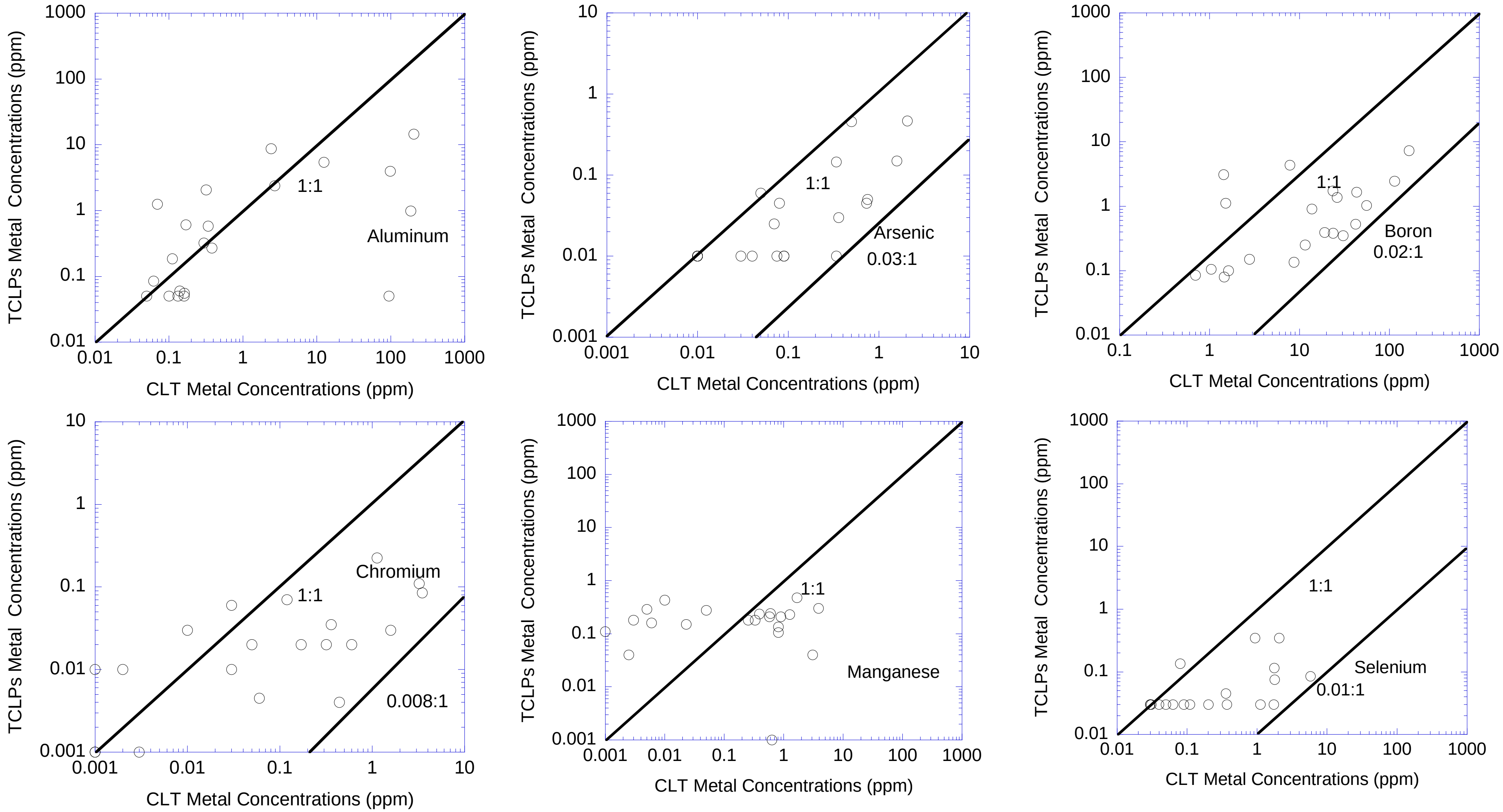


Figure 4.11. Comparison of peak effluent concentrations of six metals from the CLTs and the TCLPs

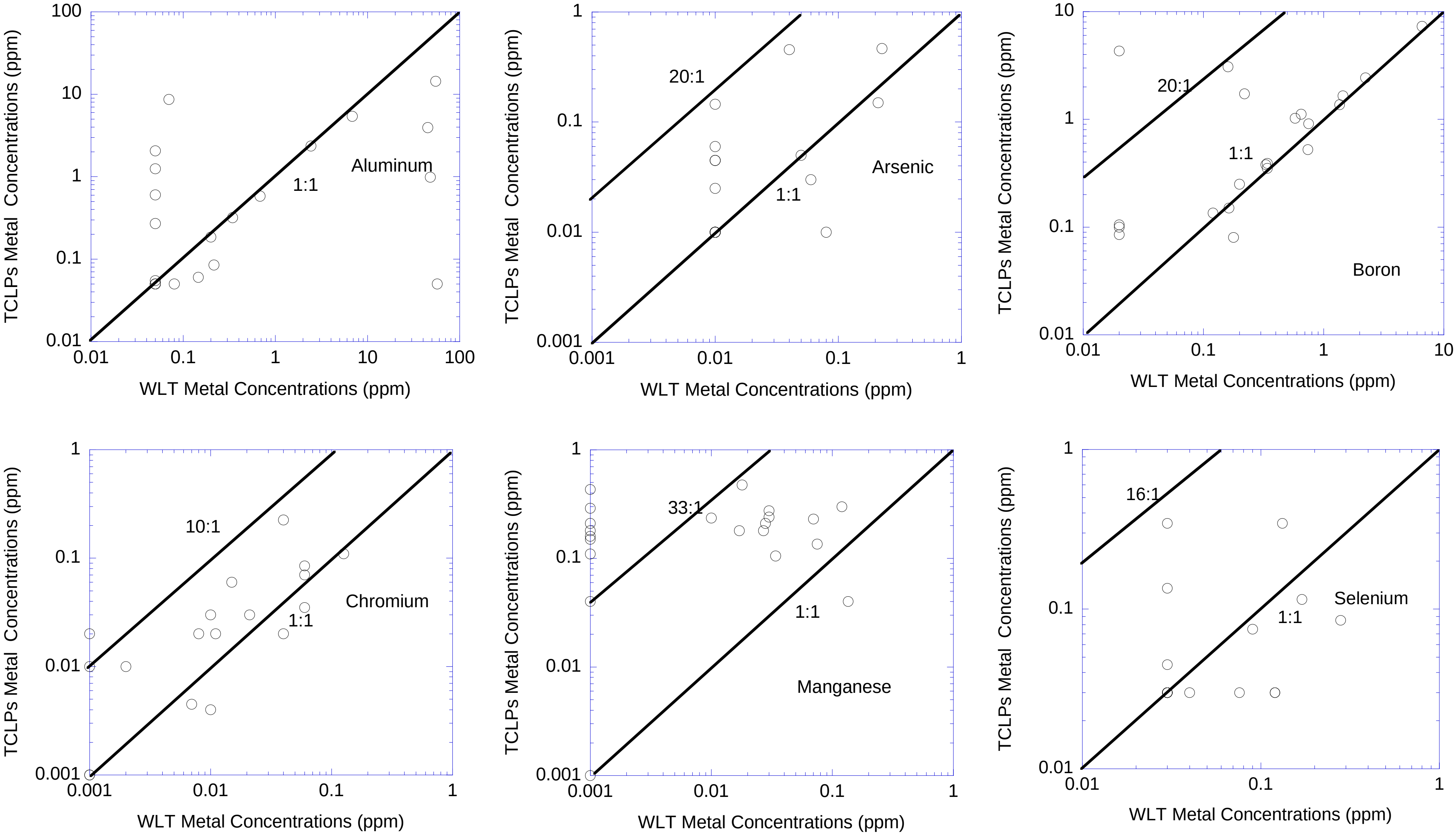


Figure 4.12. Comparison of peak effluent concentrations of six metals from the WLTs and the TCLPs

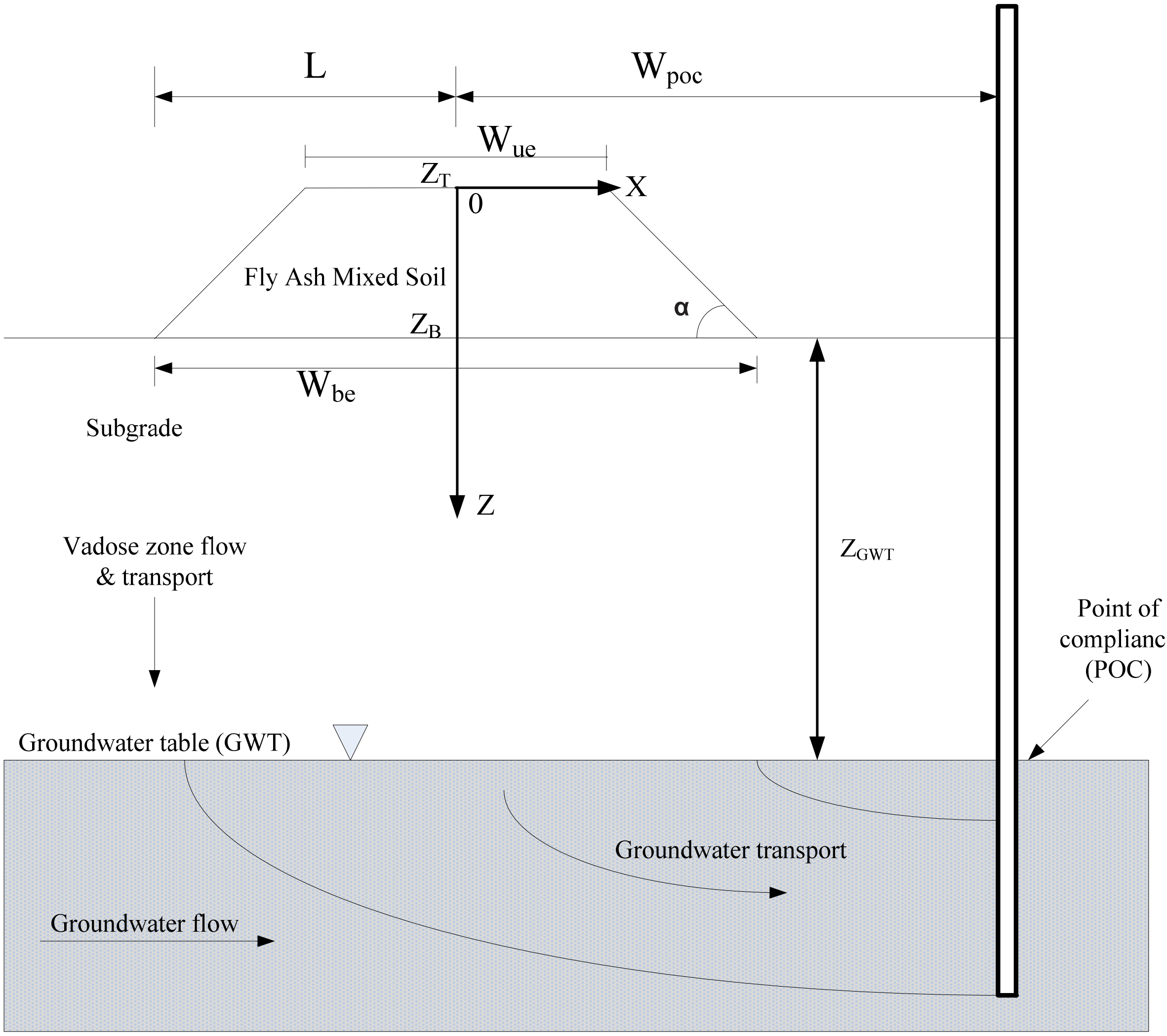


Figure 4.13. Conceptual model for embankment structure

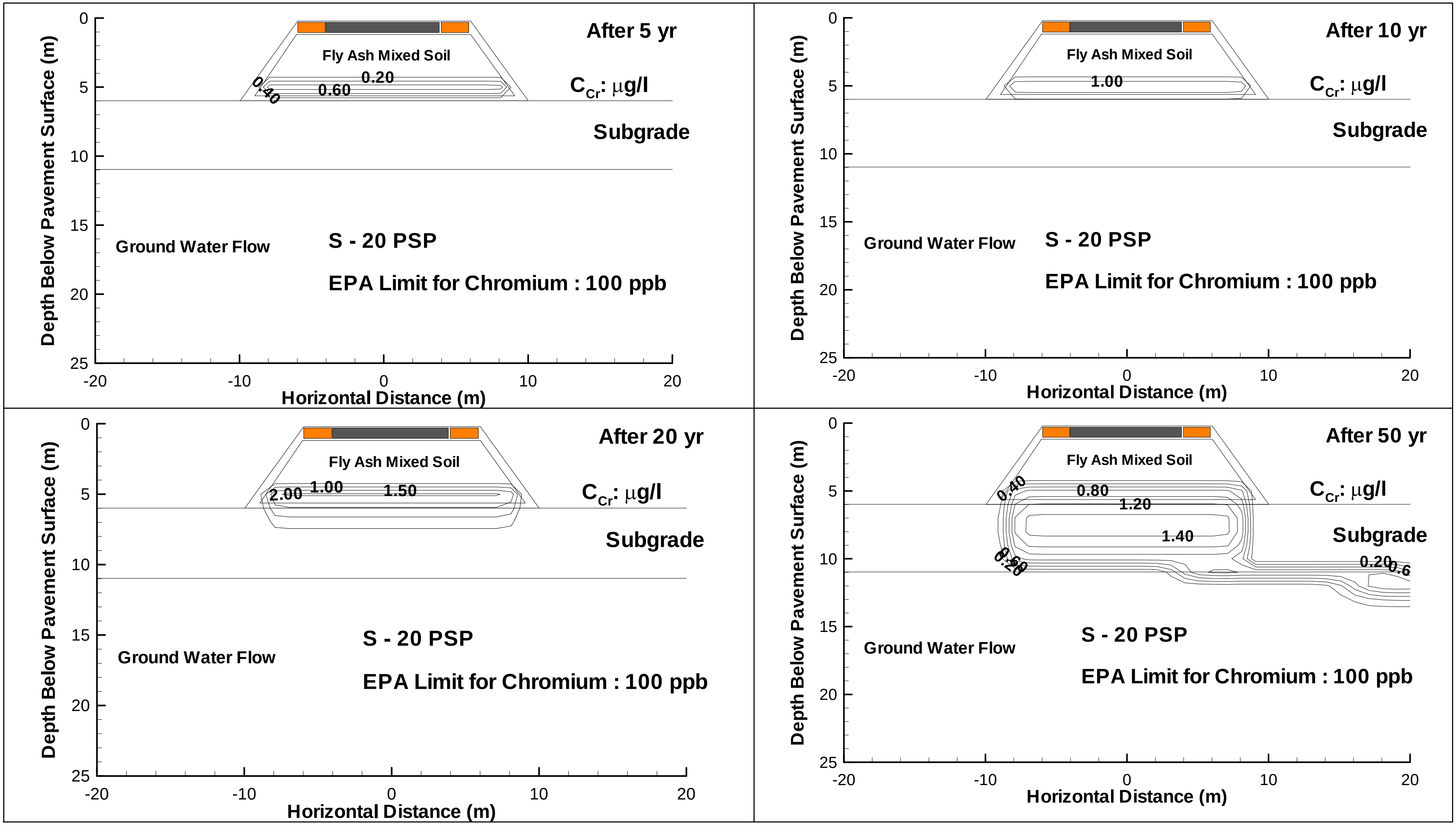


Figure 4.14. Predicted Cr concentrations in vadose zone and ground water (Note: 20 PSP designate the specimens with 20 % Paul Smith Precipitator fly ash.)

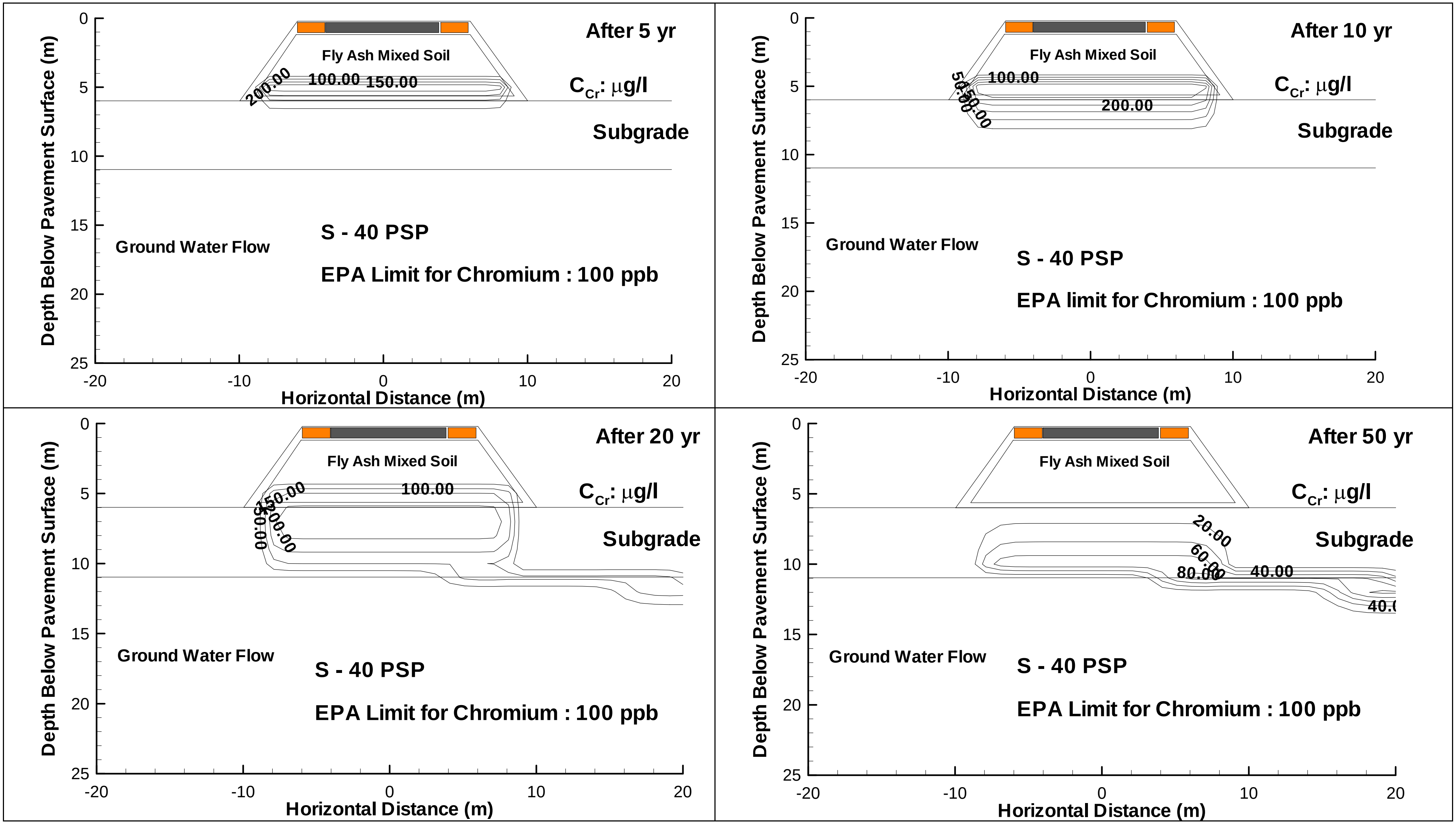


Figure 4.15. Predicted Cr concentrations in vadose zone and ground water (Note: 40 PSP designate the specimens with 40 % Paul Smith Precipitator fly ash.)

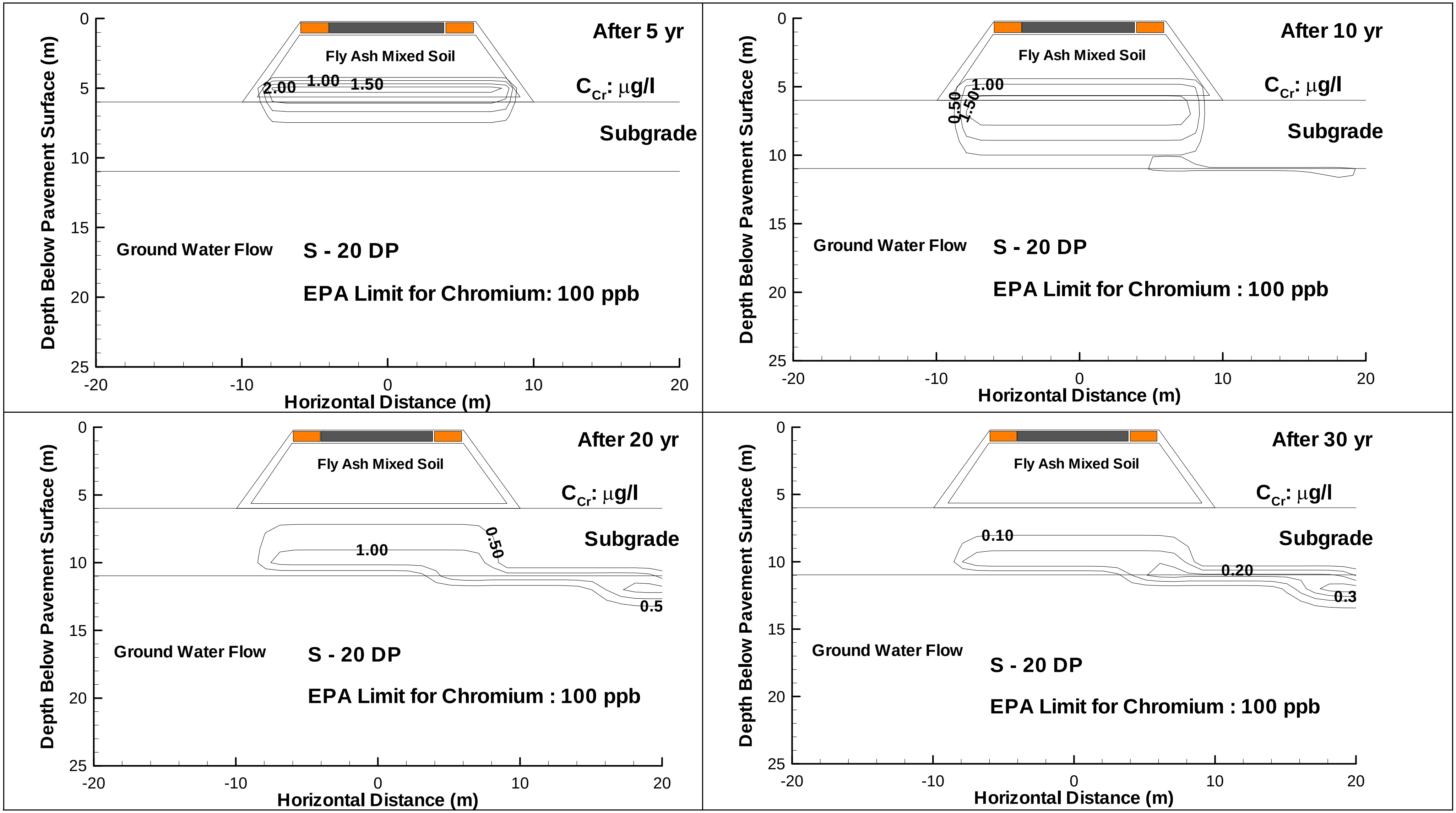


Figure 4.16 Predicted Cr concentrations in vadose zone and ground water (Note: 20 DP designate the specimens with 20 % Dickerson Precipitator fly ash.)

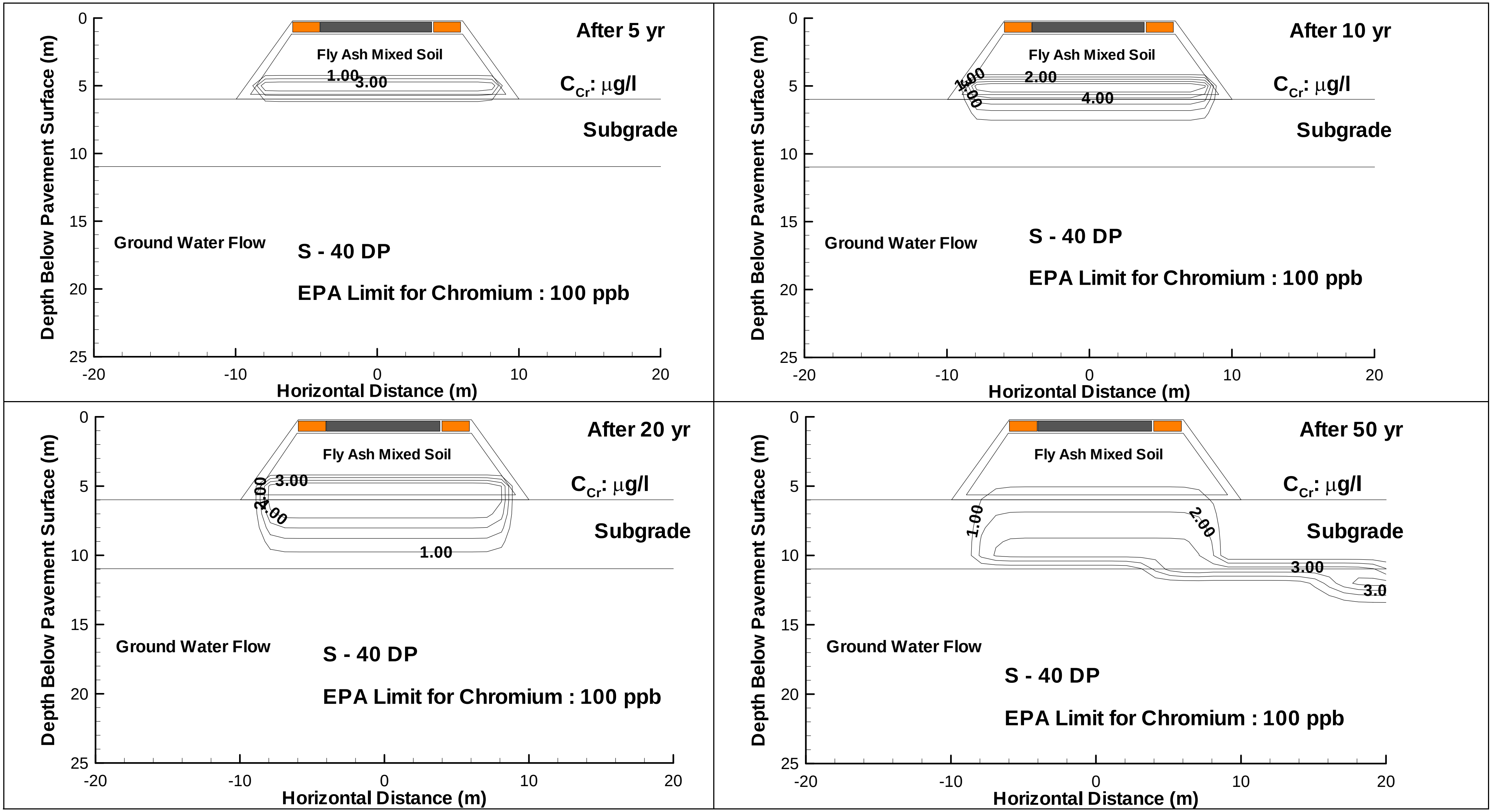


Figure 4.17 Predicted Cr concentrations in vadose zone and ground water (Note: 40 DP designate the specimens with 40 % Dickerson Precipitator fly ash.)

REFERENCES

ACAA (2008). "*2008 Coal Combustion Product Production and Use*", American Coal Ash Association, Denver, Colorado

Al-Abed, S.R., Jegadeesan, G. and Pinto, P. (2008). "Influence of Trace Metal Distribution on its Leachability from Coal Fly Ash", *Fuel*, Vol. 87, pp. 1887-1893.

Allison, J.D., Brown, D.S., Novo-gradac, K.J. (1991). "MINTEQA2/PRODEFA2, A Geochemical Assesment Model for Environmental Systems. Version 3.11 Databases and Version 3.0 User`s Manual", US EPA, Athens.

ASTM D854 (2005). "*Standard test methods for specific gravity of soil solids by water pycnometer*", Annual Book of ASTM Standards, Vol. 04.01, American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.

ASTM D1293 (2005). "*Standard test method for pH of water*", Annual Book of ASTM Standards, Vol. 04.01, American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.

ASTM D3987 (1992). "*Standard test method for shake extraction of solid waste with water*", Annual Book of ASTM Standards, Vol. 04.01, American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.

ASTM C618 (2008). " Standard specification for coal fly ash and raw or calcined Natural pozzolan for use in concrete", Annual Book of ASTM Standards, Vol. 04.01, American Society for Testing and Materials, West Conshohocken, Pennsylvania, USA.

Baba A., Gurdal G., Sengunalp, F., and Ozay, O. (2008). "Effects of Leachant Temperature and pH on Leachability of Metals from Fly Ash. A Case Study: Can Thermal Power Plant, Province of Canakkale, Turkey." *Environmental Monit. Assess.* Vol. 139, pp. 287-298.

Baykal, G., Edincliler, A., Saygili, A. (2004). "Highway Embankment Construction Using Fly Ash in Cold Regions", *Resources, Conversation and Recycling*, Vol. 42 - 3, 209-222.

Bin-Shafique, S., Benson, C., Edil, T. and Hwang, K. (2006). Leachate Concentrations from Water leach and Column Leach Tests on Fly – Ash Stabilized Soil, Environmental Engineering Science, 23(1), 51-65.

Brookins, D. G., *Eh-pH Diagrams for Geochemistry*, (1988). Springer-Verlag Berlin Heidelberg, United States.

Brown, S., Christensen, B. Lombi, E., McLaughin, M., McGrath, S., Colpaert, J., and Vangronsveld, J. (2005). "An Inter-Laboratory Study to Test the Ability of Amendments to Reduce the Availibility of Cd, Pb, and Zn In Situ.", *Environmental Pollution*, Vol. 138, pp. 34-45.

Cetin, B., Aydilek, A.H., and Guney, Y. (2010). "Stabilization of Recycled Base Material Using High Carbon Fly Ash", *Resources, Conservation and Recycling*, Vol. 54, pp. 879-892.

Chen, G.G., He, Z.L., Stoffella, P.J., Yang, X.E., Yu, S., Yang, J.Y., and Calvert, D.V. (2006). "Leaching Potential of Heavy Metals (Cd, Ni, Pb, Cu, Zn) from Acidic Sandy Soil Amended with Dolomite Phosphate Rock (DPR) Fertilizers", *Journal of Trace Elements in Medicine and Biology*, Vol. 20, pp. 127 – 133.

Chichester, D.L. and Landsberger, S. (1996). "Determination of the leaching dynamics of metals from municipal solid waste incinerator fly ash using a column test", *Journal of Air and Waste Management Association*, Vol. 46, pp. 643-649.

Cornelis, G., Johnson, C.H., Van Gerven, T., Vandecasteele, C (2008). "Leaching Mechanisms of Oxyanionic Metalloid and Metal Species in Alkaline Solid Wastes", *Applied Geochemistry*, Vol. 23, 955-976.

Cornell, R.M., and Schwertmann, U. (2003). *The Iron Oxides : Structure, Properties, Reactions, Occurences and Uses,* Second Edition Wiley – VCH, Weinheim.

Cotton , A.F, and Wilkinson, G. (1999)., *Advanced Inorganic Chemistry*, 5th ed. John Wiley & Sons, Inc., New York

Demirkan, M.M., Seagren, E.A., and Aydilek, A.H. (2006). “Reuse of Fly Ash Amended Petroleum Contaminated Soils in Highway Embankments”, *Journal of the Transportation Research Board*, No. 1975, pp. 104-111.

DiGioia, A. M. and Nuzzo, W. L. (1972). “Fly Ash as Structural Fill,” *J. Power Div.,* ASCE, New York, Vol. 98 (1), pp. 77-92.

Dijkstra, J.J., Van der Sloot, H.A., and Comans, R.N.J (2002). “Process Identification and Model Development of Contaminant Transport in MSWI Bottom Ash”, *Waste Management*, Vol. 22(5), 531.

Dijkstra, J.J., Meeussen, J.C.L and Comans, R.N.J (2004). “Leaching of Heavy Metals From Contaminated Soils : An Experimental and Modeling Study”, *Environmental Science and Technology*, Vol. 38(16), 4390.

Dixit, S., and Herring, J.G. (2003). “Comparison of Arsenic (V) and Arsenic (III) Sorption onto Iron Oxide Minerals; Implications for Arsenic Mobility”, *Environmental Science and technology*, Vol. 37, 4182-4189.

Dutta, B.K., Khanra and S., Mallick, D. (2009). “Leaching of elements from coal fly ash: Assesment of its potential for use in filling abandoned coal mines”, *Journal of Fuel*, Vol. 88, pp. 1314-1323.

Dzombak, D.A. and Morrel, F.M.M. (1990). , *Surface Complexation Modeling: Hydrous Ferric Oxide* , John Wiley and Sons, New York.

Edil, T.B., Sandstorm, L.K., and Berthouex, P.M. (1992). "Interaction of inorganic leachate with compacted pozzolanic fly ash", *Journal of Geotechnical Engineering*, Vol.118, No. 9, pp. 1410-1430.

Espana, J.S., Pamo, E.L., Santofimia, E., Aduvire, O., Reyes, J., and Barettino,D. (2005). "Acid Mine Drainage in the Iberian Pyrite Belt (Odiel River Water Shed, Huelva, Spain):Geochemistry, mineralogy and Environmental Implication", *Applied Geochemistry*, Vol. 20, pp. 1320-56.

Garavaglia, R., and Caramuscio, P. (1994). "Coal Fly – Ash Leaching Behavior and Solubility Controlling Solids ", Maastricht, Neth, 87.

Garrabrants, A.C., Sanchez, F., and Kosson, D.S.(2004). "Changes in Constituent Equilibrium Leaching and Pore Water Characteristics of a Portland Cement Mortar as a Result of Carbonation", *Waste Management*, Vol. 24, pp. 19 - 36.

Gelhar, L.W., Welty, C., and Rehfeldt, K.R. (1992). "A critical review of data on field-scale dispersion in aquifers", *Water Resources Research*, Vol. 28, No. 7, pp. 1955–1974.

Ghosh, A. and Subbarao, C. (1998). "Hydraulic conductivity and leachate characteristics of stabilized fly ash", *Journal of Environmental Engineering*, Vol. 124, No. 9, pp. 812-820.

Goh, A. T. C., and Tay, J. H. (1993). "Municipal Solid Waste Incinerator Fly Ash for Geotechnical Applications," *J. of Geotech. Engrg.*, ASCE, New York, Vol. 119 (5), pp. 811-825.

Goswami, R.K. and Mahanta, C. (2007). "Leaching Characteristics of Residual Lateric soils Stabilized with Fly Ash and Lime for Geotechnical Applications", *Waste Management*, Vol. 27, pp. 466 – 481.

Jackson, B.P., Miller, W.P., Schumann, A.W., and Sumner, M.E. (1999). “Trace Element Solubility from Land Application of Fly Ash / Organic Waste Mixtures”, *Journal of Environmental Quality*, Vol. 28 (2), pp. 639.

Jegadeesan, G., Al-Abed, S.R., and Pinto, P. (2008). “Influence of Trace Metal Distribution on its Leachability from Coal Fly Ash”, *Fuel*, Vol. 87, pp. 1887-1893.

Jing, C., Liu, S., Korfiatis, P., Meng, X. (2006). “Leaching Behavior of Cr (III) in Stabilized / Solidified Soil”, *Chemosphere*, Vol. 64, 379-385.

Jo, H.Y., Min, S.H., Lee, T.Y., Ahn, H.S., Lee, H.S, Yang, J.Y., and Hong, J.K. (2007). “Environmental Feasibility of Using Coal Ash as a Fill Material to Raise Ground Level ”, *Journal of Hazardous Materials*, Vol. 154, pp. 933 – 945.

Kenkel, J. (2003). *ANAlytical Chemistry for Technicians*, Lewis Publishers, Boca Raton, FL.

Kumpiene, J., Lagerkvist, A., and Maurice, C. (2007). “Stabilization of Pb and Cu Contaminated Soil Using Coal Fly Ash and Peat, *Environmental Pollution*, Vol. 145, pp. 365 – 373.

Komonweeraket, K. Benson, C.H., Edil, T.B., and Bleam, W.F.(2010). “Mechanisms Controlling Leaching of Heavy Metals from Soil Stabilized with Fly Ash”, Geo Engineering Report No. 02-14, Geo Engineering Program, University of Wisconsin-Madison, Madison, WI.

Langmuir, D. (1997). *Aqueous Environmental Geochemistry*, Prentice – Hall, Inc., Vol. 47, New Jersey.

Leuz, A.K., Monch, H., Johnson, A.C. (2006b). “Sorption of Sb(III) and Sb(V) to Geothite: Influence on Sb(III) Oxidation and Mobilization”, *Environmental Science and Technology*, Vol. 40, 7277 - 7282.

Lim, T.T., Tay, J.H., Tan, L.C., Choa, V., and The, C.I. (2004). "Changes in Mobility and Speciation of Heavy Metals in Clay – Amended Incinerator Fly Ash", *Environmental Geology*, Vol. 47, 1-10.

Li, L, Benson, C.H., Edil, T.B., and Hatipoglu, B. (2007). "Groundwater Impacts from Coal Ash in Highways", *Waste and Resource Management*, Vol. 159, pp. 151 – 163.

Malferrari, D., Brigatti, M.F., Laurora, and A., Pini, S. (2008). "Heavy Metals in Sediments from Canals for Water Supplying and Drainage: Mobilization and Control Strategies", *Journal of Hazardous Materials*, Vol. 161, pp. 723-729.

Morar, D.L. (2007). "Leaching of Metals from Fly Ash – Amended Permeable Reactive Barriers", M.S. Thesis, University of Maryland – College Park.

Naik, T.R., Singh, S.S., and Ramme, B.W. (2001). " Performance and Leaching Assessment of Flowable Slurry", *Journal of Environmental Engineering*, Vol.127, No.4, pp.359-368.

Ogunro, V.O. and Inyang, H.I. (2003). "Relating batch and column diffusion coefficients for leachable contaminants in particulate waste materials", *Journal of Environmental Engineering, ASCE*, Vol. 129, Issue 10, pp. 930-942.

Pagenkopf, G.K., and Connolly, J.M., (1982). "Retention of Boron by Coal Ash", *Environmental Science & Technology*, Vol. 16, No. 9, 609 - 613.

Pandian, N.S., Rajasekhar, C., and Sridharan, A. (1996). "Fly Ash as a Pre-Filter Material for the Retention of Lead Ions", *Journal of Testing and Evaluation*, Vol.24, No.3, pp.181-186.

Papini, M. P., Kahie, Y. D., Troia, B., and Majone, M. (1999). "Adsorption of Lead at Variable pH onto a Natural Porous Medium: Modeling of Batch and Column Experiments," *Environ. Sci. and Technol.,* Vol. 33, pp. 4457-4464.

Pavageau, M., Morin, H., Seby, F., Guiman, C., Krupp, E. Pecheyran, C., Poulleau, J., Donard, O.F.X.(2004). "Partioning of Metal Species During an Enriched Fuel Combustion Experiment. Speciation in the Gaseous and Particulates Phases, *Environmental Science and Technology*, Vol. 38, 2252-2263.

Peacock, C.L. and Sherman, D.M. (2004). "Vanadium (V) Adsorption onto Geothite (α – FeOOH) at pH 1.5 to pH 12: A Surface Complexation Model Based on an Initio Molecular Geometries and EXAFS Spectroscopy", *Geochim. Cosmochim*, Vol. 68, pp. 1723 - 1733.

Piantone, P., Bodenan, F., Chatelet – Sniduro, L., (2004). "Minerological Study of Secondary Mineral Phases from Weathered MSWI Bottom Ash: Implications for the Modelling and Trapping of Heavy Metals", *Applied Geochemistry*, Vol. 19, 1981-1904.

Rai, D. and Zachara, J.M. (1984). "Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration Review", Vol. 1, Electric Power Institute Rep. EPRI, EA - 3356 .

Ricou, P., Lecuyer, I., and Le Cloirec, P. (1999). "Removal of Cu^{2+}, Zn^{2+} and Pb^{2+} By Adsorption Onto Fly Ash and Fly Ash/Lime Mixing", *Wat. Sci. Tech.*, Vol. 39, pp. 239 – 247.

Sauer, J.J., Benson, C.H., and Edil, T.B. (2005). "Leaching of Heavy Metals from Organic Soils Stabilized with High Carbon Fly Ash", Geo Engineering Report No. 05-01, Geo Engineering Program, University of Wisconsin – Madison, Madison, WI.

Samaras, P., Papadimitriou, C.A., Haritou, I., Zouboluis, A.I. (2008). "Investigation of Sewage Sludge Stabilization Potential by the Addition of Fly Ash and Lime", *Journal of Hazardous Materials*, Vol. 154, pp. 1052-1059.

Soco, E., and Kalembkiewicz, J. (2007). “Investigations of Sequential Leaching Behavior of Cu and Zn from Coal Fly Ash and Their Mobility in Environmental Conditions”, *Journal of Hazardous Materials*, Vol, 145, 482-487.

Sparks, D.L. (2003). *Environmental Soil Chemistry*, Academic Press, California, USA, 300 p.

Srivastava, S., Chaudhary, R., and Khale, D. (2008). “ Influence of pH, Curing Time and Environmental Stress on the Immobilization of Hazardous Waste Using Activated Fly Ash”, *Journal of Hazardous Materials*, Vol. 153, pp. 1103 – 1109.

Stumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry*, *Chemical Equilibria and Rates in Natural Waters*, 3rd ed. John Wiley & Sons, Inc., New York, 1022 p.

Sushil, S., and Batra, V.S. (2006). “Analysis of Fly Ash Heavy Metal Content and Disposal in Three Thermal Power Plants in India”, *Journal of Fuel*, Vol. 85, pp. 2676 – 2679.

Suzuki, K., and Ono, Y. (2008). “Leaching Characteristics of Stabilized/Solidified Fly Ash Generated from Ash – Melting Plant”, *Journal of Chemosphere*, Vol. 71, pp. 922 – 932.

Theis, T.M and Wirth, J. L. (1977). “Sorptive Behavior of Trace Metals on Fly Ash in Aqueous Systems,” Envir. Sci. and Technol., Vol. 11(12), pp. 1096 – 1100.

van der Hoek, E.E., van Elteren, J.T., Comans, R.N.J., (1996). “Determination of As, Sb, and Se Speciation in Fly Ash Leachates”, *Internat. Environ*, Vol. 63, 67-79.

Vitkova, M., Ettler, V., Sebek, O.,and Mihaljevic, M. (2008). “Metal – ContamiNAnt Leaching from Lead Smelter Fly Ash Using pH – Stat Experiments”, *Mineralogical Magazine*, Vol. 72, pp. 521 – 524.

Wang, W., Qin, Y., Song, D., and Wang, K. (2008). “Column Leaching of Coal and Its Combustion Residues, Shizuishan, ChiNA”, *International Journal of Coal Geology*, Vol. 75, pp. 81 -87.

Wang, J., Ban, H., Teng, X., Wang, H.,and Ladwig, K. (2006). "Impacts of pH and Ammonia on the Leaching of Cu(II) and Cd(II) from Coal Fly Ash", *Journal of Chemosphere*, Vol. 64, pp. 1892 – 1898.

Wang, T., Wang, J, Tang, Y., Shi, H., and Ladwig, K (2009). "Leaching Characteristics of Arsenic and Selenium from Coal Fly Ash: Role of Calcium", *Journal of Energy & Fuels*, Vol. 23, pp. 2959 – 2966.

Wehrer, M. and Totsche, K.U. (2008). "Effective Rates of Heavy Metal Release from Alkaline Wastes – Quantified by Column Outflow Experiments and Inverse Simulations",*Journal of Contaminant Hydrology*, Vol. 101, pp. 53 – 66.

Whalley, C., Hursthouse, A., Rowlat, S., Iqbal-Zahid, P., Vaughan, H., and Durant, R. (1999), "Chromium Speciation in Natural Waters Draining Contaminated Land, Glasgow, U.K." *Water Air Soil Pollution*, Vol. 112, pp. 389 – 405.

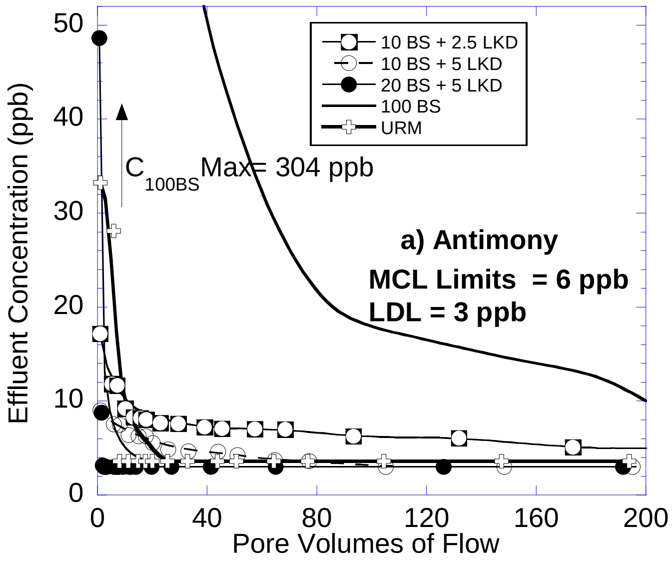
Yan, R., Gauthier, D., and Flamant, G. (2001). "Volatility and Chemistry of Trace Elements in a Coal Combustor", *Fuel*, Vol. 80, pp. 2217 – 2226.

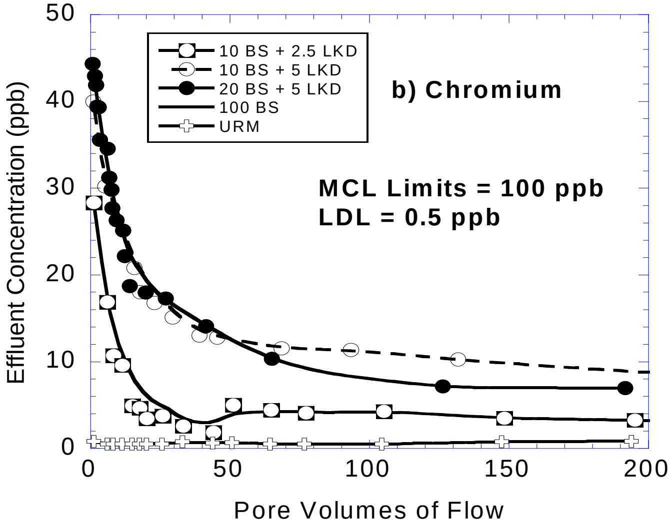
Yoon, S., Balunaini, U., Yildirim, Z.I., Prezzi, M.,and Siddiki, N. (2009). "Construction of Embankment with Fly and Bottom Ash Mixture, Field Performance Study", *J.Mat. in Civ. Engrg*, Vol. 21 – 6, pp. 271 – 278.

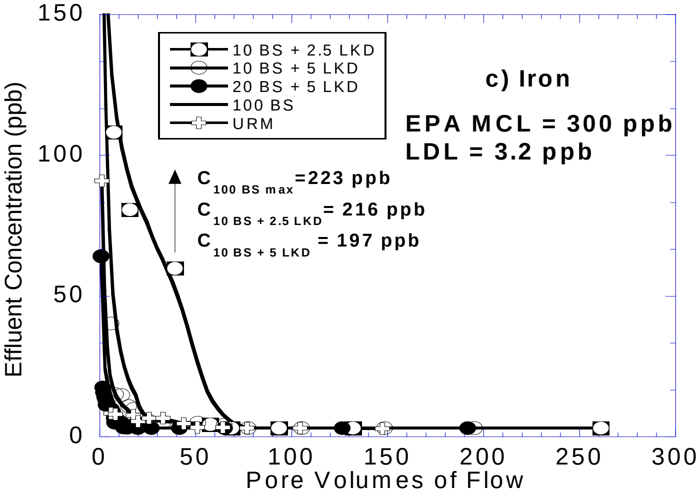
Zhang, J., and Solis, R. (2008). "Fly Ash Stabilized Gypsiferous Soil as Embankment Material", *Earth & Environmental Science*, Vol. 6, pp. 809 – 814.

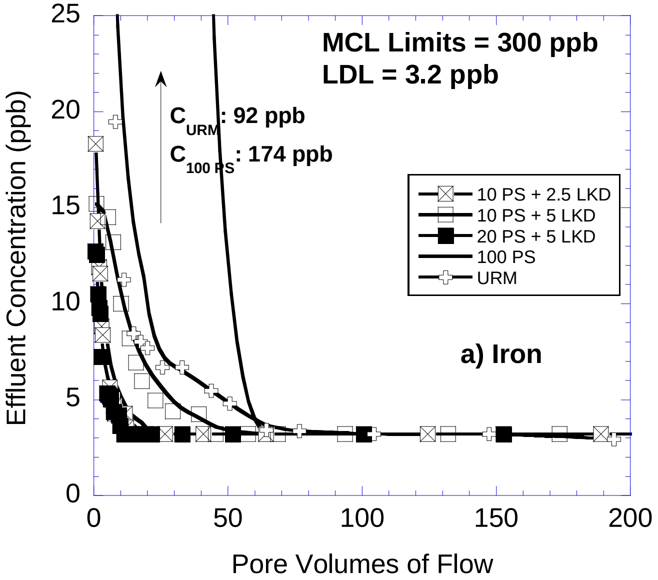
APPENDIX A

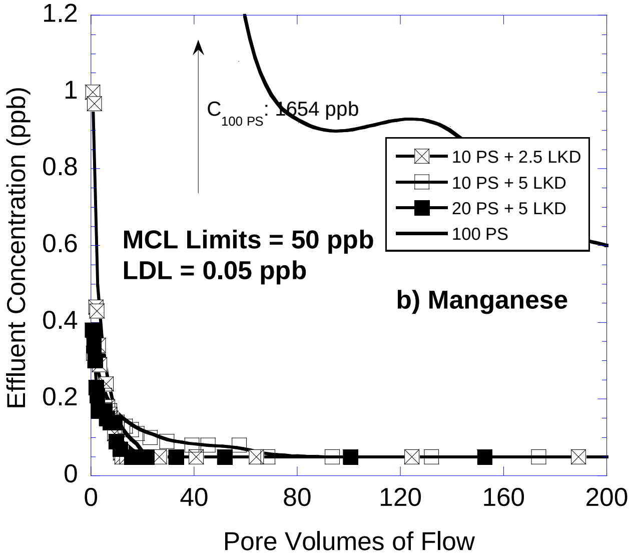
Elution Curves for Metals for High Carbon Fly Ash Stabilized Base Layer

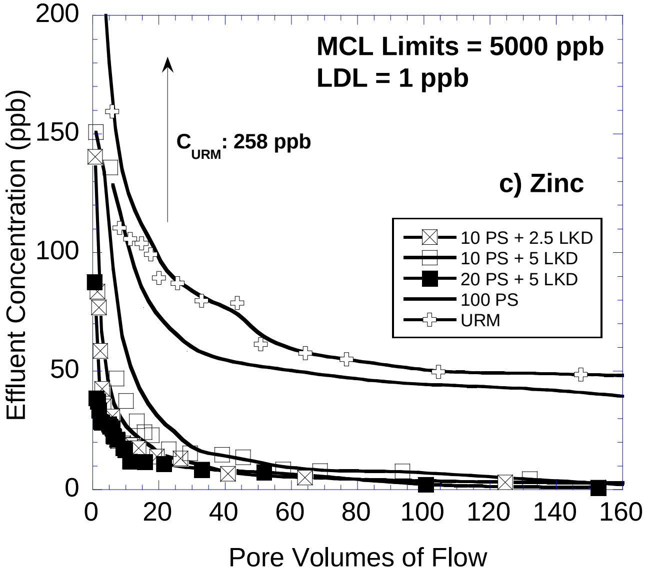

a) Antimony
MCL Limits = 6 ppb
LDL = 3 ppb
C_{100BS}Max= 304 ppb
10 BS + 2.5 LKD
10 BS + 5 LKD
20 BS + 5 LKD
100 BS
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
0
10
20
30
40
50
0
40
80
120
160
200

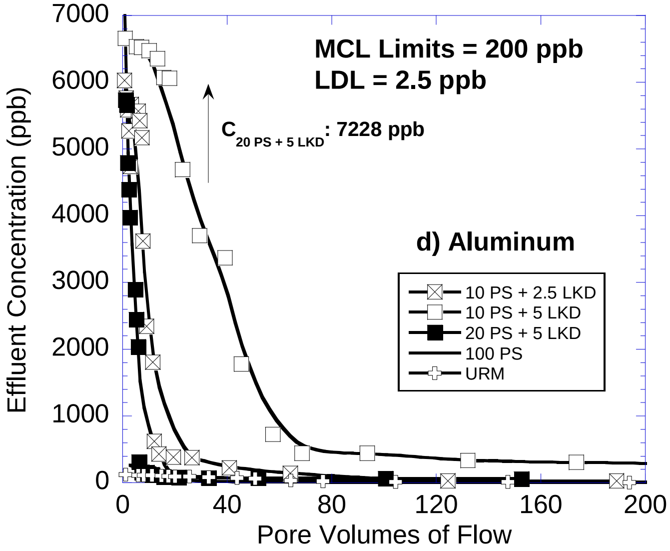

b) Chromium
MCL Limits = 100 ppb
LDL = 0.5 ppb
10 BS + 2.5 LKD
10 BS + 5 LKD
20 BS + 5 LKD
100 BS
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
0
10
20
30
40
50
0
50
100
150
200

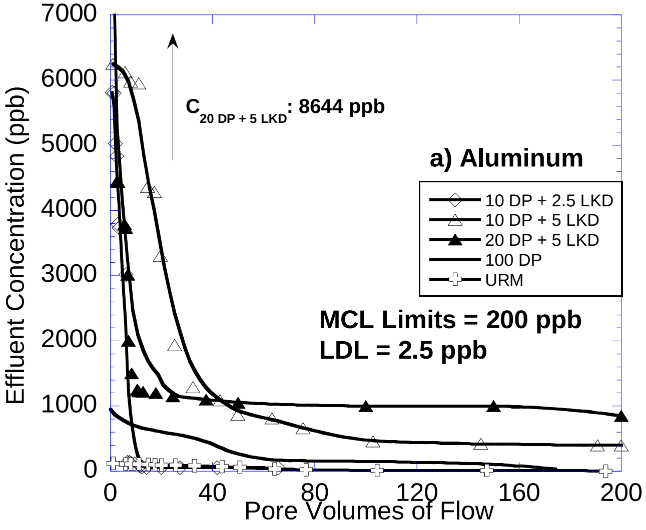

c) Iron
EPA MCL = 300 ppb
LDL = 3.2 ppb
$C_{100\ BS\ max}$=223 ppb
$C_{10\ BS\ +\ 2.5\ LKD}$= 216 ppb
$C_{10\ BS\ +\ 5\ LKD}$= 197 ppb
10 BS + 2.5 LKD
10 BS + 5 LKD
20 BS + 5 LKD
100 BS
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
0
50
100
150
0
50
100
150
200
250
300

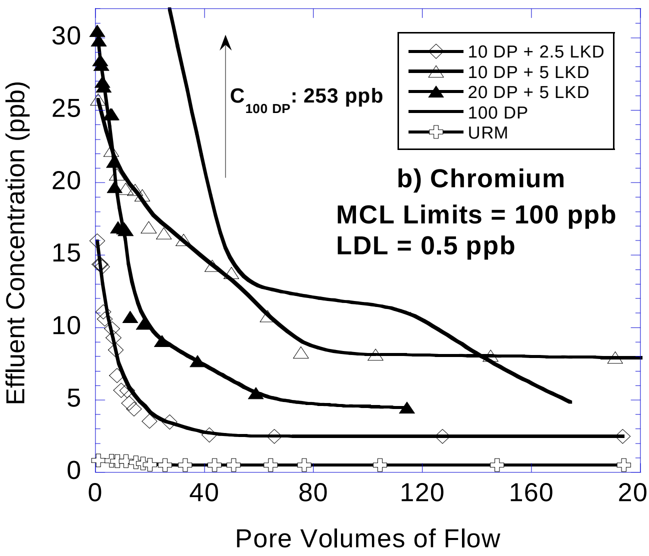

MCL Limits = 300 ppb
LDL = 3.2 ppb
C_{URM}: 92 ppb
$C_{100\ PS}$: 174 ppb
10 PS + 2.5 LKD
10 PS + 5 LKD
20 PS + 5 LKD
100 PS
URM
a) Iron
Effluent Concentration (ppb)
Pore Volumes of Flow
0
5
10
15
20
25
0
50
100
150
200

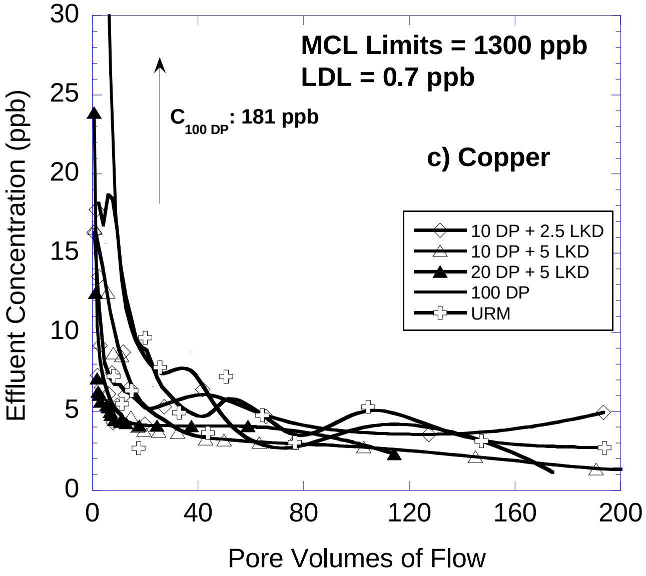

$C_{100\ PS}$: 1654 ppb
10 PS + 2.5 LKD
10 PS + 5 LKD
20 PS + 5 LKD
100 PS
MCL Limits = 50 ppb
LDL = 0.05 ppb
b) Manganese
Effluent Concentration (ppb)
Pore Volumes of Flow
0
0.2
0.4
0.6
0.8
1
1.2
0
40
80
120
160
200

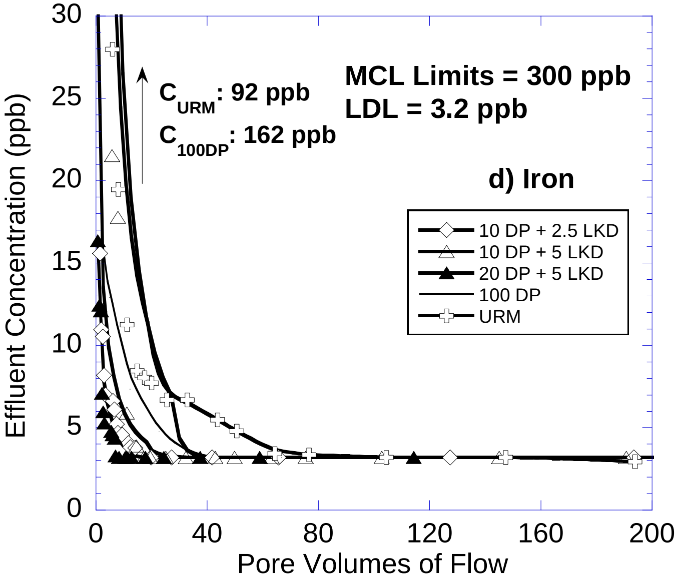

MCL Limits = 5000 ppb
LDL = 1 ppb
C_{URM}: 258 ppb
c) Zinc
10 PS + 2.5 LKD
10 PS + 5 LKD
20 PS + 5 LKD
100 PS
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
0
50
100
150
200
0
20
40
60
80
100
120
140
160

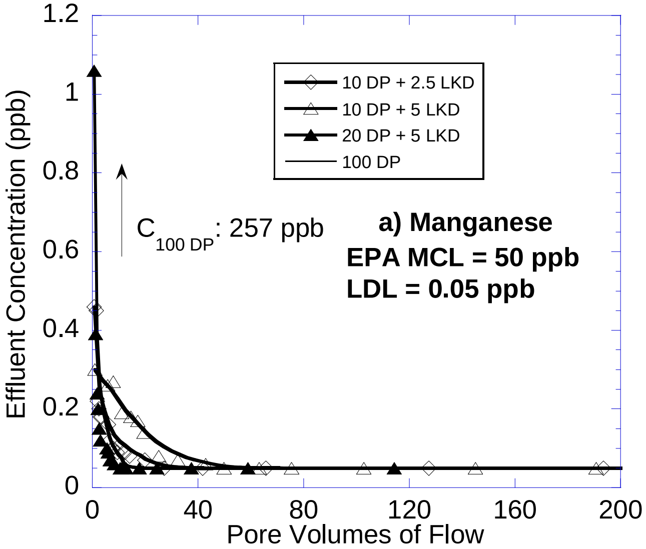

MCL Limits = 200 ppb
LDL = 2.5 ppb
$C_{20\ PS\ +\ 5\ LKD}$: 7228 ppb
d) Aluminum
10 PS + 2.5 LKD
10 PS + 5 LKD
20 PS + 5 LKD
100 PS
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
0
1000
2000
3000
4000
5000
6000
7000
0
40
80
120
160
200

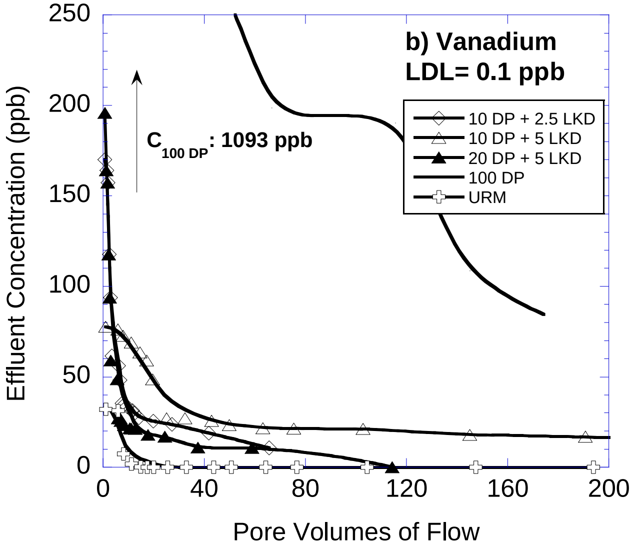

a) Aluminum
C$_{20\ DP + 5\ LKD}$: 8644 ppb
MCL Limits = 200 ppb
LDL = 2.5 ppb
10 DP + 2.5 LKD
10 DP + 5 LKD
20 DP + 5 LKD
100 DP
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
7000
6000
5000
4000
3000
2000
1000
0
0
40
80
120
160
200

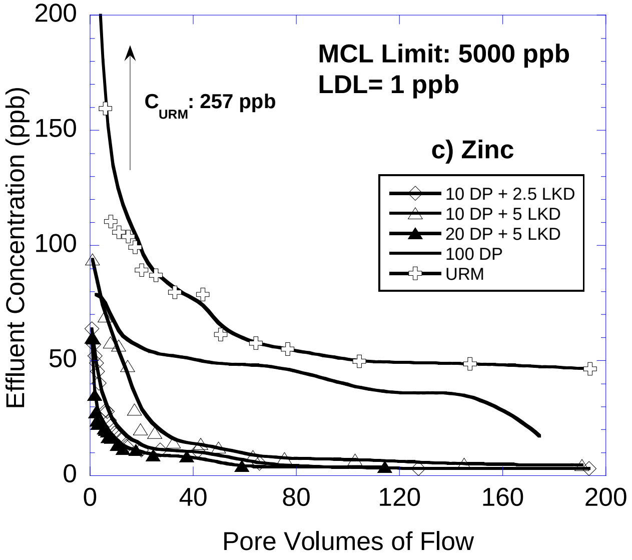

b) Chromium
C$_{100\ DP}$: 253 ppb
MCL Limits = 100 ppb
LDL = 0.5 ppb
10 DP + 2.5 LKD
10 DP + 5 LKD
20 DP + 5 LKD
100 DP
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
30
25
20
15
10
5
0
0
40
80
120
160
200


c) Copper
MCL Limits = 1300 ppb
LDL = 0.7 ppb
C$_{100\ DP}$: 181 ppb
10 DP + 2.5 LKD
10 DP + 5 LKD
20 DP + 5 LKD
100 DP
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
30
25
20
15
10
5
0
0
40
80
120
160
200


d) Iron
C$_{URM}$: 92 ppb
C$_{100DP}$: 162 ppb
MCL Limits = 300 ppb
LDL = 3.2 ppb
10 DP + 2.5 LKD
10 DP + 5 LKD
20 DP + 5 LKD
100 DP
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
30
25
20
15
10
5
0
0
40
80
120
160
200

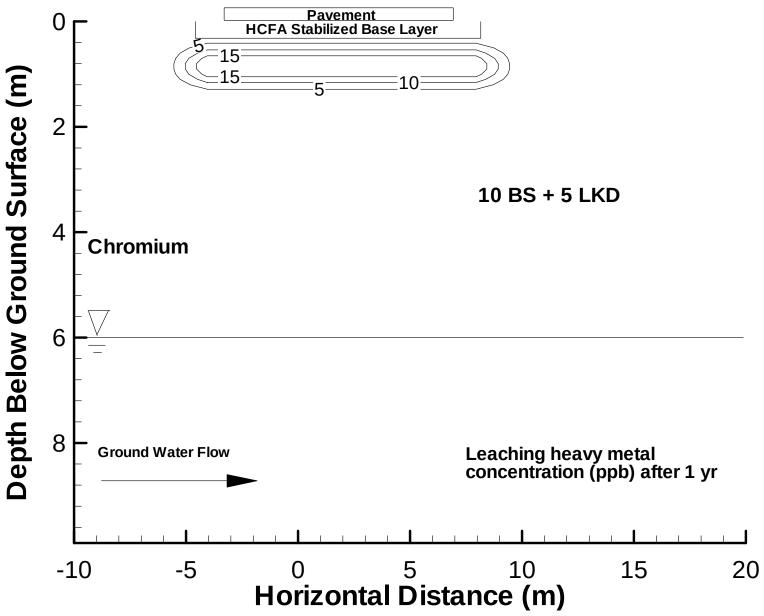

a) Manganese
EPA MCL = 50 ppb
LDL = 0.05 ppb
C100 DP: 257 ppb
10 DP + 2.5 LKD
10 DP + 5 LKD
20 DP + 5 LKD
100 DP
Effluent Concentration (ppb)
Pore Volumes of Flow
0
0.2
0.4
0.6
0.8
1
1.2
0
40
80
120
160
200

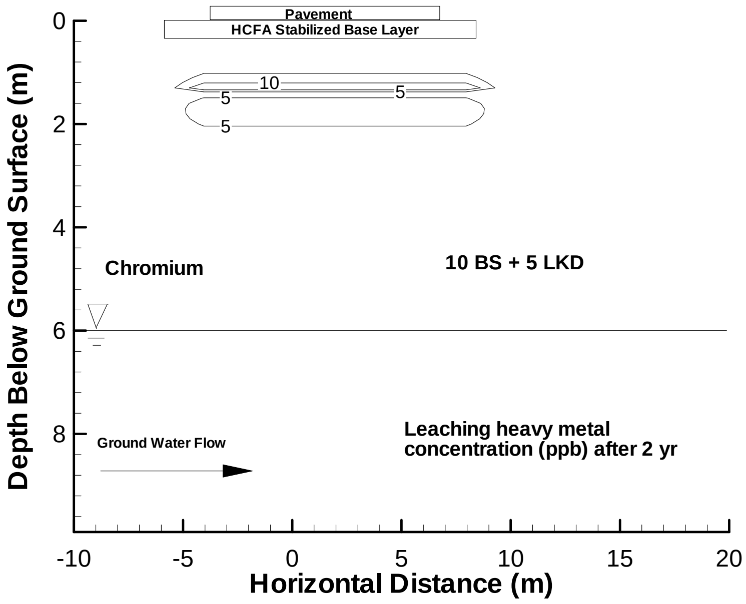

b) Vanadium
LDL= 0.1 ppb
C100 DP: 1093 ppb
10 DP + 2.5 LKD
10 DP + 5 LKD
20 DP + 5 LKD
100 DP
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
0
50
100
150
200
250
0
40
80
120
160
200

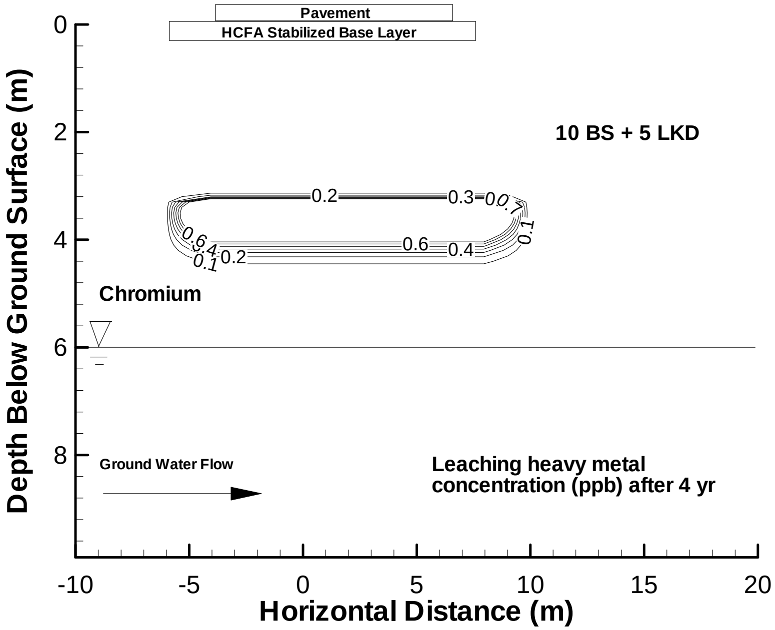

MCL Limit: 5000 ppb
LDL= 1 ppb
CURM: 257 ppb
c) Zinc
10 DP + 2.5 LKD
10 DP + 5 LKD
20 DP + 5 LKD
100 DP
URM
Effluent Concentration (ppb)
Pore Volumes of Flow
0
50
100
150
200
0
40
80
120
160
200

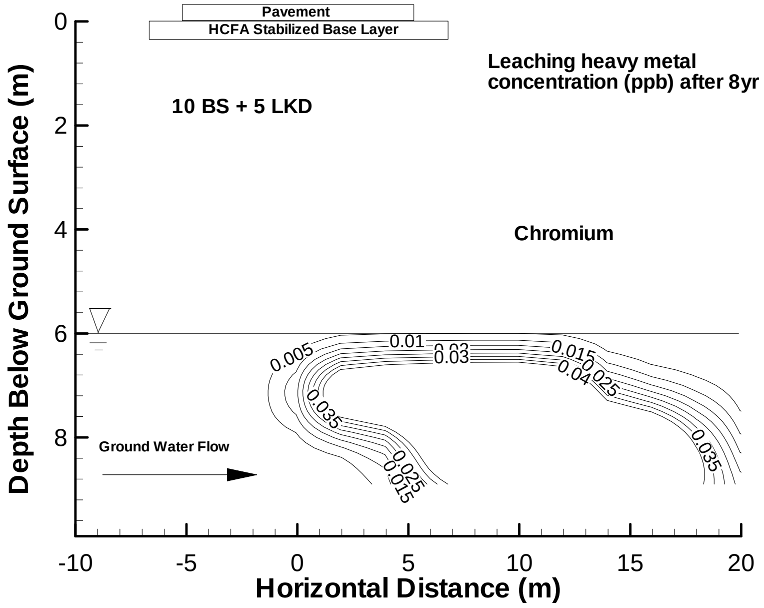
APPENDIX B

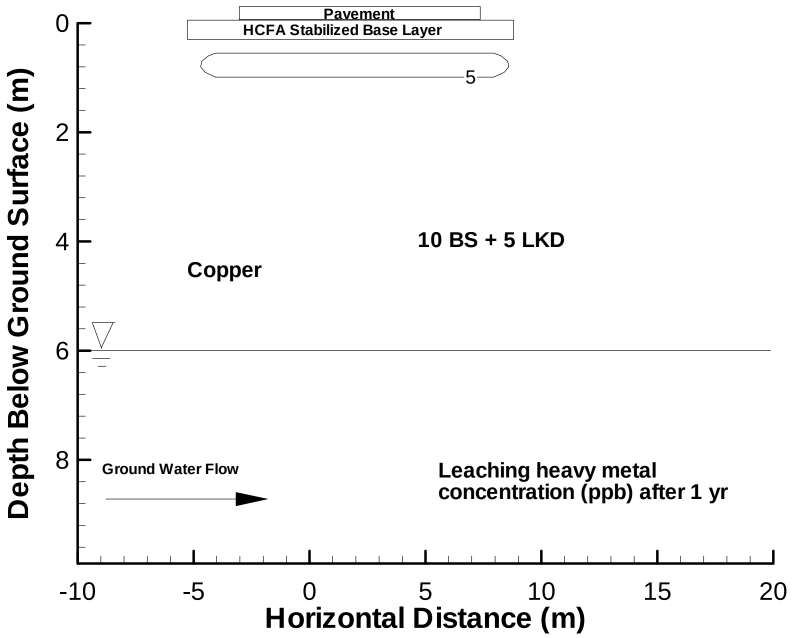
Predicted Cr concentrations in vadose zone and ground water for High Carbon Fly Ash Stabilized Base Layer

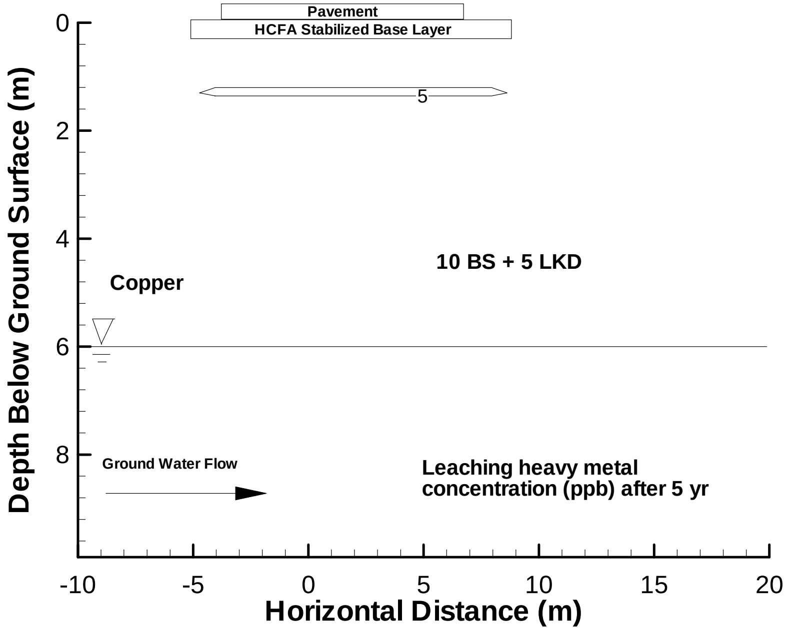

Pavement
HCFA Stabilized Base Layer
5
15
15
5
10
10 BS + 5 LKD
Chromium
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

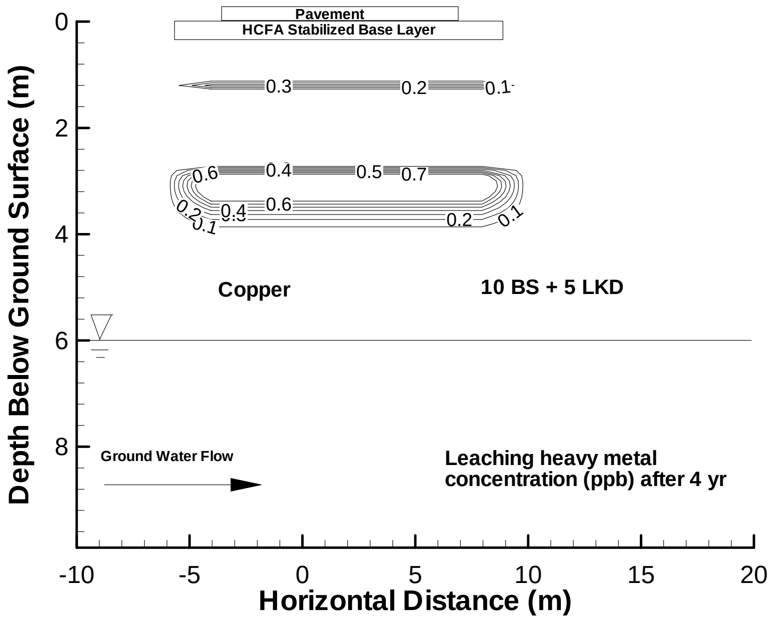

Pavement
HCFA Stabilized Base Layer
10
5
5
5
10 BS + 5 LKD
Chromium
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

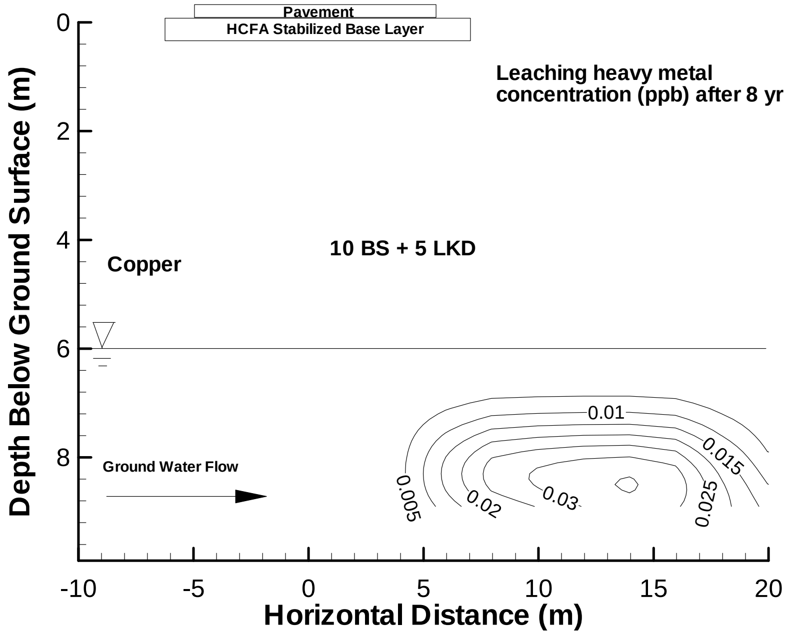

Pavement
HCFA Stabilized Base Layer
10 BS + 5 LKD
0.2
0.3
0.7
0.1
0.6
0.4
0.1
0.2
0.6
0.4
Chromium
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

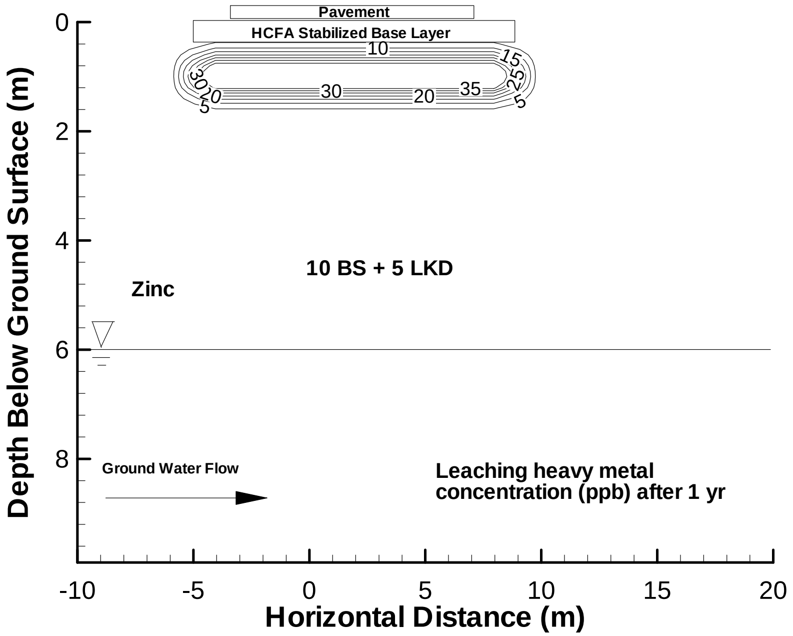

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8yr
10 BS + 5 LKD
Chromium
0.005
0.01
0.03
0.03
0.015
0.04
0.025
0.035
0.025
0.015
0.035
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

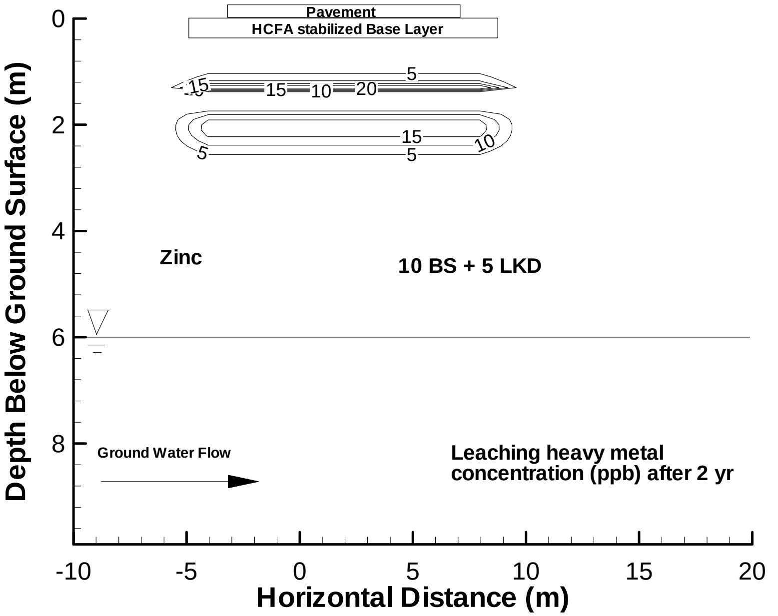

Pavement
HCFA Stabilized Base Layer
5
10 BS + 5 LKD
Copper
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

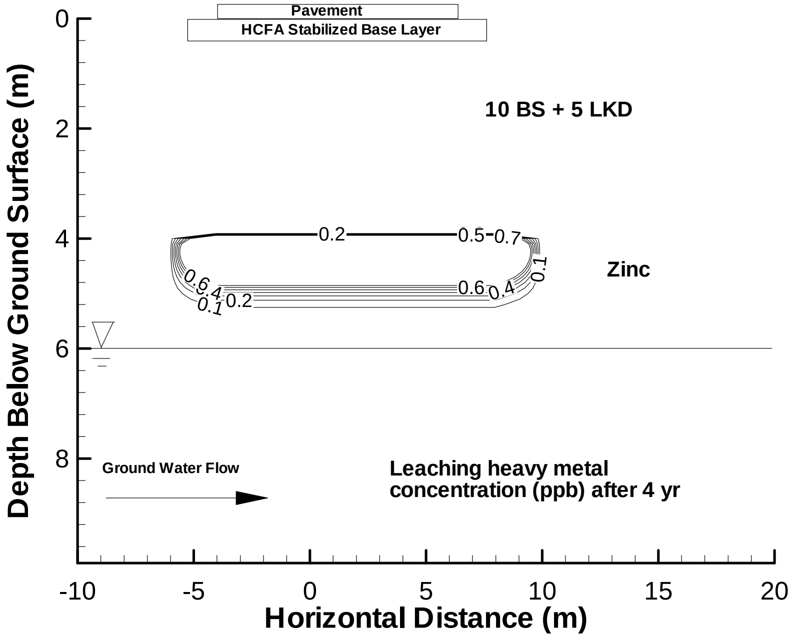

Pavement
HCFA Stabilized Base Layer
5
10 BS + 5 LKD
Copper
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 5 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

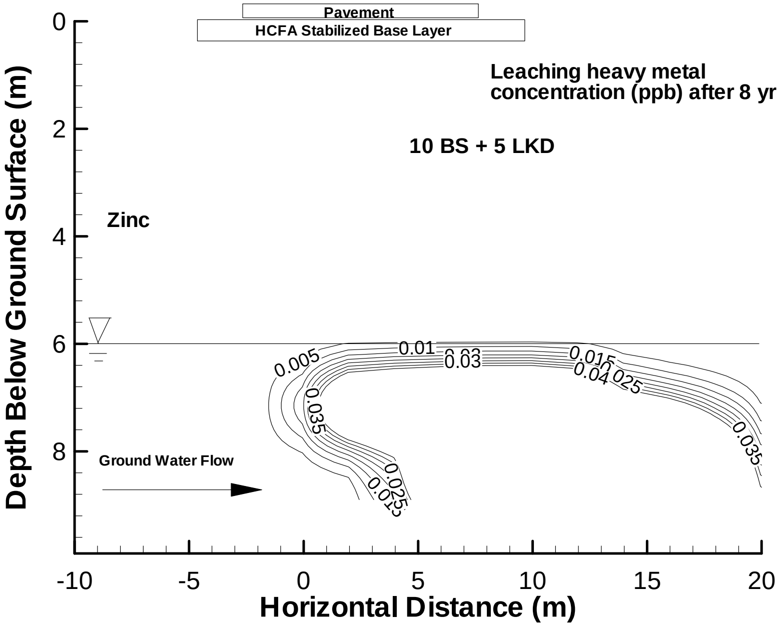

Pavement
HCFA Stabilized Base Layer
0.3
0.2
0.1
0.6
0.4
0.5
0.7
0.2
0.4
0.6
0.1
0.2
0.1
Copper
10 BS + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

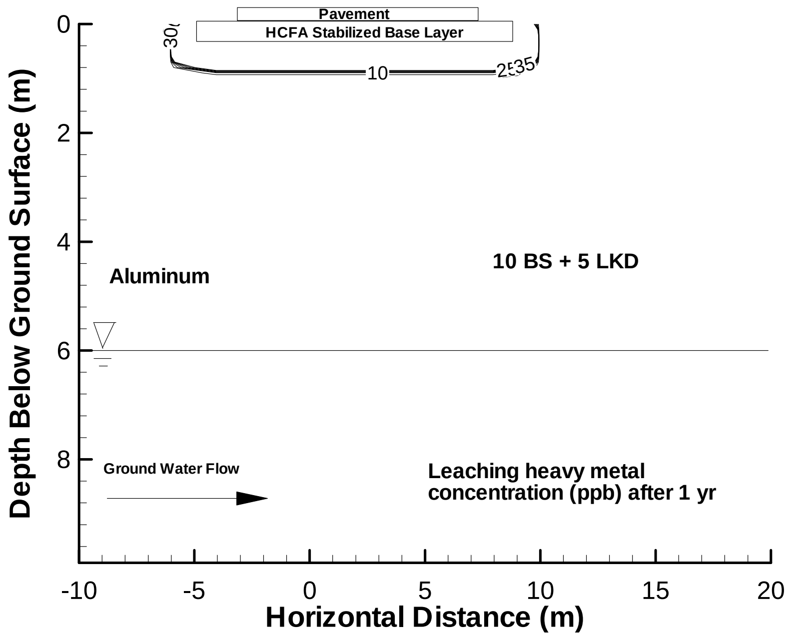

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal
concentration (ppb) after 8 yr
10 BS + 5 LKD
Copper
0.01
0.015
0.005
0.02
0.03
0.025
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

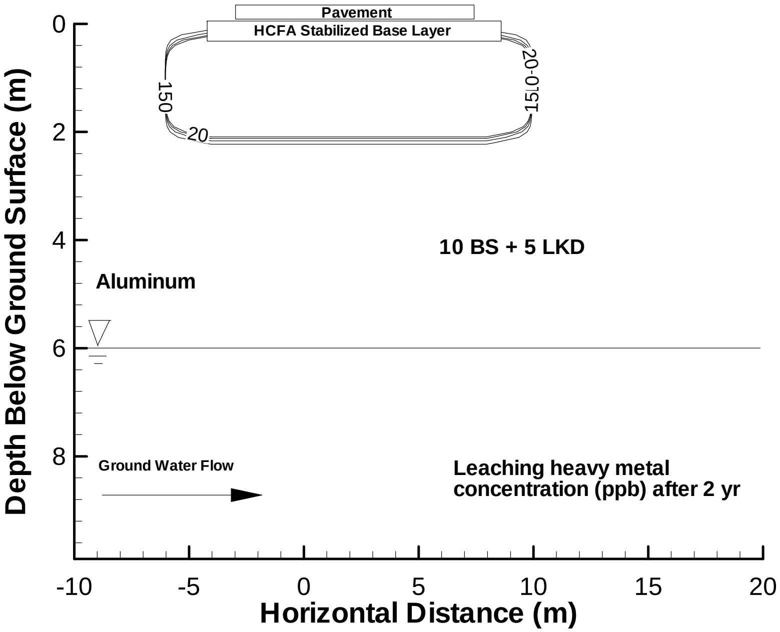

Pavement
HCFA Stabilized Base Layer
10
15
30
20
30
20
35
25
5
5
10 BS + 5 LKD
Zinc
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20

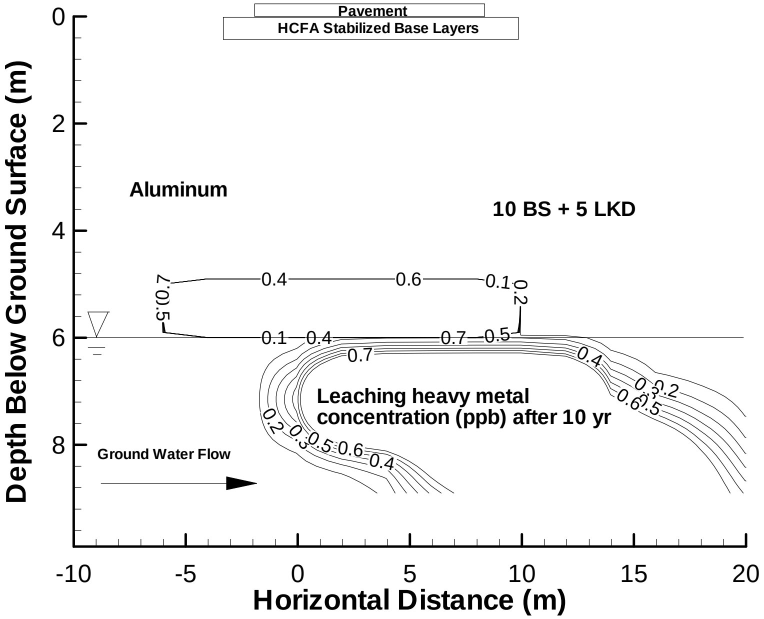

Pavement
HCFA stabilized Base Layer
5
15
15
10
20
15
10
5
5
Zinc
10 BS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20

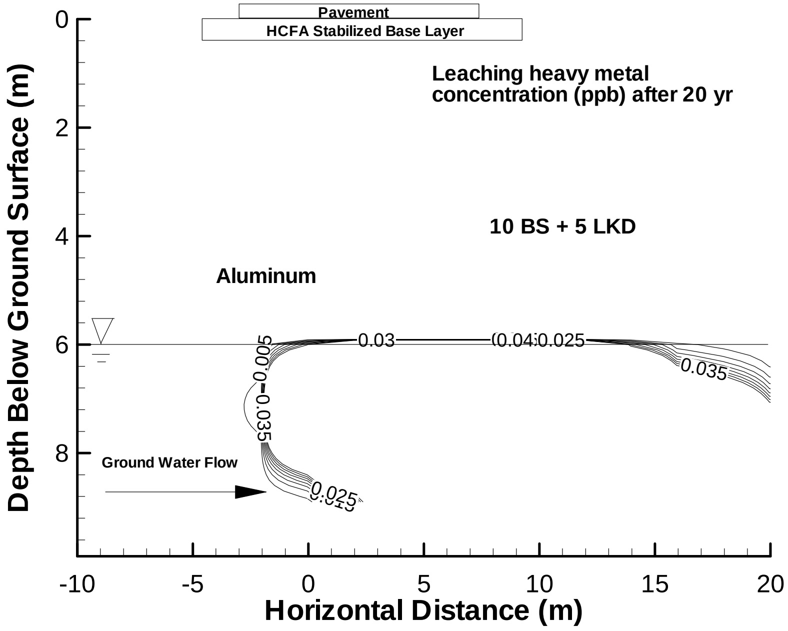

Pavement
HCFA Stabilized Base Layer
10 BS + 5 LKD
0.2
0.5
0.7
0.1
0.6
0.4
0.2
0.1
0.6
0.4
Zinc
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20

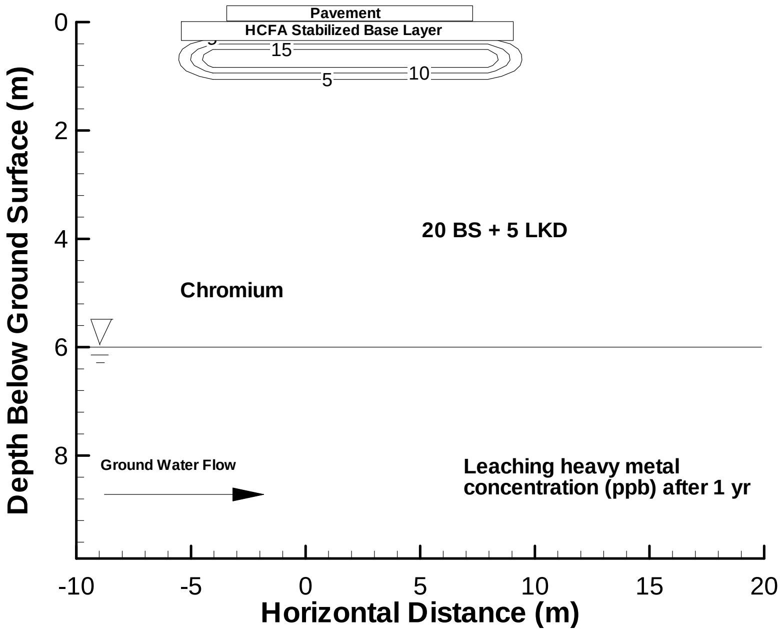

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
10 BS + 5 LKD
Zinc
0.005
0.01
0.03
0.03
0.015
0.04
0.025
0.035
0.035
0.025
0.015
Ground Water Flow
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20

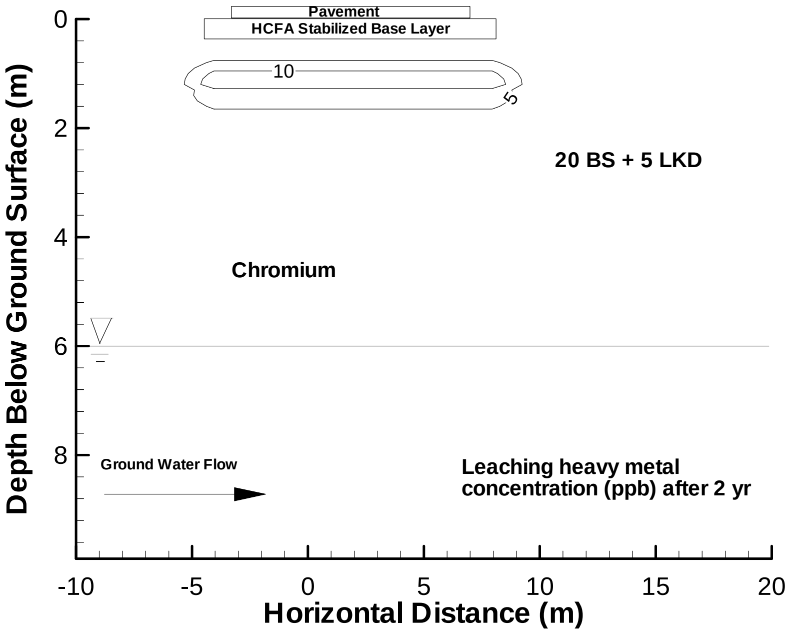

Pavement
HCFA Stabilized Base Layer
30
10
25
35
Aluminum
10 BS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

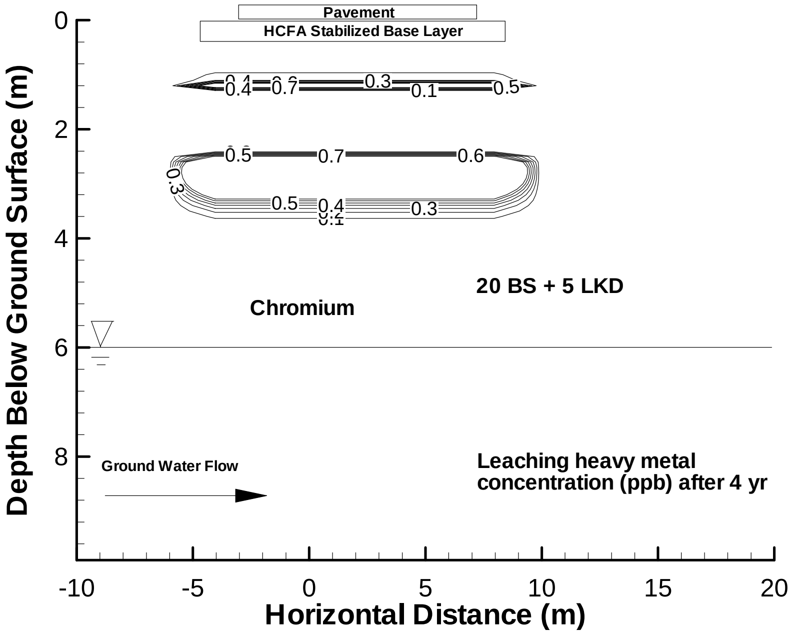

Pavement
HCFA Stabilized Base Layer
150
20
20
0
15
Aluminum
10 BS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

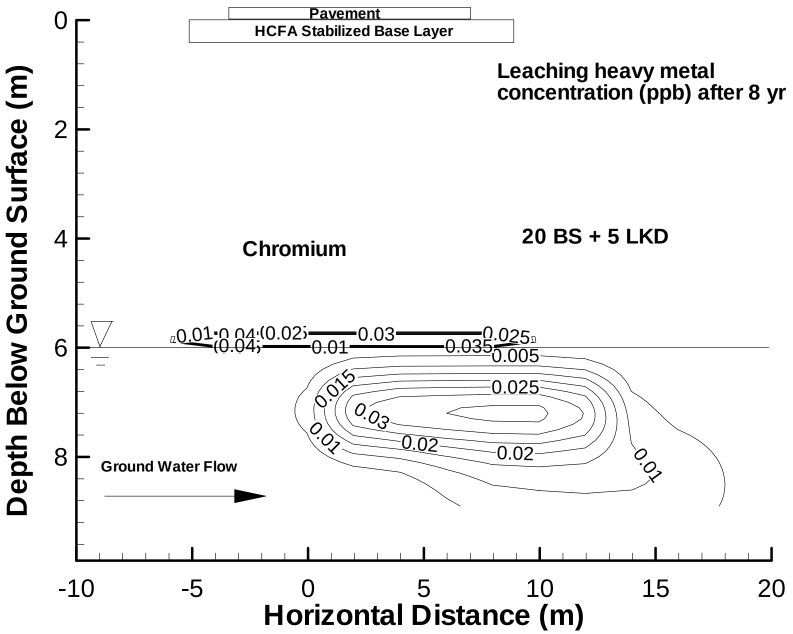

Pavement
HCFA Stabilized Base Layers
Aluminum
10 BS + 5 LKD
0.4
0.6
0.1
0.2
0.5
0.1
0.4
0.7
0.5
0.7
0.4
0.2
0.6
0.5
0.2
0.3
0.5
0.6
0.4
Leaching heavy metal concentration (ppb) after 10 yr
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

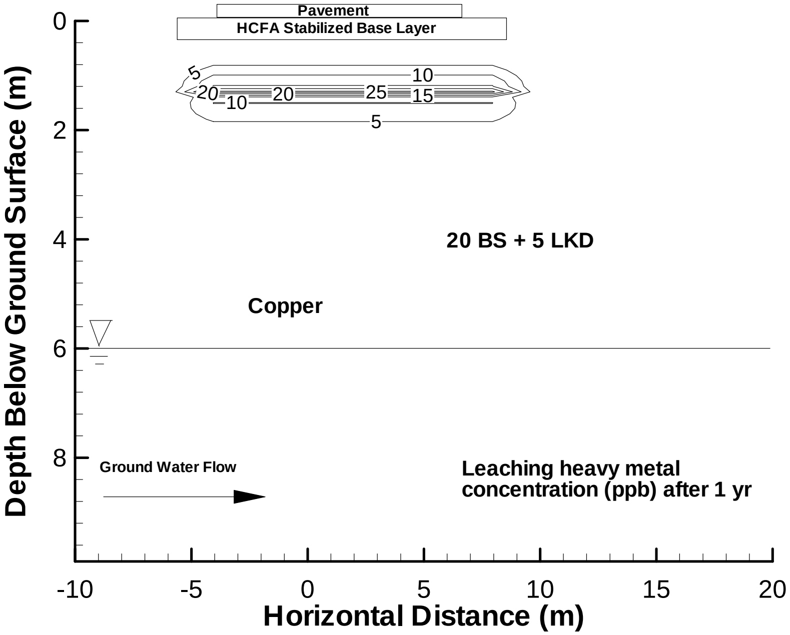

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 20 yr
10 BS + 5 LKD
Aluminum
0.03
0.04
0.025
0.035
0.035
0.025
0.015
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

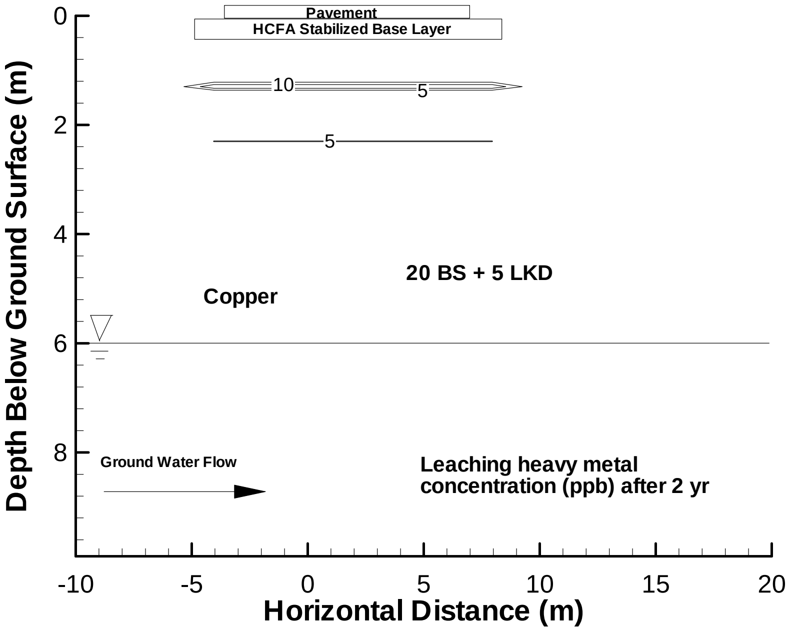

Pavement
HCFA Stabilized Base Layer
15
5
10
20 BS + 5 LKD
Chromium
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

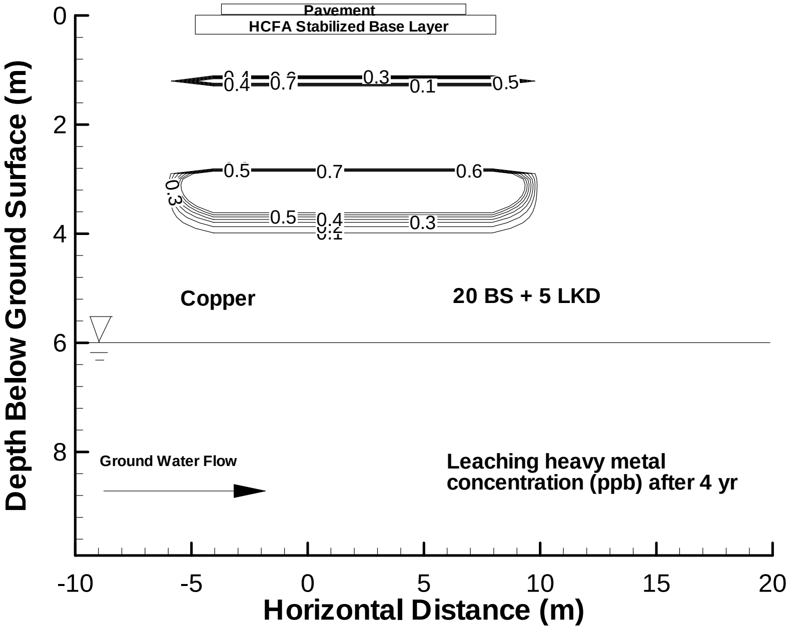

Pavement
HCFA Stabilized Base Layer
10
5
20 BS + 5 LKD
Chromium
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

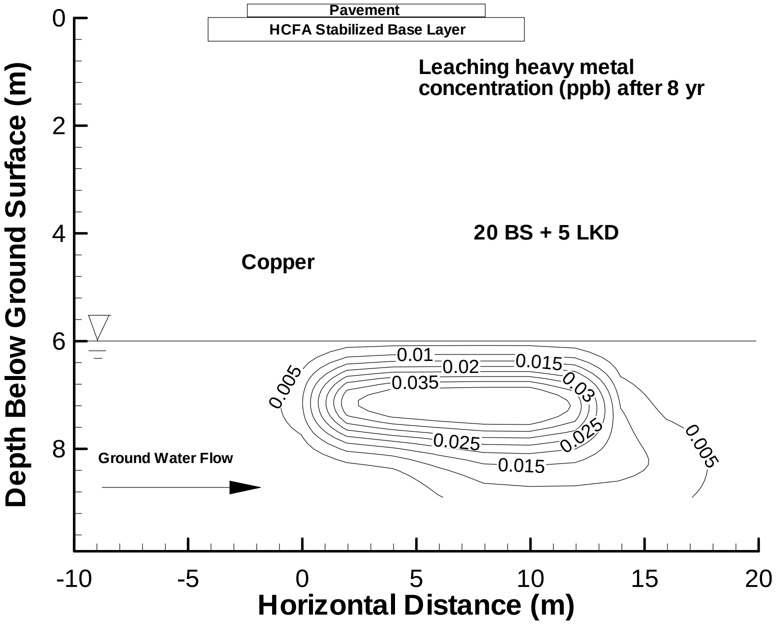

Pavement
HCFA Stabilized Base Layer
0.4
0.7
0.3
0.1
0.5
0.5
0.7
0.6
0.3
0.5
0.4
0.3
0.1
20 BS + 5 LKD
Chromium
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

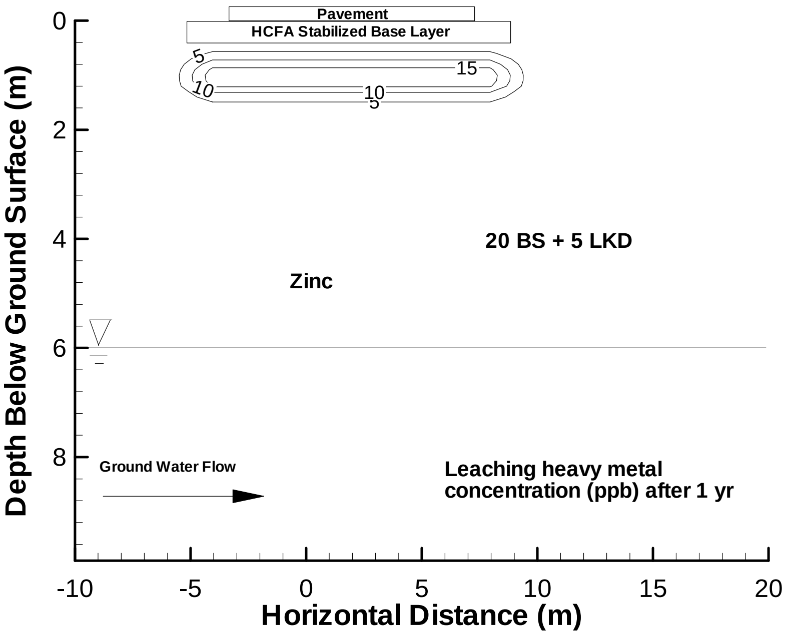

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
20 BS + 5 LKD
Chromium
0.01
(0.02)
0.03
0.025
(0.04)
0.01
0.035
0.005
0.025
0.015
0.03
0.01
0.02
0.02
0.01
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

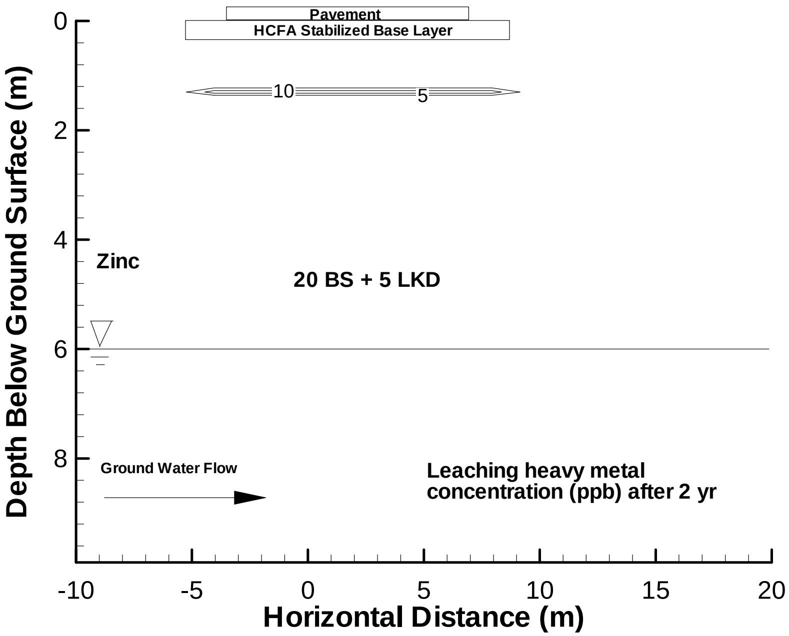

Pavement
HCFA Stabilized Base Layer
5
10
20
20
25
15
10
5
20 BS + 5 LKD
Copper
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

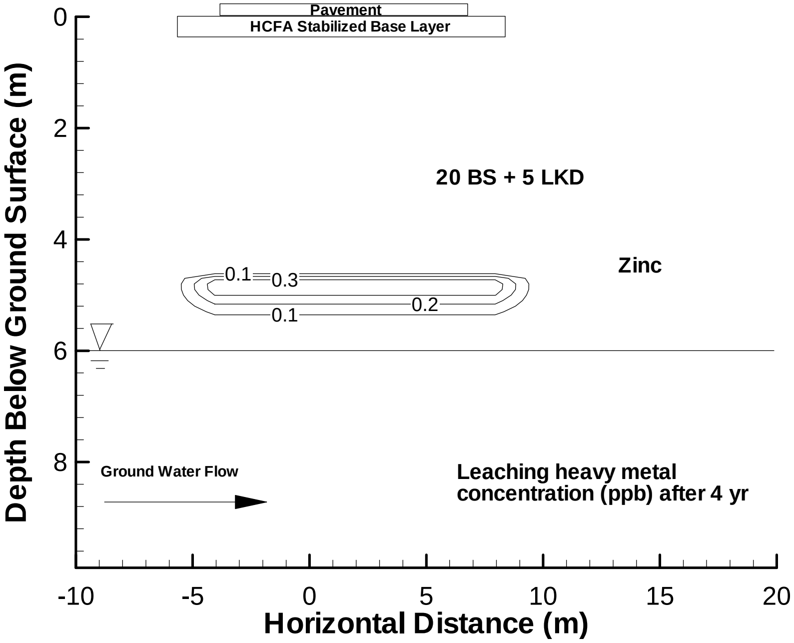

Pavement
HCFA Stabilized Base Layer
10
5
5
20 BS + 5 LKD
Copper
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

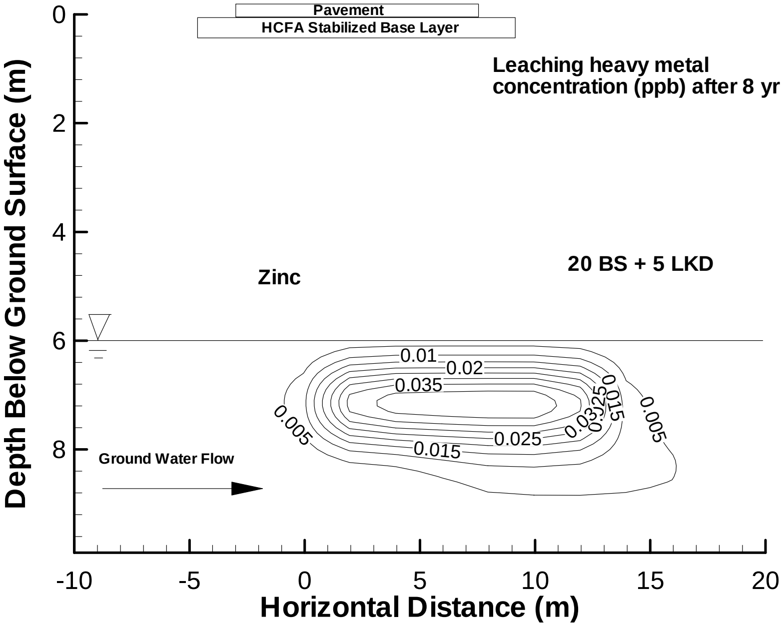

Pavement
HCFA Stabilized Base Layer
0.4
0.7
0.3
0.1
0.5
0.5
0.7
0.6
0.3
0.5
0.4
0.2
0.1
0.3
Copper
20 BS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

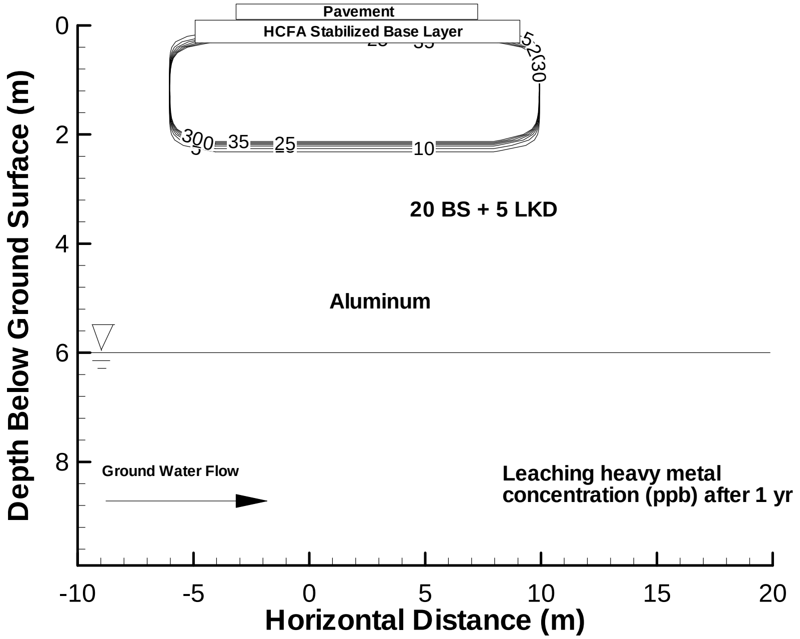

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
20 BS + 5 LKD
Copper
0.01
0.02
0.015
0.005
0.035
0.03
0.025
0.025
0.015
0.005
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20


Pavement
HCFA Stabilized Base Layer
5
15
10
10
5
20 BS + 5 LKD
Zinc
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

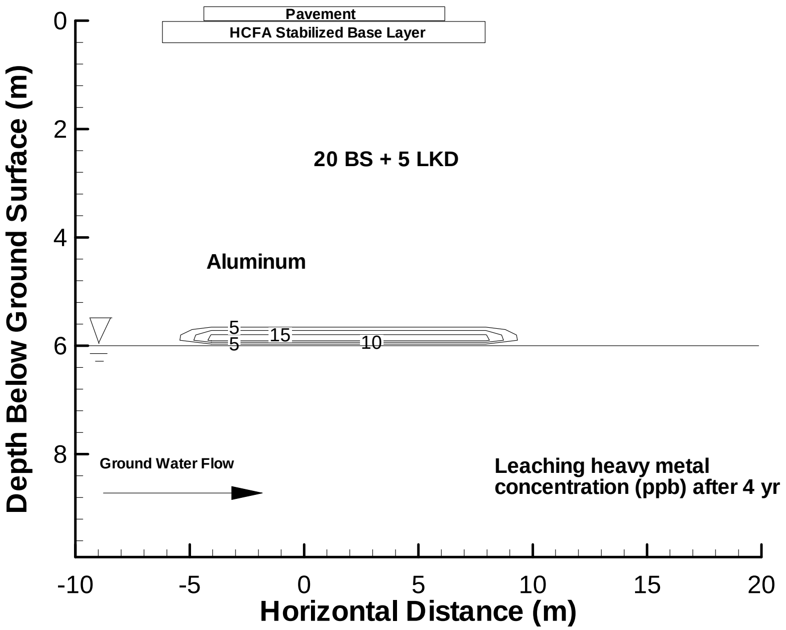

Pavement
HCFA Stabilized Base Layer
10
5
Zinc
20 BS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20


Pavement
HCFA Stabilized Base Layer
20 BS + 5 LKD
Zinc
0.1
0.3
0.1
0.2
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

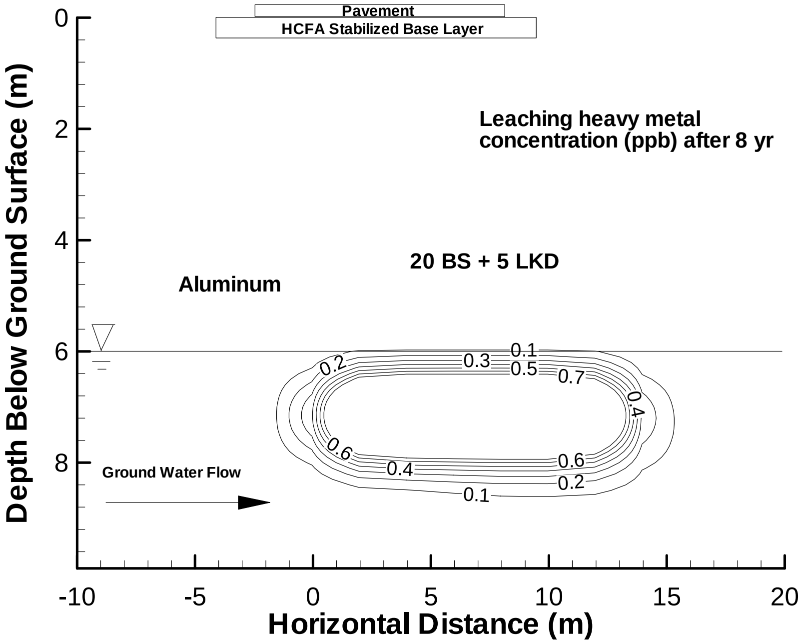

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
Zinc
20 BS + 5 LKD
0.01
0.02
0.035
0.015
0.025
0.03
0.005
0.025
0.015
0.005
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20



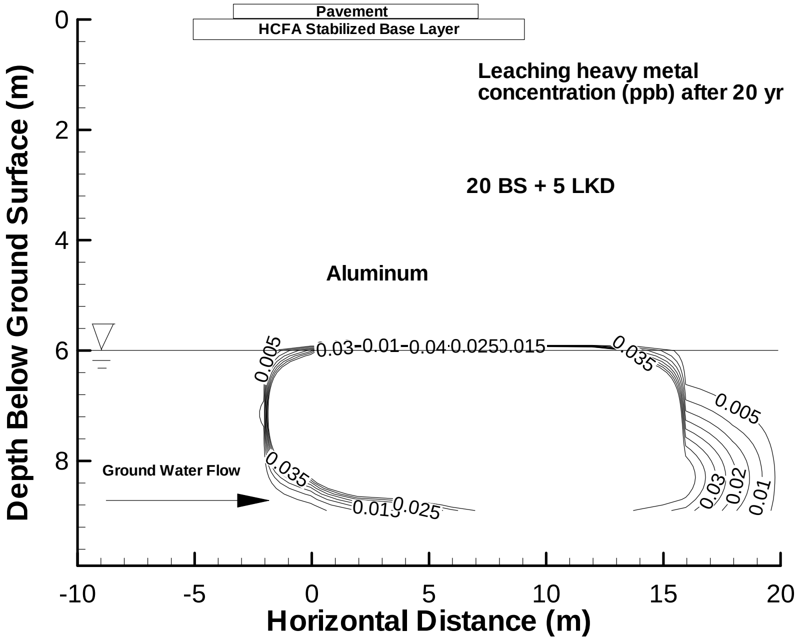
Pavement
HCFA Stabilized Base Layer
20 BS + 5 LKD
Aluminum
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
25
35
30
30
35
25
10



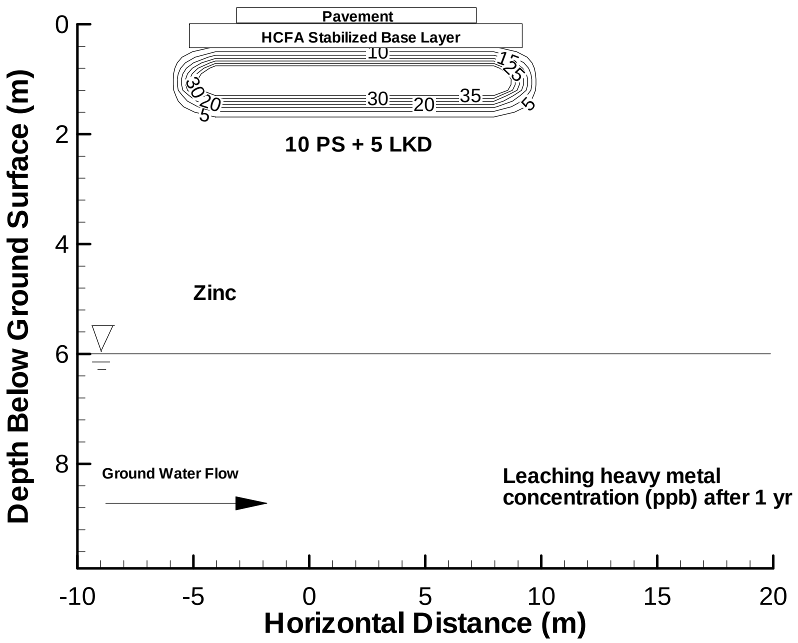
Pavement
HCFA Stabilized Base Layer
20 BS + 5 LKD
Aluminum
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
5
15
5
10

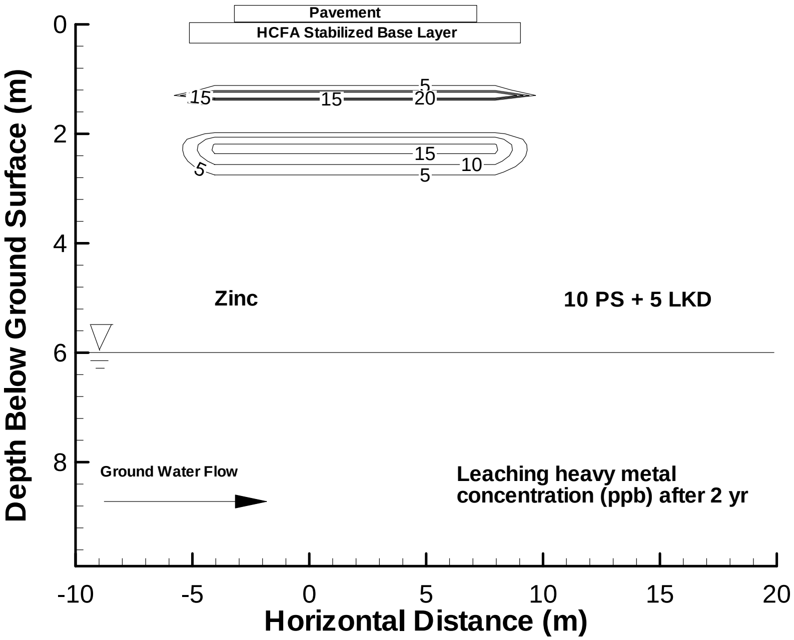


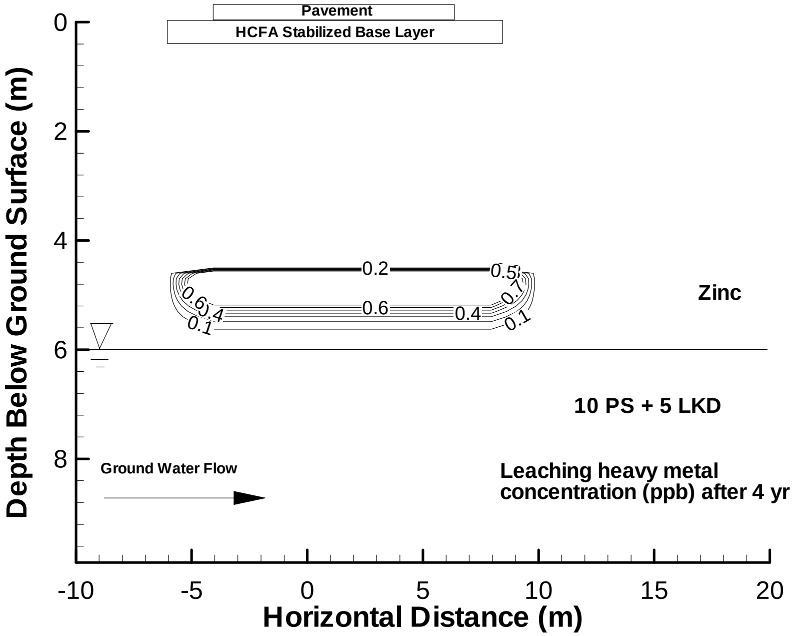
Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
20 BS + 5 LKD
Aluminum
Ground Water Flow
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
0.1
0.2
0.3
0.5
0.7
0.4
0.6
0.4
0.6
0.2
0.1

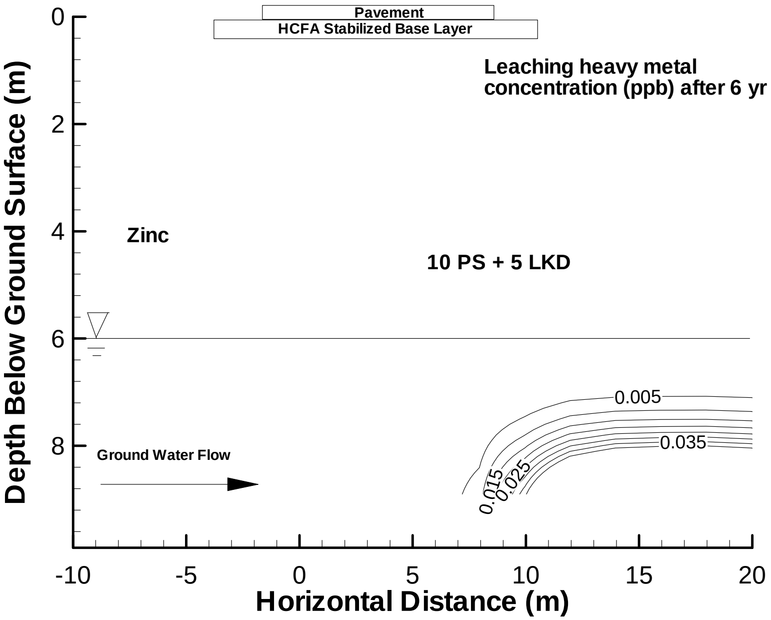


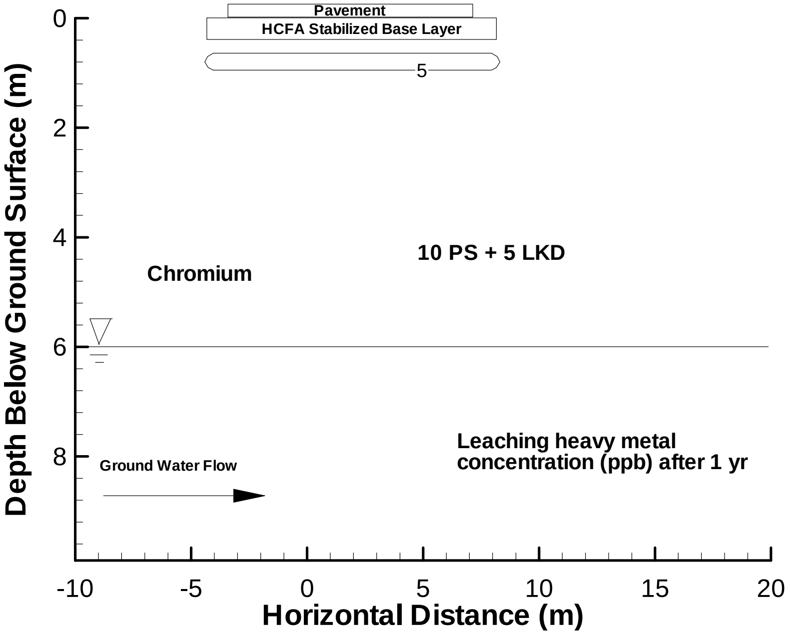
Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 20 yr
20 BS + 5 LKD
Aluminum
Ground Water Flow
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
0.005
0.03
0.01
0.04
0.025
0.015
0.035
0.005
0.035
0.015
0.025
0.03
0.02
0.01

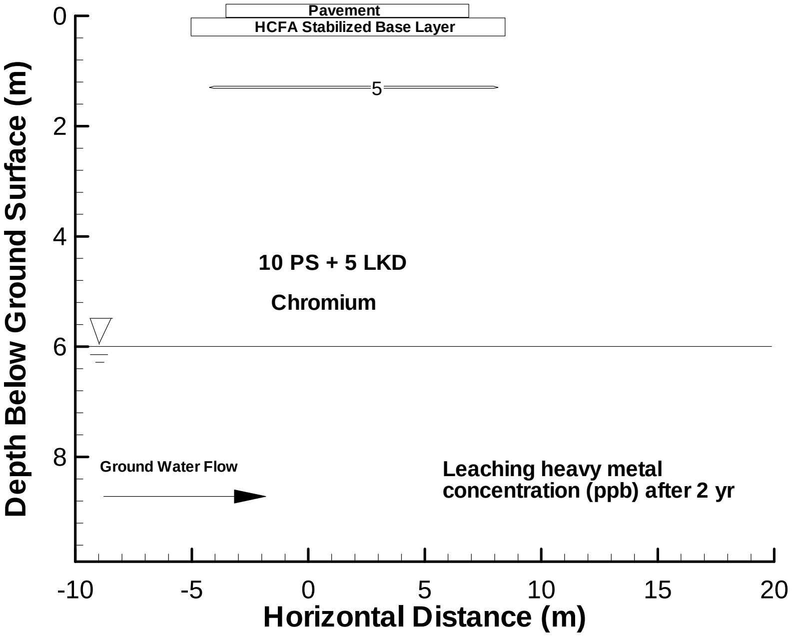

Pavement
HCFA Stabilized Base Layer
10
15
25
30
20
30
20
35
5
5
10 PS + 5 LKD
Zinc
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

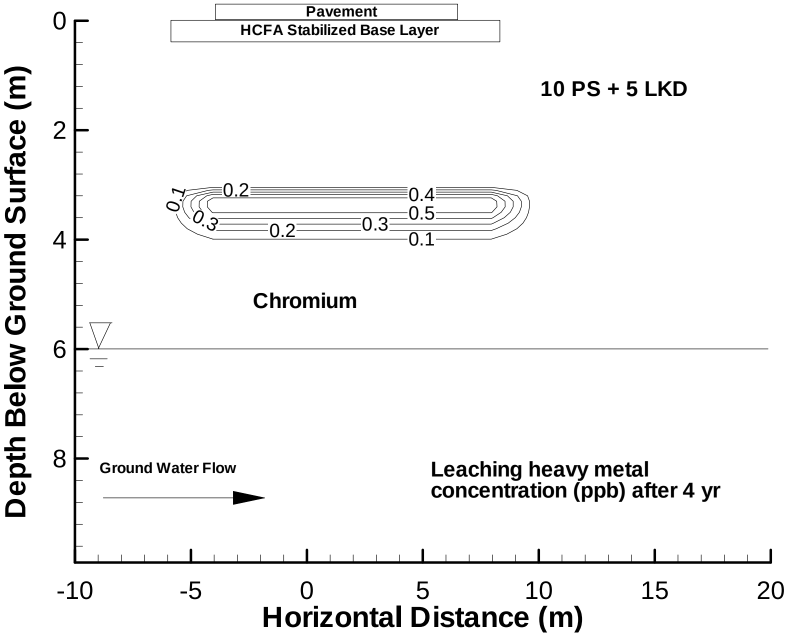

Pavement
HCFA Stabilized Base Layer
5
15
15
20
15
10
5
5
Zinc
10 PS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

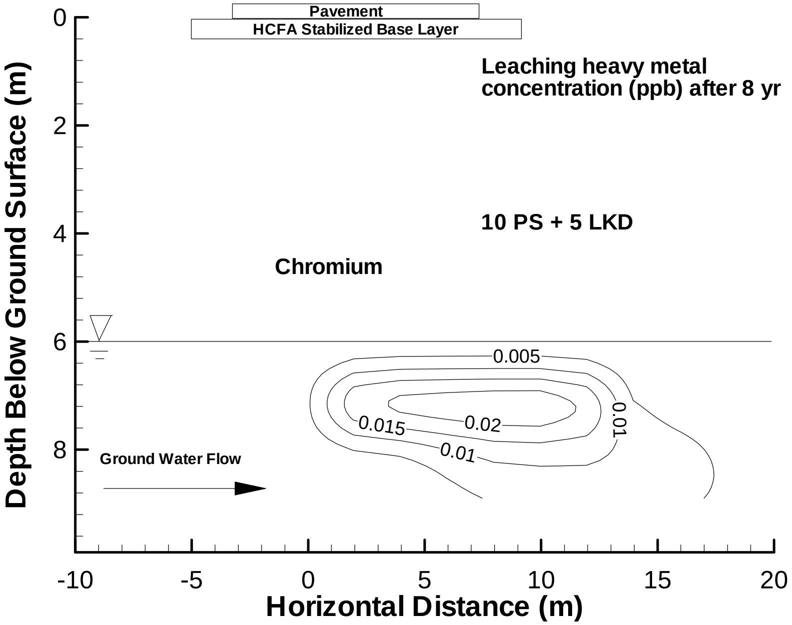

Pavement
HCFA Stabilized Base Layer
0.2
0.5
0.7
0.6
0.4
0.6
0.4
0.1
0.1
Zinc
10 PS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

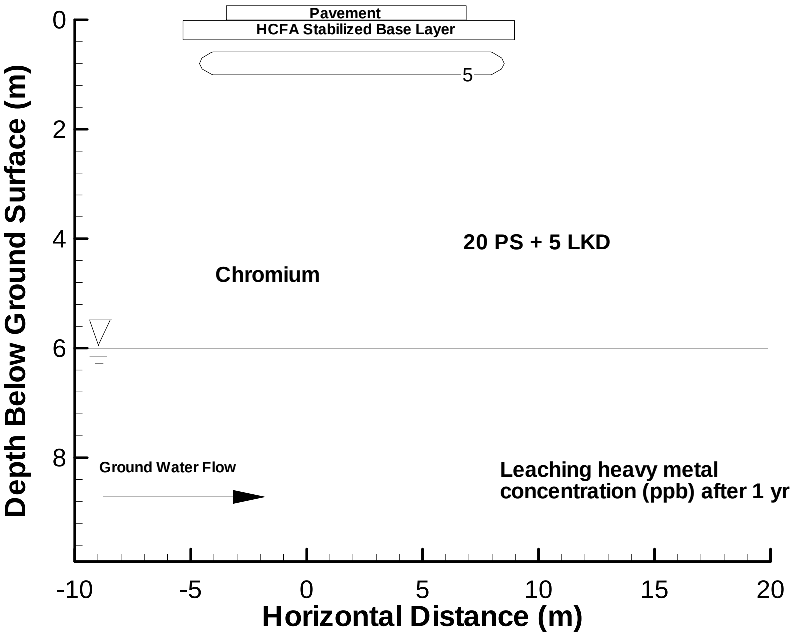

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 6 yr
Zinc
10 PS + 5 LKD
0.005
0.035
0.015
0.025
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)


Pavement
HCFA Stabilized Base Layer
5
10 PS + 5 LKD
Chromium
Leaching heavy metal concentration (ppb) after 1 yr
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

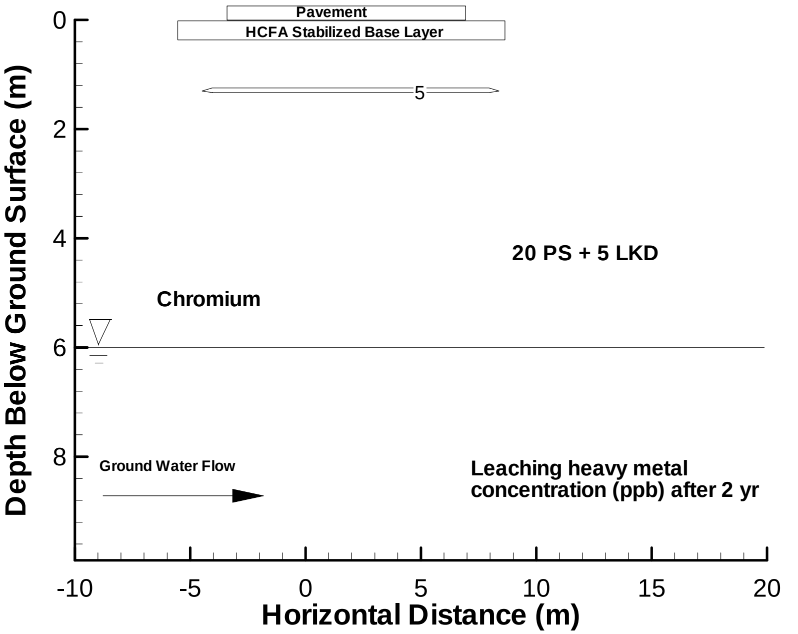

Pavement
HCFA Stabilized Base Layer
5
10 PS + 5 LKD
Chromium
Leaching heavy metal concentration (ppb) after 2 yr
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20


Pavement
HCFA Stabilized Base Layer
10 PS + 5 LKD
0.1
0.2
0.4
0.5
0.3
0.2
0.3
0.1
Chromium
Leaching heavy metal concentration (ppb) after 4 yr
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

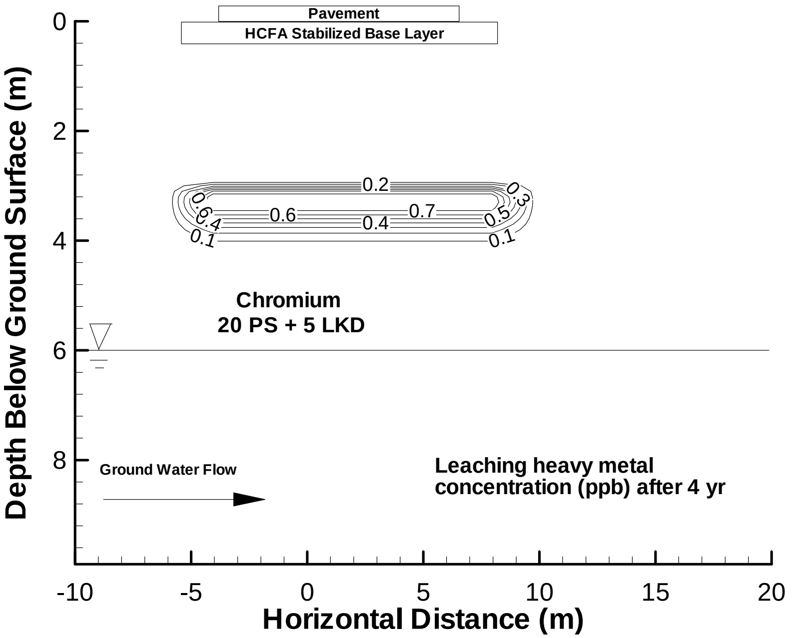

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
10 PS + 5 LKD
Chromium
0.005
0.015
0.02
0.01
0.01
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20



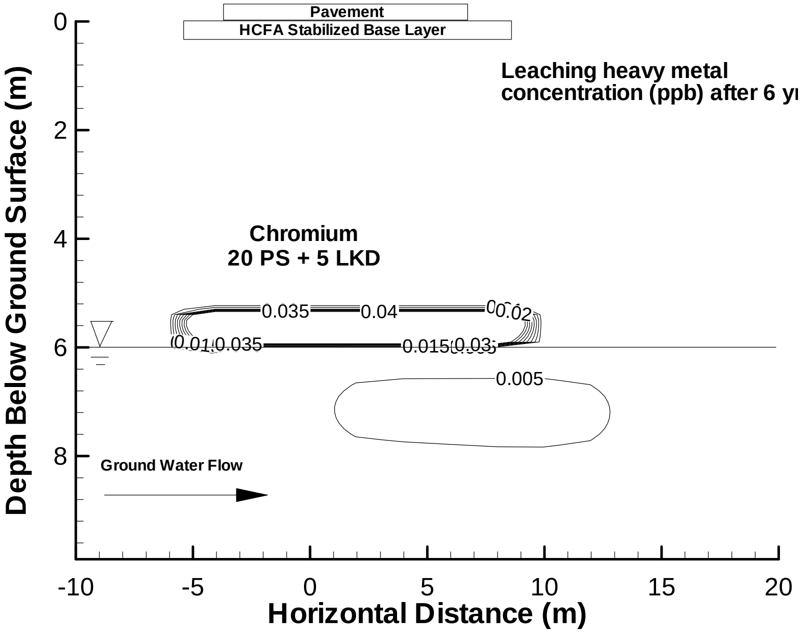
Pavement
HCFA Stabilized Base Layer
5
20 PS + 5 LKD
Chromium
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)



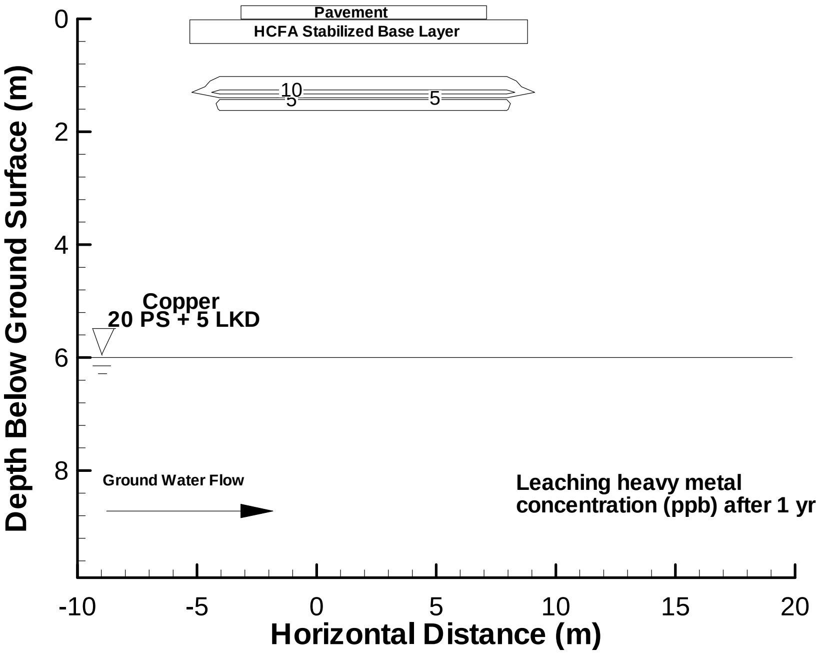
Pavement
HCFA Stabilized Base Layer
5
20 PS + 5 LKD
Chromium
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

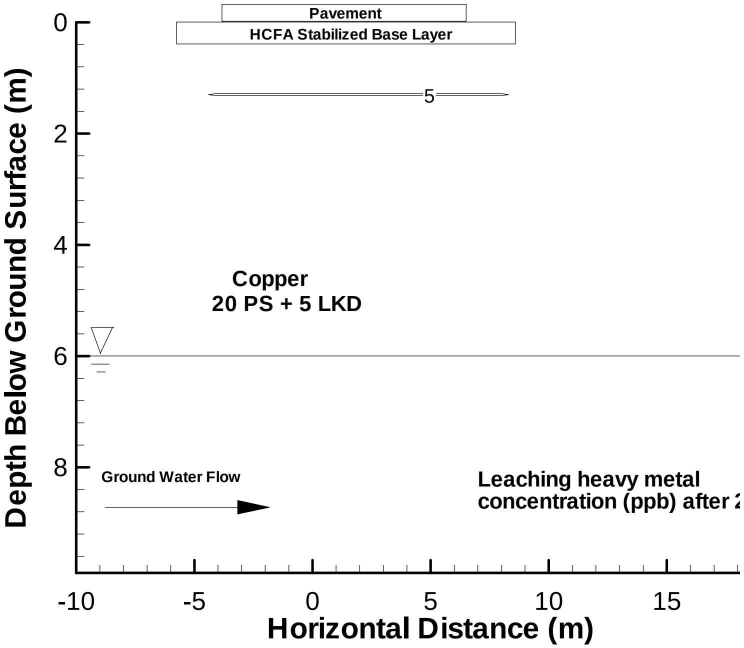


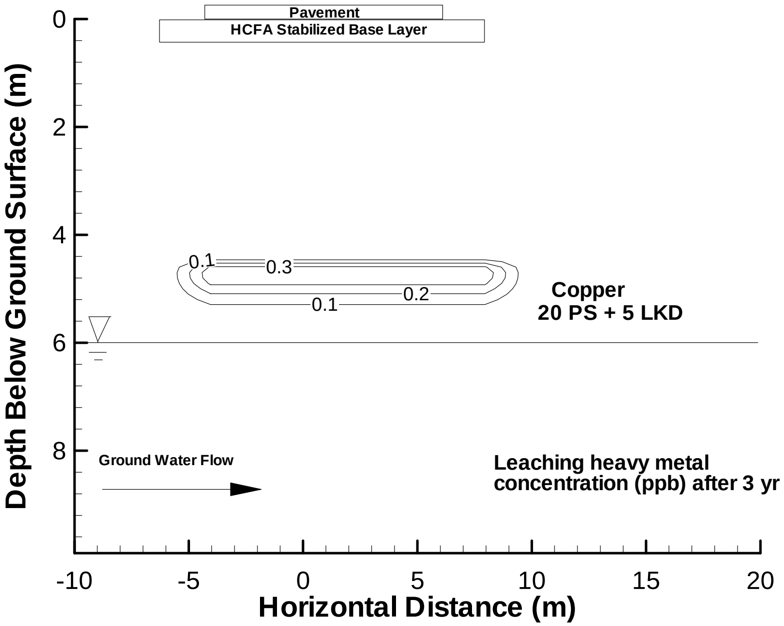
Pavement
HCFA Stabilized Base Layer
0.2
0.3
0.6
0.4
0.6
0.4
0.7
0.5
0.1
0.1
Chromium
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

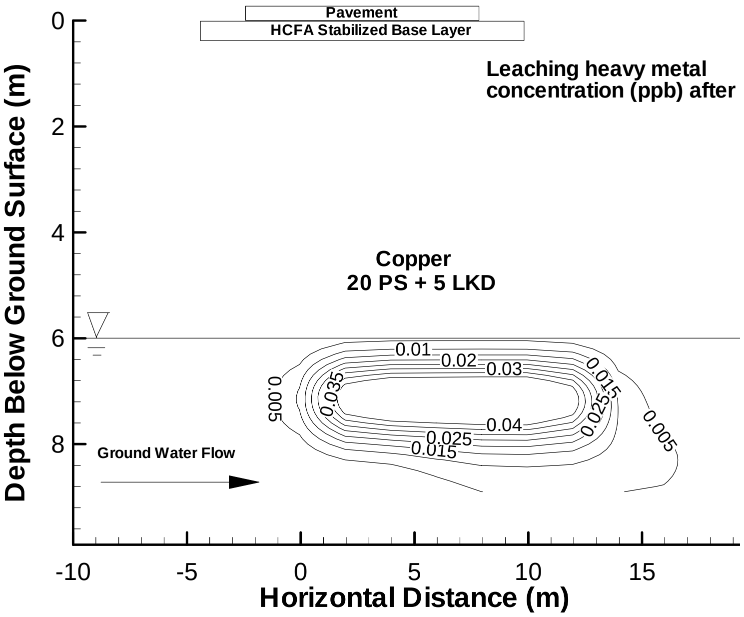


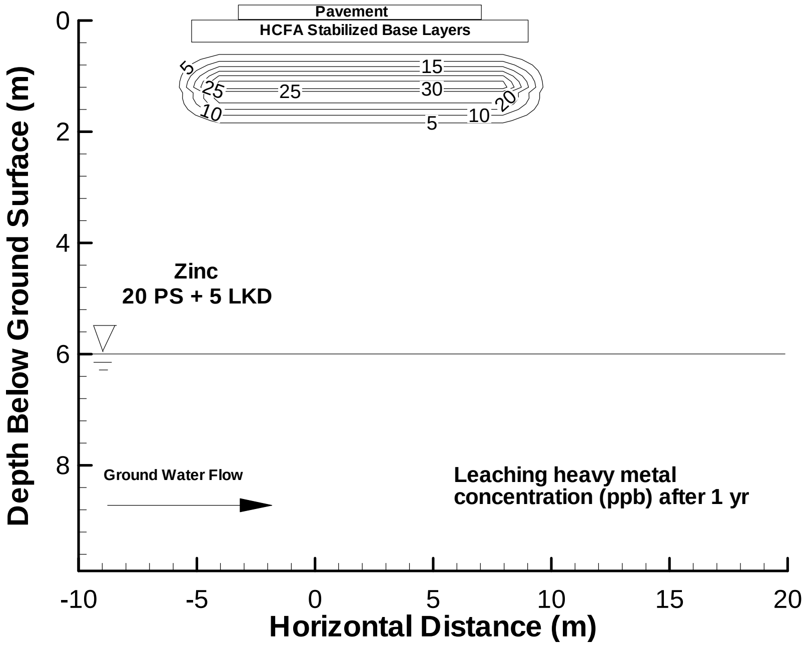
Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 6 yr
Chromium
20 PS + 5 LKD
0.035
0.04
0.02
0.01
0.035
0.015
0.03
0.005
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

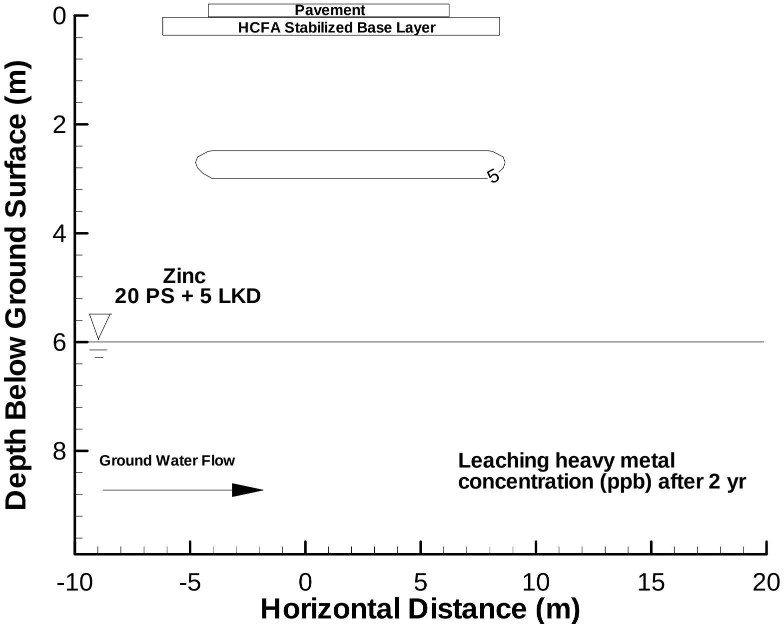

Pavement
HCFA Stabilized Base Layer
10
5
5
Copper
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

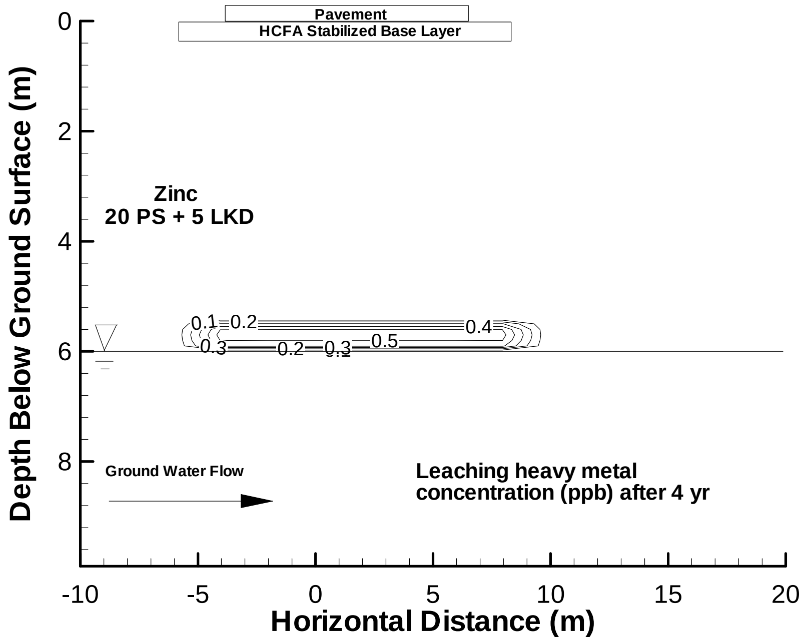

Pavement
HCFA Stabilized Base Layer
5
Copper
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 2
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
Horizontal Distance (m)

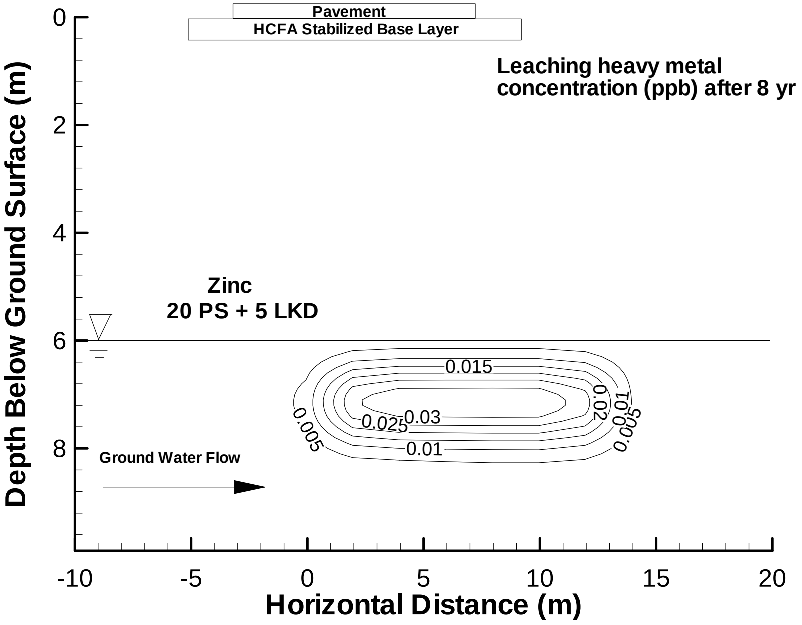

Pavement
HCFA Stabilized Base Layer
0.1
0.3
0.2
0.1
Copper
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 3 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

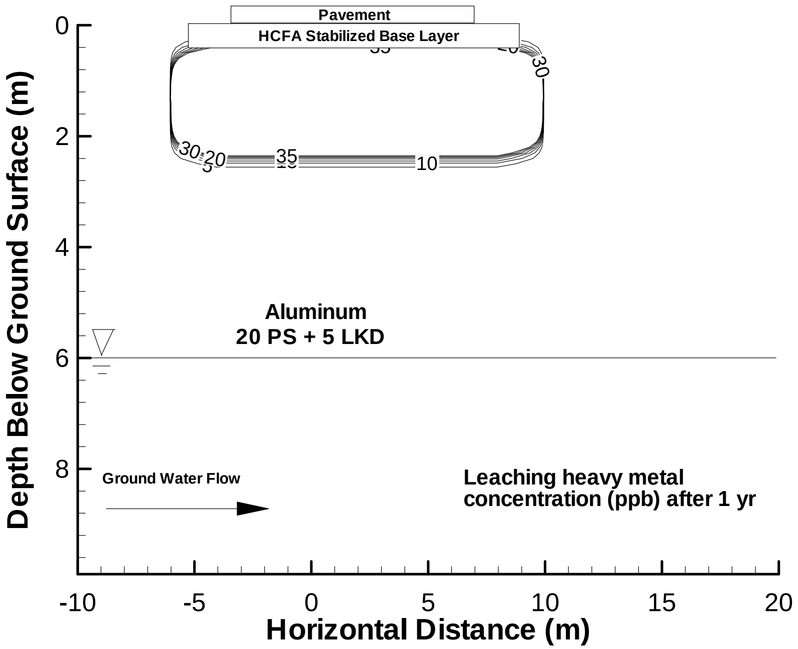

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal
concentration (ppb) after
Copper
20 PS + 5 LKD
0.01
0.02
0.03
0.015
0.035
0.005
0.04
0.025
0.025
0.015
0.005
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
Horizontal Distance (m)

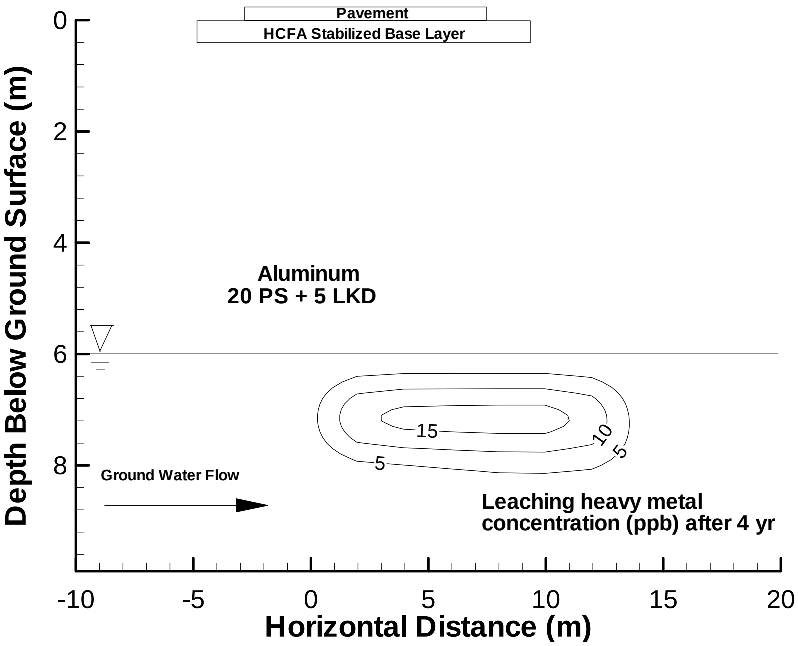

Pavement
HCFA Stabilized Base Layers
15
30
25
25
5
10
20
10
5
Zinc
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

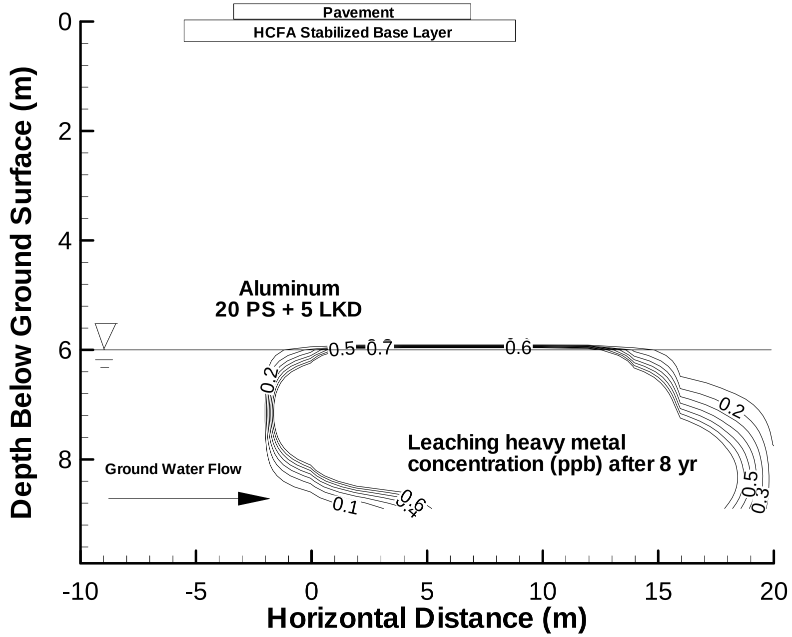

Pavement
HCFA Stabilized Base Layer
5
Zinc
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

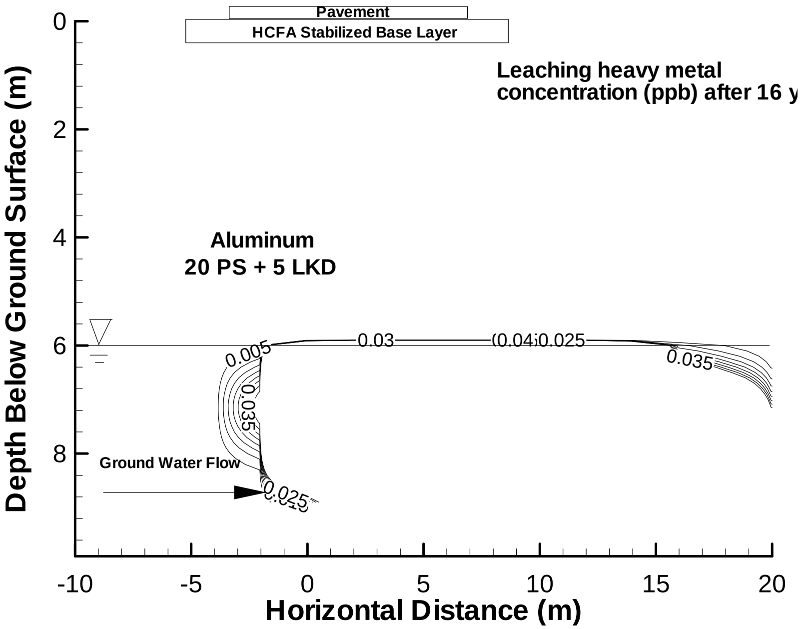

Pavement
HCFA Stabilized Base Layer
Zinc
20 PS + 5 LKD
0.1
0.2
0.4
0.3
0.2
0.3
0.5
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

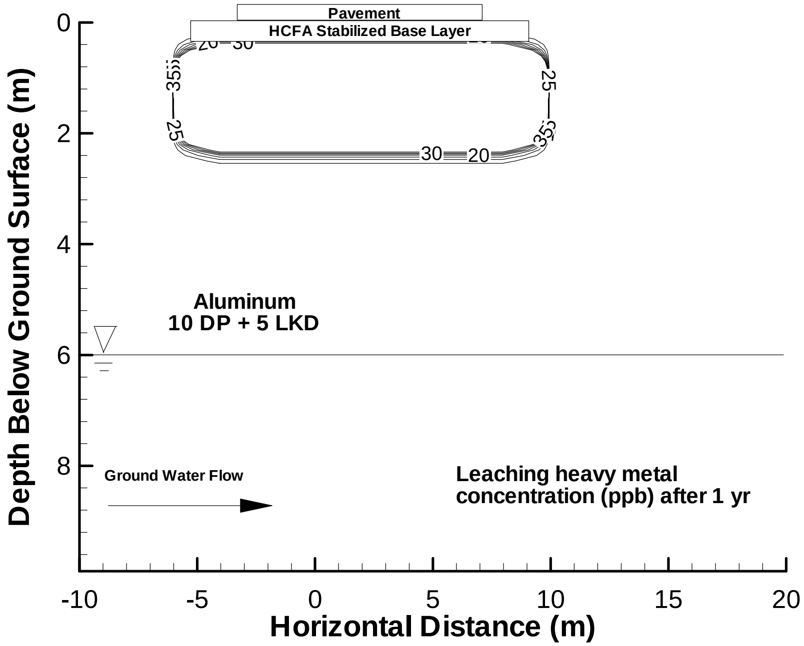

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
Zinc
20 PS + 5 LKD
0.015
0.005
0.025
0.03
0.02
0.01
0.005
0.01
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

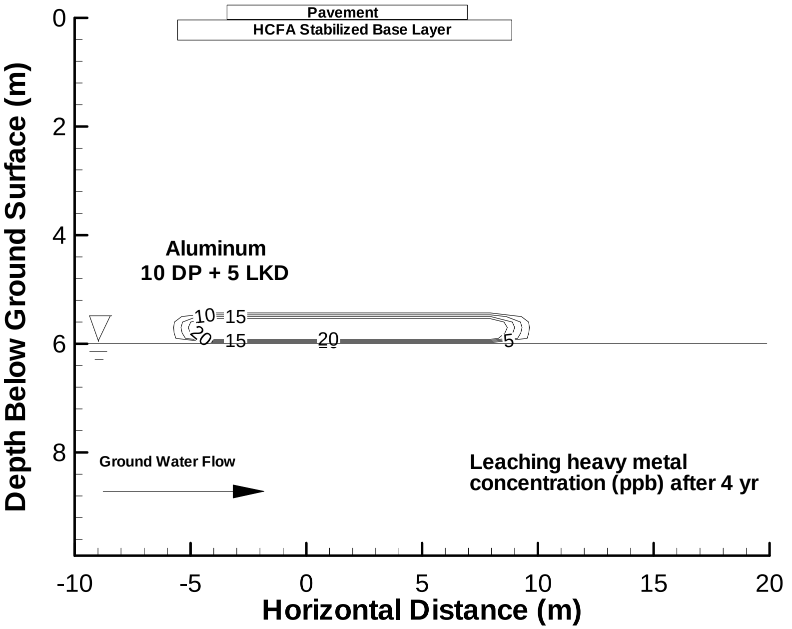

Pavement
HCFA Stabilized Base Layer
Aluminum
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
30
20
35
10
5
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

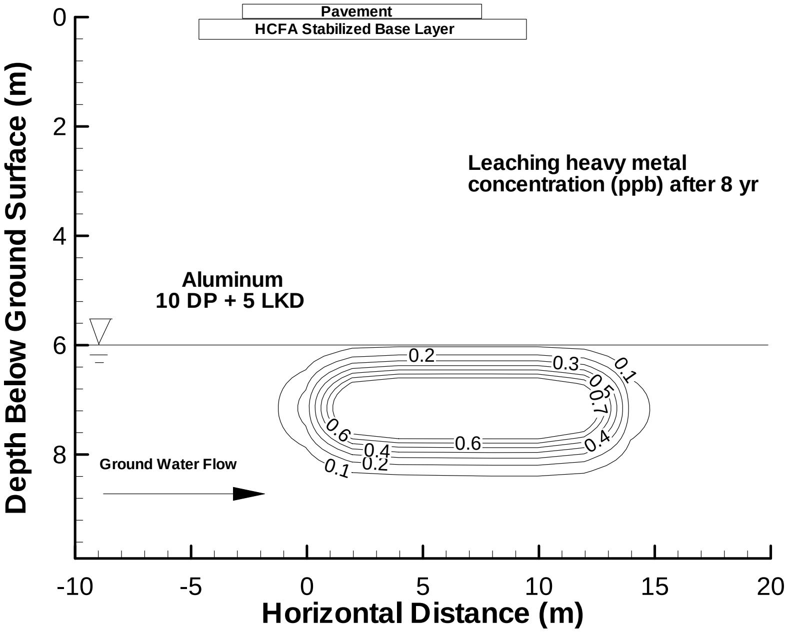

Pavement
HCFA Stabilized Base Layer
Aluminum
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
15
10
5
5
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

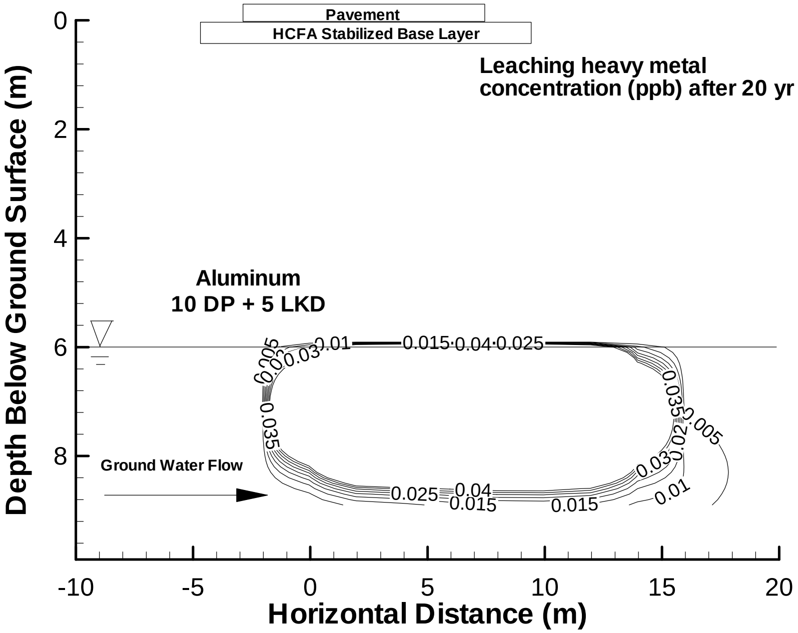

Pavement
HCFA Stabilized Base Layer
Aluminum
20 PS + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 8 yr
0.5
0.7
0.6
0.2
0.2
0.1
0.6
0.5
0.3
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

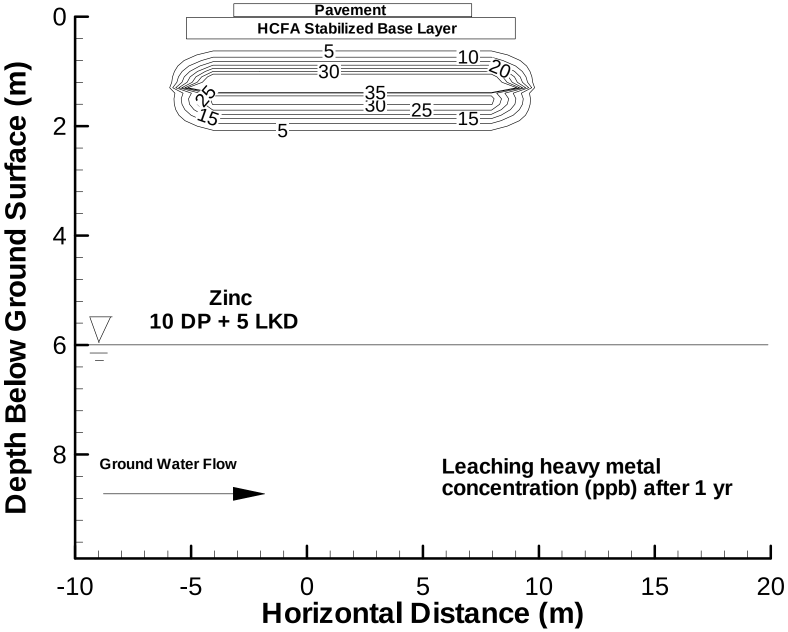

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 16 y
Aluminum
20 PS + 5 LKD
Ground Water Flow
0.005
0.03
0.04
0.025
0.035
0.035
0.025
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

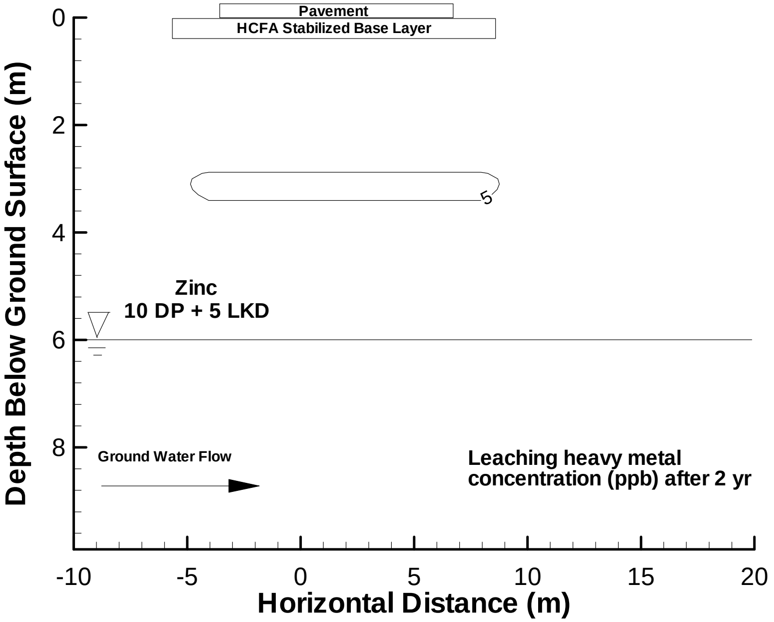

Pavement
HCFA Stabilized Base Layer
Aluminum
10 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
20
30
35
25
25
35
30
20
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20

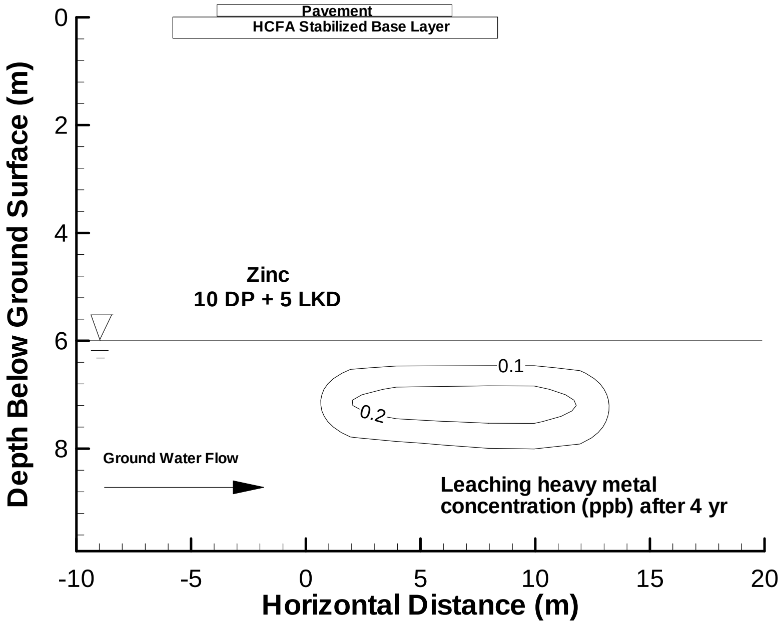

Pavement
HCFA Stabilized Base Layer
Aluminum
10 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
10
15
20
15
20
5
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20

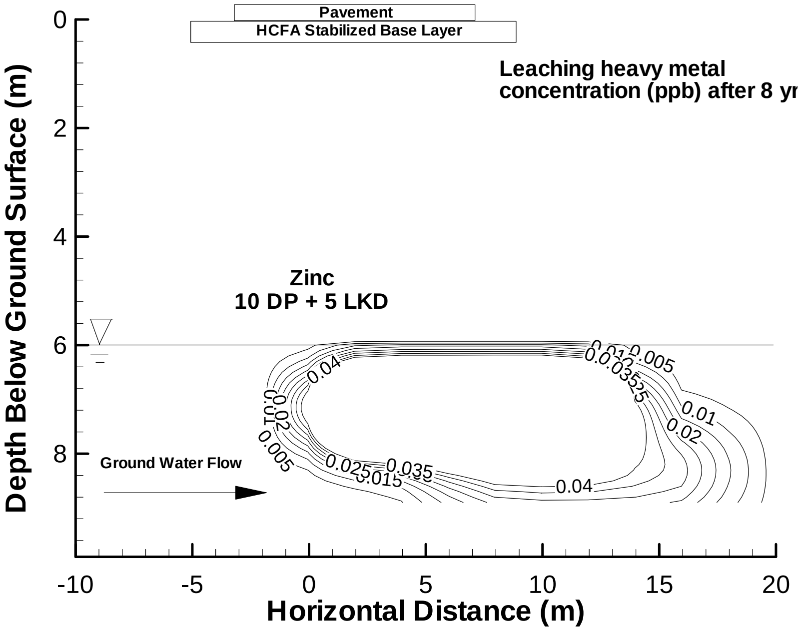

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
Aluminum
10 DP + 5 LKD
Ground Water Flow
0.2
0.3
0.1
0.5
0.7
0.6
0.6
0.4
0.4
0.2
0.1
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20

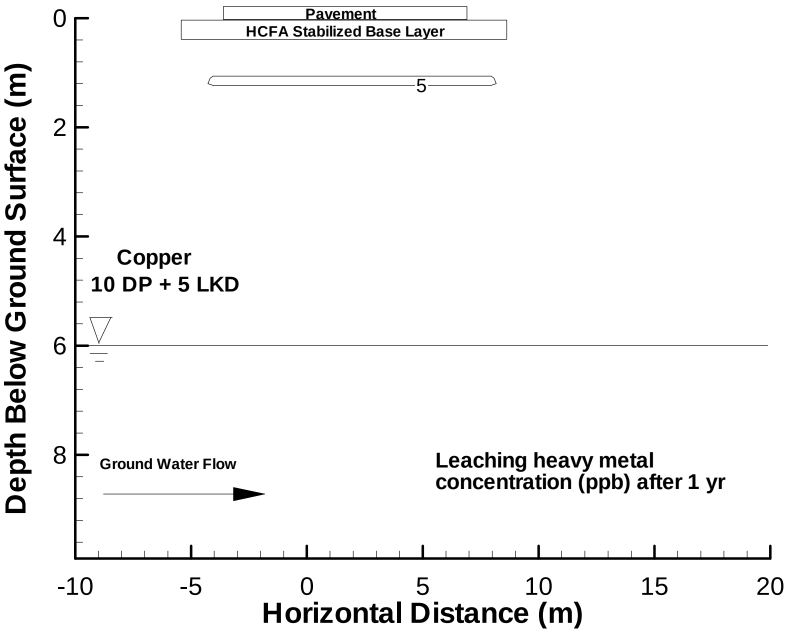

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 20 yr
Aluminum
10 DP + 5 LKD
Ground Water Flow
0.005
0.03
0.01
0.015
0.04
0.025
0.035
0.035
0.02
0.005
0.03
0.01
0.025
0.04
0.015
0.015
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20

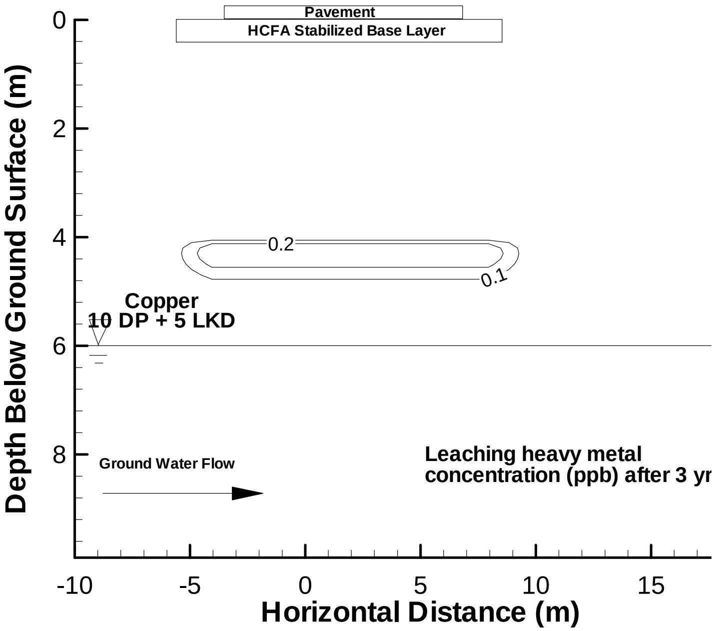

Pavement
HCFA Stabilized Base Layer
5
10
20
30
35
30
25
25
15
15
5
Zinc
10 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

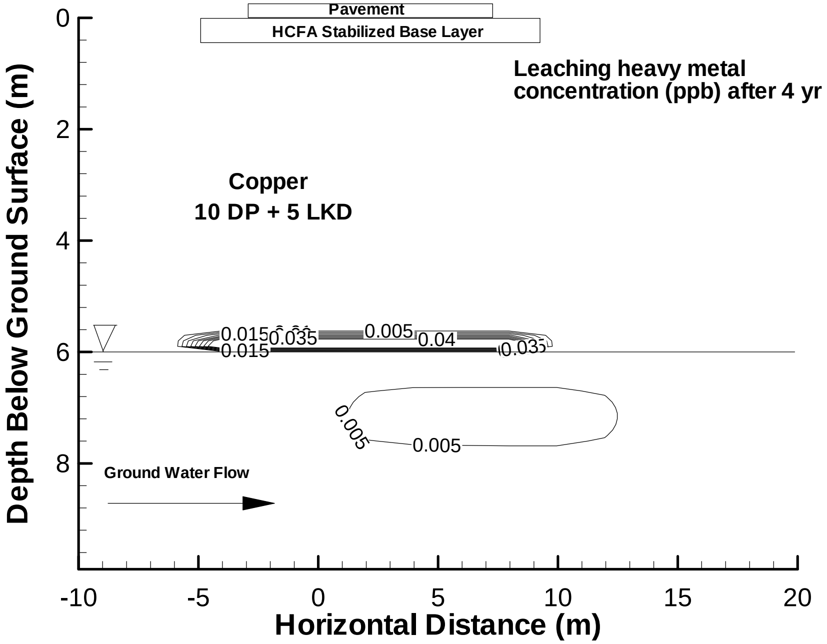

Pavement
HCFA Stabilized Base Layer
5
Zinc
10 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

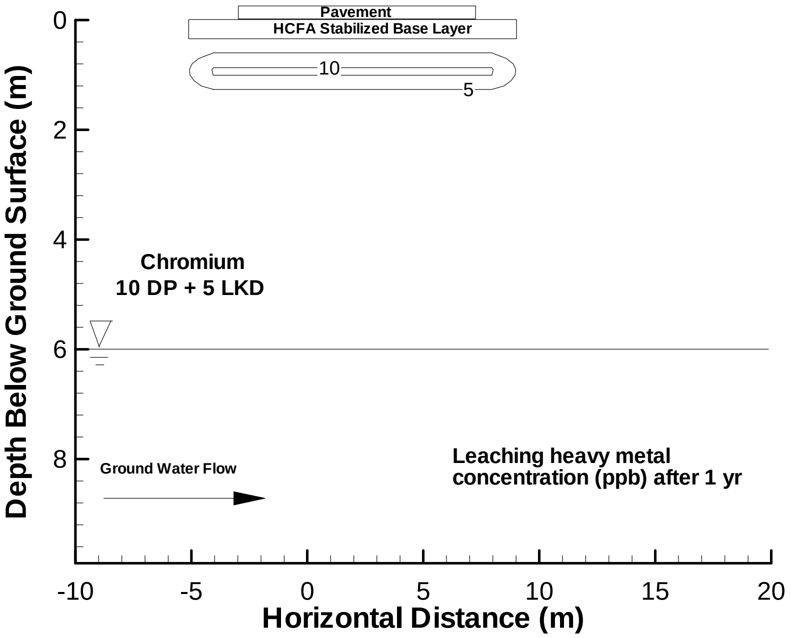

Pavement
HCFA Stabilized Base Layer
Zinc
10 DP + 5 LKD
0.1
0.2
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

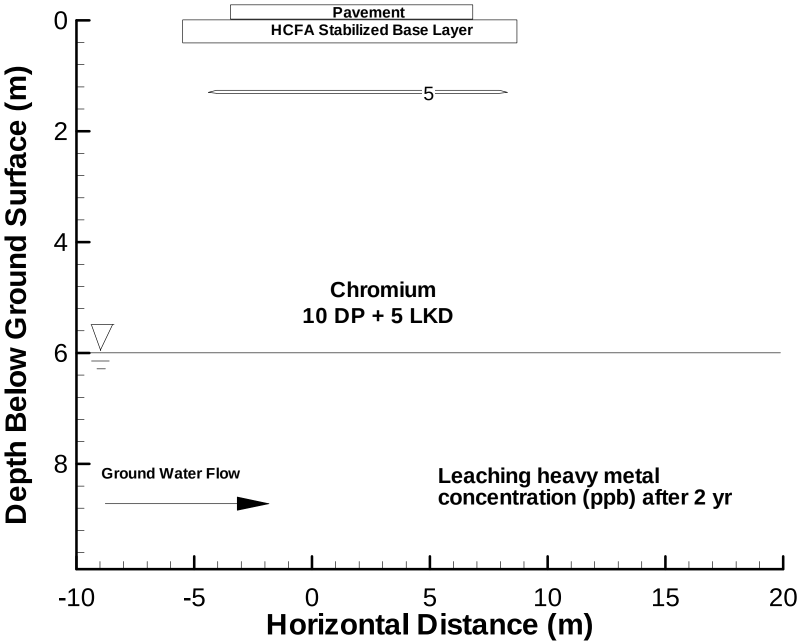

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 8 yr
Zinc
10 DP + 5 LKD
0.04
0.005
0.01
0.02
0.025
0.035
0.01
0.02
0.01
0.02
0.005
0.025
0.015
0.035
0.04
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

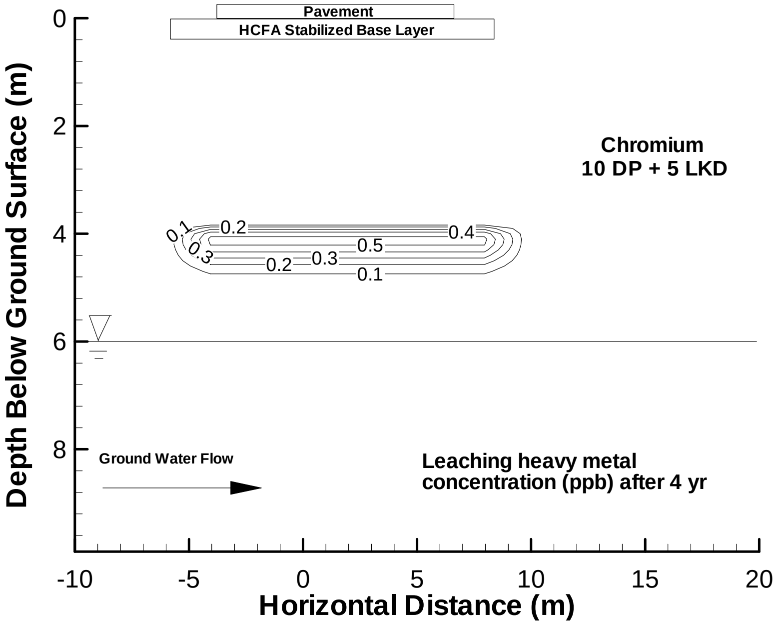

Pavement
HCFA Stabilized Base Layer
5
Copper
10 DP + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

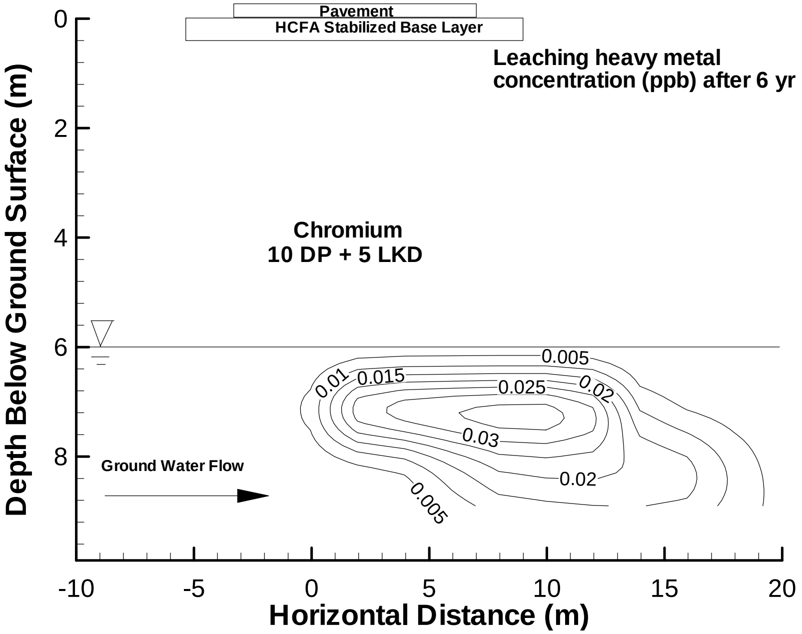

Pavement
HCFA Stabilized Base Layer
0.2
0.1
Copper
10 DP + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 3 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
Horizontal Distance (m)

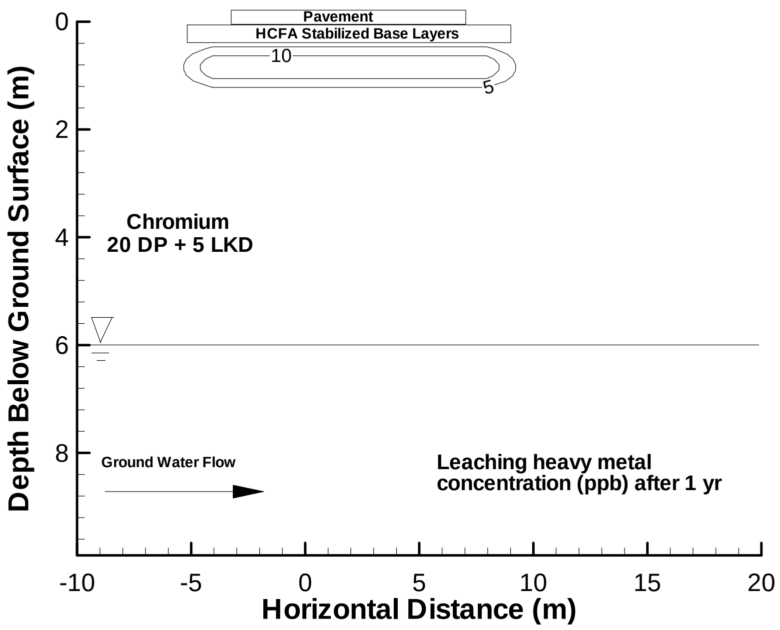

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal
concentration (ppb) after 4 yr
Copper
10 DP + 5 LKD
0.015
0.035
0.005
0.04
0.015
0.035
0.005
0.005
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

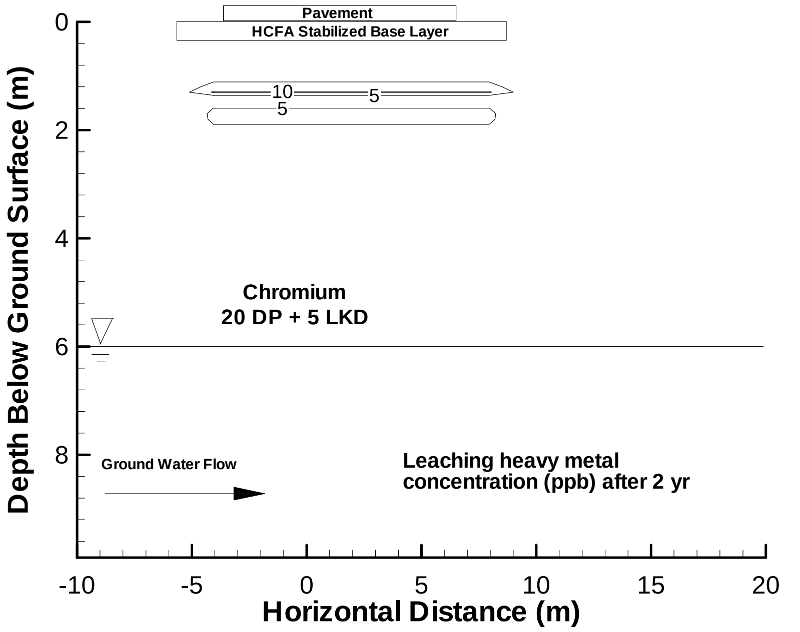

Pavement
HCFA Stabilized Base Layer
10
5
Chromium
10 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

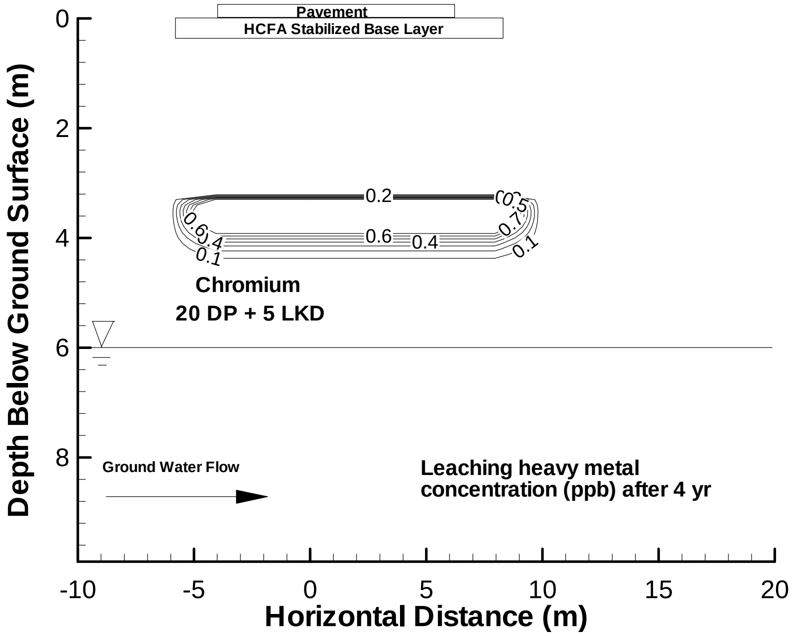

Pavement
HCFA Stabilized Base Layer
5
Chromium
10 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

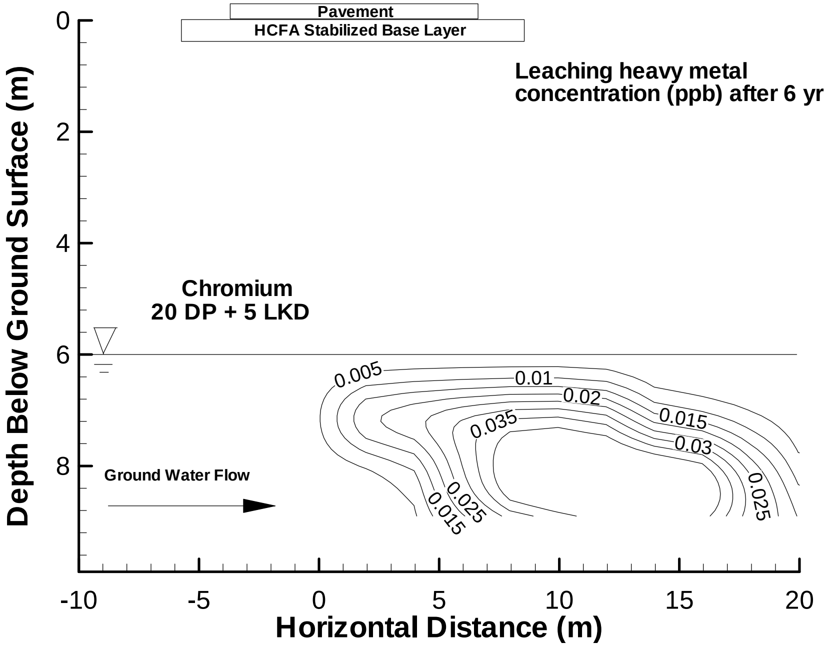

Pavement
HCFA Stabilized Base Layer
Chromium
10 DP + 5 LKD
0.1
0.2
0.4
0.3
0.5
0.2
0.3
0.1
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

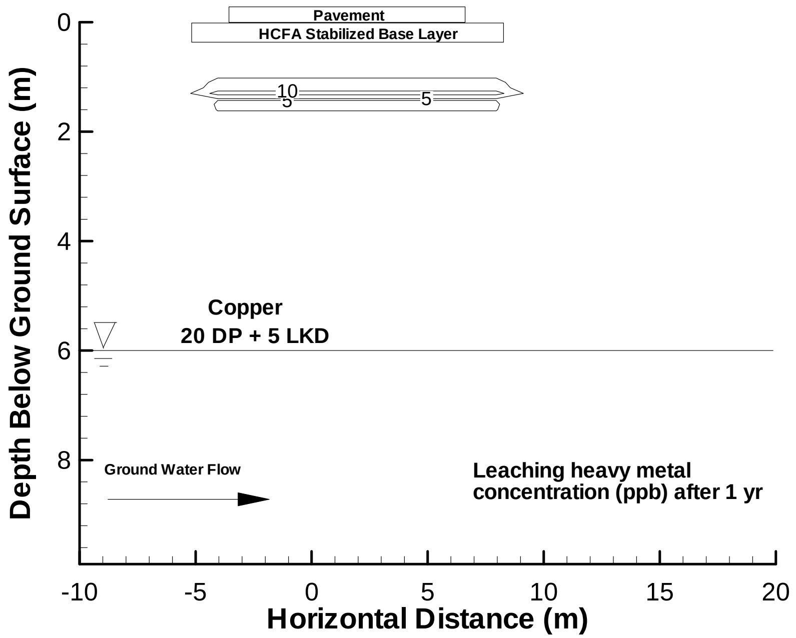

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 6 yr
Chromium
10 DP + 5 LKD
0.005
0.01
0.015
0.025
0.02
0.03
0.02
0.005
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

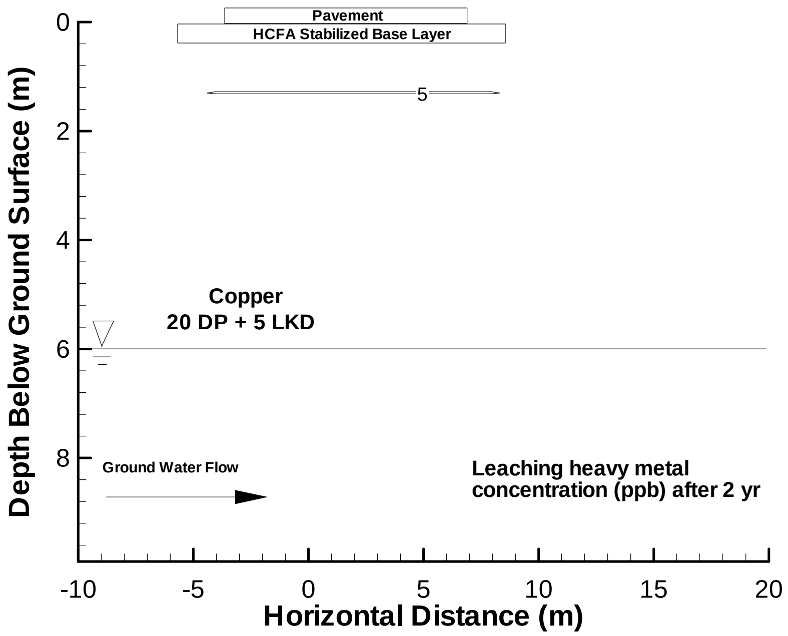

Pavement
HCFA Stabilized Base Layers
10
5
Chromium
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

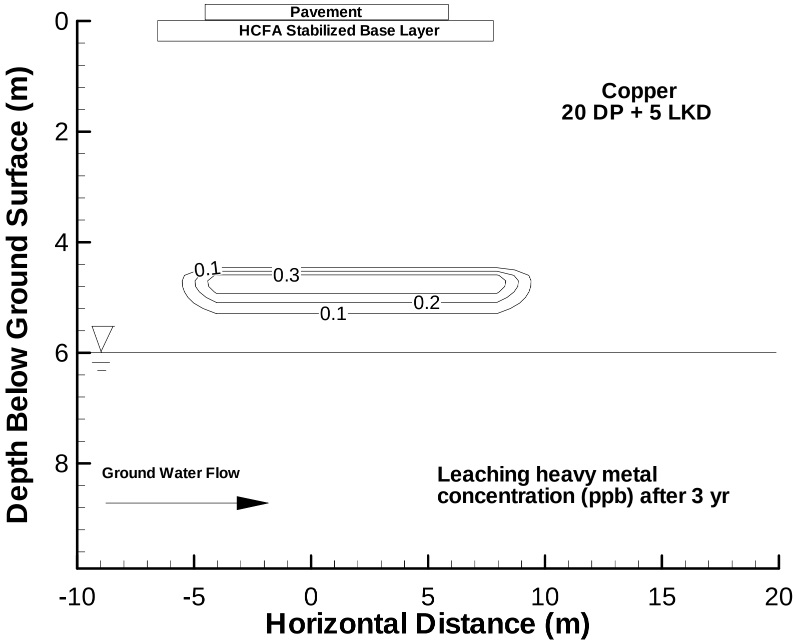

Pavement
HCFA Stabilized Base Layer
10
5
5
Chromium
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

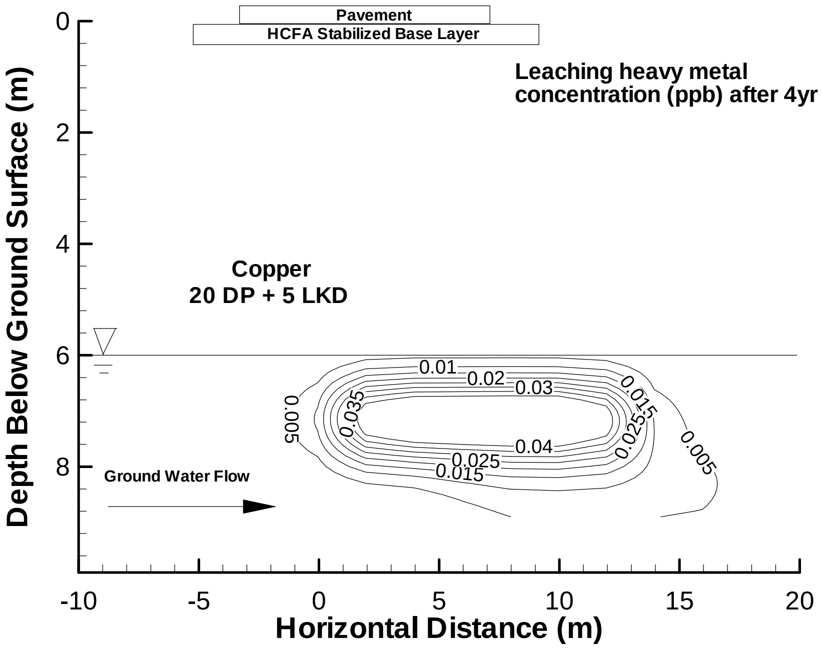

Pavement
HCFA Stabilized Base Layer
0.2
0.5
0.7
0.6
0.4
0.6
0.4
0.1
0.1
Chromium
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal concentration (ppb) after 4 yr
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

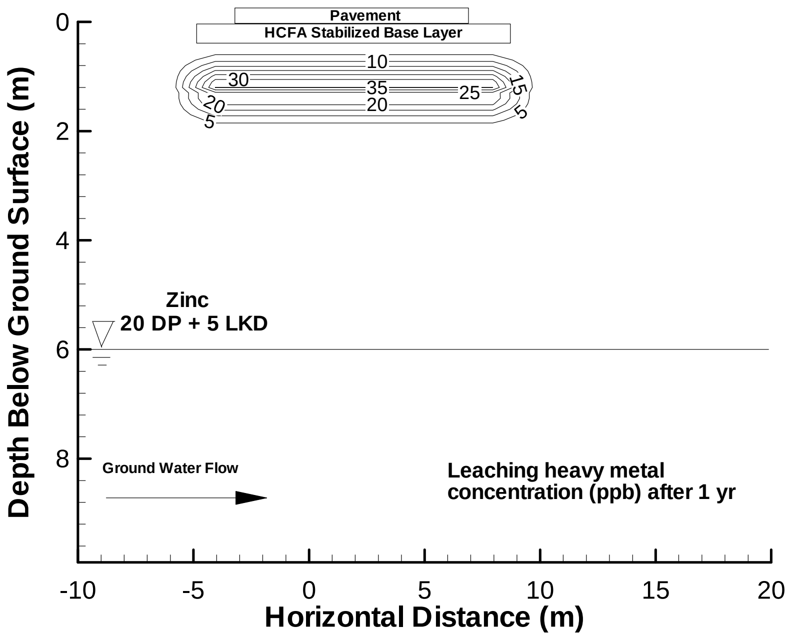

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal concentration (ppb) after 6 yr
Chromium
20 DP + 5 LKD
0.005
0.01
0.02
0.015
0.035
0.03
0.025
0.015
0.025
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
Horizontal Distance (m)
-10
-5
0
5
10
15
20

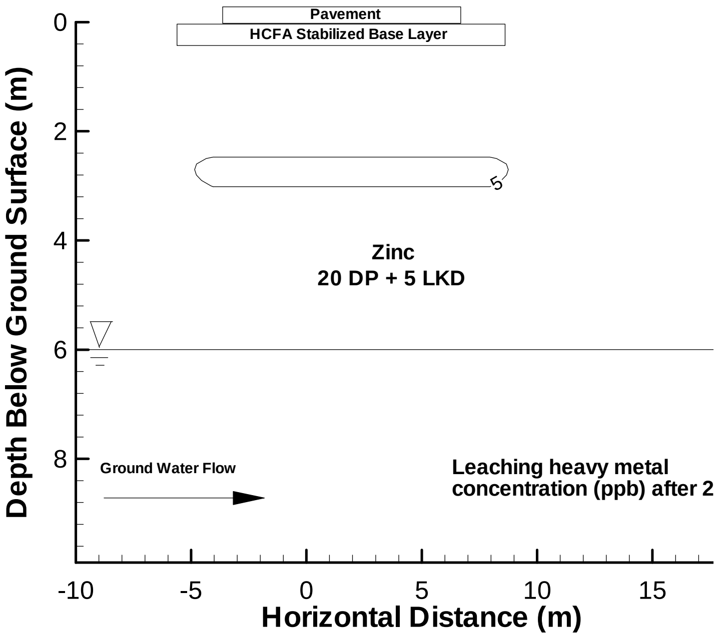

Pavement
HCFA Stabilized Base Layer
10
5
5
Copper
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

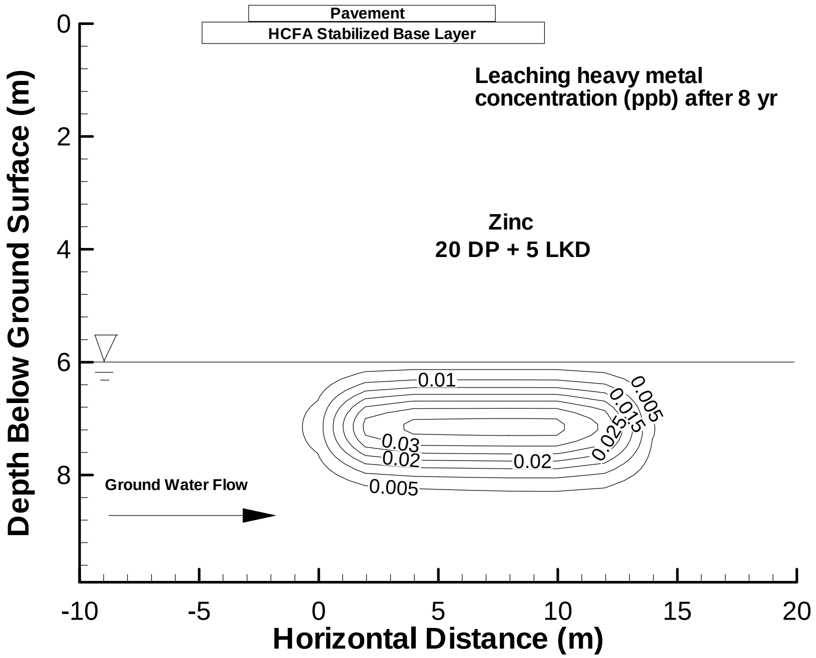

Pavement
HCFA Stabilized Base Layer
5
Copper
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 2 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

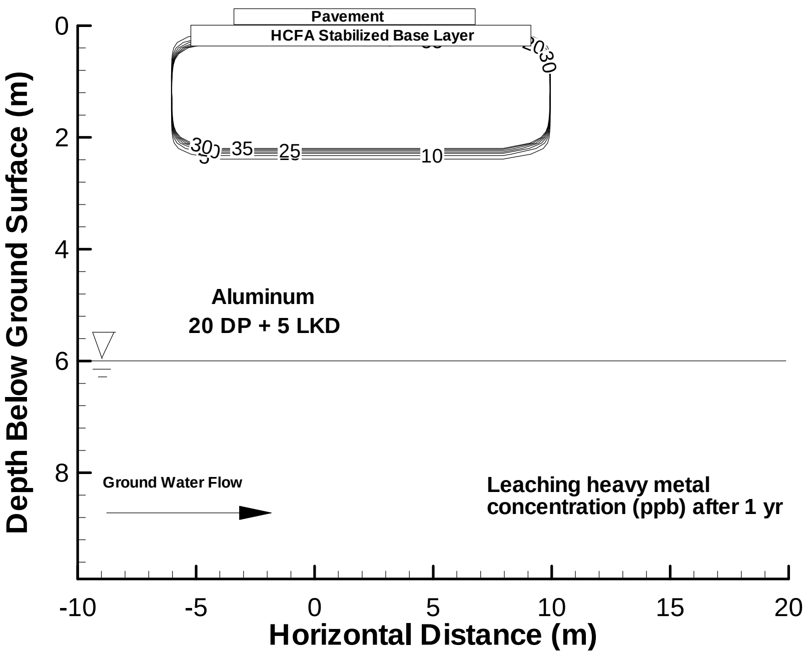

Pavement
HCFA Stabilized Base Layer
Copper
20 DP + 5 LKD
0.1
0.3
0.2
0.1
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 3 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

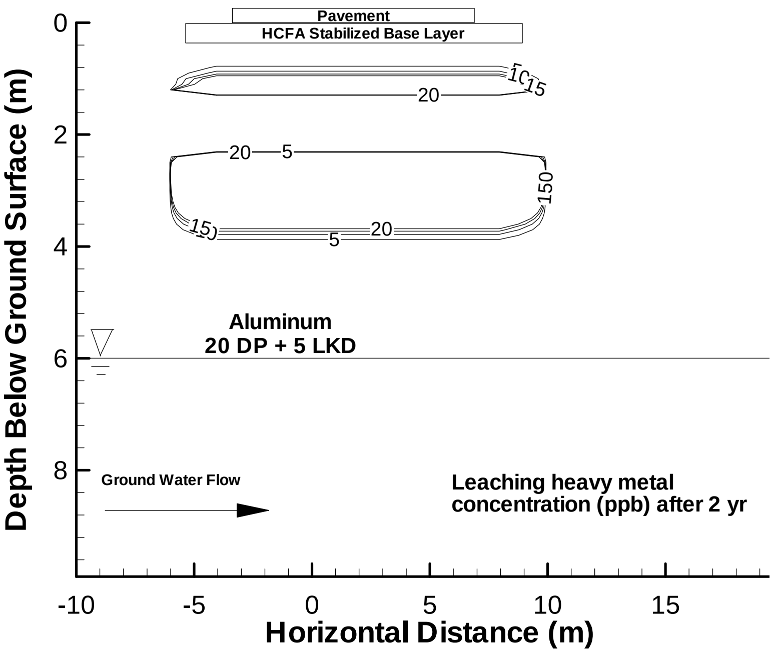

Pavement
HCFA Stabilized Base Layer
Leaching heavy metal
concentration (ppb) after 4yr
Copper
20 DP + 5 LKD
0.01
0.02
0.03
0.005
0.035
0.015
0.025
0.04
0.025
0.015
0.005
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

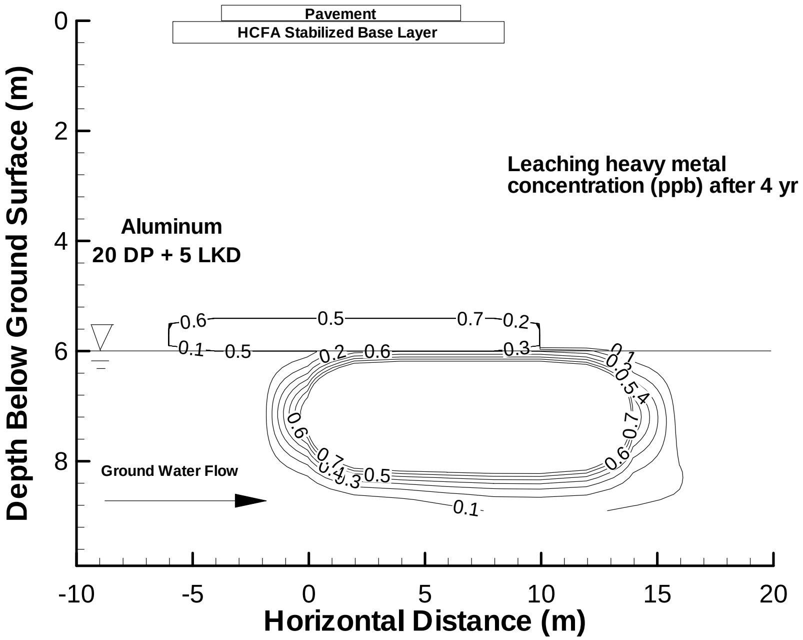

Pavement
HCFA Stabilized Base Layer
10
30
35
25
15
20
20
5
5
Zinc
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 1 yr
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)

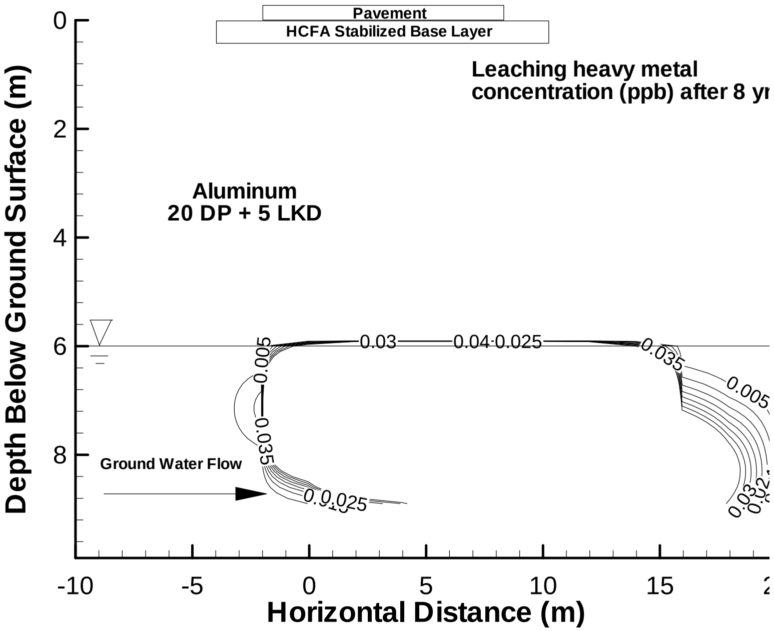

Pavement
HCFA Stabilized Base Layer
5
Zinc
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 2
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
Horizontal Distance (m)


Pavement
HCFA Stabilized Base Layer
Leaching heavy metal
concentration (ppb) after 8 yr
Zinc
20 DP + 5 LKD
0.01
0.005
0.015
0.025
0.03
0.02
0.02
0.005
Ground Water Flow
Depth Below Ground Surface (m)
0
2
4
6
8
-10
-5
0
5
10
15
20
Horizontal Distance (m)


Pavement
HCFA Stabilized Base Layer
Aluminum
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 1 yr
30
35
25
10
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20


Pavement
HCFA Stabilized Base Layer
Aluminum
20 DP + 5 LKD
Ground Water Flow
Leaching heavy metal
concentration (ppb) after 2 yr
10
15
20
20
5
150
15
5
20
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15


Pavement
HCFA Stabilized Base Layer
Leaching heavy metal
concentration (ppb) after 4 yr
Aluminum
20 DP + 5 LKD
Ground Water Flow
0.6
0.5
0.7
0.2
0.1
0.5
0.2
0.6
0.3
0.1
0.5
0.4
0.7
0.6
0.6
0.7
0.4
0.3
0.5
0.1
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15
20


Pavement
HCFA Stabilized Base Layer
Leaching heavy metal
concentration (ppb) after 8 yr
Aluminum
20 DP + 5 LKD
Ground Water Flow
0.005
0.03
0.04
0.025
0.035
0.005
0.035
0.025
0.03
Depth Below Ground Surface (m)
Horizontal Distance (m)
0
2
4
6
8
-10
-5
0
5
10
15

COMPARATIVE EVALUATION OF LABORATORY LEACHING TESTS

TABLE OF CONTENTS

1 Introduction

More than 50% of the electricity demand in the United States is met from coal-fired power plants, which burn over 1 billion metric tons of coal annually to provide electricity to homes, businesses, and industries (Kim 2006). This generation of electricity results in production of coal combustion by-products (CCBs) that require proper handling and disposal or beneficial reuse. For example, fly ash, one of the main types of CCBs, is the collected particulate matter from the exhaust gases of coal power plants. The CCB disposal problem has been exacerbated by increases in electricity demand, which have led to higher rates of coal burning, producing more CCBs. This coupled with the high levels of hazardous metals in CCBs and the large landfill space required, has resulted in CCB disposal receiving increasing attention. Correspondingly, there have been increased efforts to research and develop new, more sustainable disposal methods for CCBs that do not compromise the well-being of the environment or endanger human health.

Disposal of CCBs presents an environmental challenge due to both environmental and human health concerns. The majority of CCBs have traditionally been placed in landfills, which may adversely affect both terrestrial and aquatic resources. In addition, decreases in available areas suitable for new landfill space has magnified the need for the development of alternative disposal and management options. For instance, 1.7 million tons of fly ash were produced at various facilities in Maryland in 2008, and nearly 745,000 tons of this ash were reused in beneficial applications throughout the state, corresponding to about 44% of the generated ash (MDE 2008). This quantity of reused fly ash represents a significant portion of fly ash that would otherwise be disposed of in a landfill, taking up large areas of space. However, the risk of contaminating groundwater supplies and harming wildlife from soil and/or water contamination are examples of issues that need to be addressed before beneficial reuse of fly ash can become widespread.

A common beneficial use of fly ash has been as a concrete additive due to its natural pozzolanic properties. However, changes in the U.S. Clean Air Act requiring the use of low sulfur and nitrogen oxide emission burners has resulted in CCBs with higher carbon contents. High carbon fly ash is problematic in concrete applications because it absorbs the air-entraining additives that are added for increasing the porosity of the concrete (Cetin 2009). As a result, there is currently a renewed emphasis on incorporating suitable CCB into construction activities. One area of CCB reuse that has received much attention is the construction of highways and roadway embankments. Both the reduction in construction materials required and large volume of fly ash that can be recycled make embankment construction an ideal candidate for beneficial fly ash reuse. Nevertheless, despite the advantages of reusing CCBs, potential impacts on groundwater quality still remain an issue when these by-products are used in construction applications.

Two major environmental concerns related to the reuse of fly ash in construction applications, such as the building of roadway base layers or highway embankments, are leaching of heavy metals and the consequences from changes in pH. Heavy metals such as As, Cr, Cu, Pb, Se, Cd, and Zn can be present in fly ash in levels up to several hundred parts per million (Bin Shafique et al. 2002, Ram et al. 2007, Shah et al. 2008). Leaching of metals from fly ash-amended materials has the potential to contaminate nearby natural waters. Although metal leaching can occur at the parts-per-billion scale, the potential to accumulate in the natural environment and various means of transport throughout ecosystems require investigation into the unintended effects of beneficial fly ash reuse. There have been numerous studies looking at heavy metal leaching from fly ash mixtures, and the general consensus is that both fly ash composition and pH have important effects on leaching behavior and speciation of metals (Fytianos et al. 1998, Bin Shafique et al. 2007, Jegadessan et al. 2008, Jo et al. 2008, Morar et al. 2010).

Work by Shah et al. (2008) showed that metal concentrations in coal fly ash collected from an Australian power plant were roughly 2-4 times the original concentration in the source coal. This was attributed to the loss of mass on ignition from the organic carbon being oxidized to carbon dioxide in the combustion process. Ram et al. (2007) also state that metal can become concentrated during the coal burning process by factors of 4-10. For example, Shah et al. (2008) measured 0.857 mg/kg of Cr(VI) in a fly ash compared to 0.065 mg/kg in the source coal. Changes in metal speciation may also occur during and after the combustion process. This is illustrated by the study of Shah et al. (2008), which showed that a fly ash had 90% of As present in the As(V) form compared to 65% in original coal material. This is important because it could also have implications for leaching behavior, and it is widely known that certain species of metals are more toxic than others. For example, As(III) is 50 times more toxic to humans than As(V) while Se(IV) had higher reported toxicity than Se(VI) (Shah et al. 2008).

The pH of the leachate from a fly ash-containing soil has a strong influence on many other natural processes that occur within the soil matrix. The speciation of metals, availability of nutrients such as nitrogen and phosphorus, soil weathering, and partitioning (and therefore transport) of pollutants are all affected by changes in pH. With respect to partitioning processes, the sorption, precipitation, and dissolution processes that largely control metal leaching behavior are all pH dependent, with dissolution of metal-containing minerals seen under acidic pH, while precipitation and complexation dominate at higher pH values (Jegadessan et al. 2008, Morar et al. 2010). The mobility and toxicity of heavy metals are related to both the amount of these metals that enter the environment from leaching processes and the metal species present.

Coupled with the increased interest in the beneficial reuse of CCBs has been an increase in the development of regulations governing their disposal and use. In particular, concerns with environmental health and human safety have prompted agencies across the country to begin to devise programs outlining proper methods to handle and dispose of fly ash and other CCBs. While the U.S. EPA has been working to create federal regulations for CCBs since 2000, there have been no laws passed. This has resulted in an opportunity for states to devise their own standards while federal regulations are being proposed. For instance, the Maryland Department of the Environment (MDE) created the Regulation of Coal Combustion Byproducts legislation (COMAR 26.04.10.00) to address the issue of safe CCB handling, processing, disposal, and reuse, and to develop procedures for disposing of or reusing fly ash in beneficial applications. Also included are activities that are prohibited based on issues of water, air, and human health quality concerns. One of the primary topics of the regulations is the risk associated with heavy metal leaching from fly ash mixtures used in construction projects, such as highway embankments.

Therefore, despite the advantages of reusing CCBs, potential impacts on groundwater quality remain an issue when these by-products are used in construction applications. Currently, the MDE requires that the CCBs or other industrial by-products be subjected to the EPA Toxicity Characteristic Leaching Procedure (TCLP) test to determine if the material can be used in field construction applications without causing groundwater and surface water contamination. However, concerns have been raised by various interested parties about the use of this testing methodology, as the testing conditions are typically harsher than those encountered in the field, the test is not material or site specific, and it neither represents the actual leachate produced in the field nor simulates a site-specific transport condition (Baba and Kaya 2004, ASTM D3987-06, Ram et al. 2007). Furthermore, the test method is used to determine if the material is hazardous or not; however, more than 15 years of research based on TCLP and column tests clearly shows that the CCBs are generally non-hazardous (Creek and Shackelford 1992, Kyper 1992, Chichester and Landsberger 1996, Edil 1998, Ghosh and Subbarao 1998, Qiao et al. 2006, Bin Shafique et al. 2006).

Concerns with the use of the TCLP test has led to interest in alternative ways of evaluating leaching of fly ash-soil mixtures. One alternative is the use of field lysimeters (Ahmed et al. 2010); however, their high costs and long testing duration stand as barriers to their widespread use. Furthermore, the composition of fly ash can vary even within daily batches. Thus, there is a demand for methodologies that can appropriately evaluate leaching potential using more standard laboratory equipment and do so at more frequent intervals. This would provide fly ash producers with more real-time data and aid in better selection of fly ash disposal or reuse options. Similarly, regulators at the state and federal level would also benefit from having a standardized way to easily gage the expected leaching behavior of a fly ash mixture, and could use this information as a tool in accessing the feasibility of beneficial reuse of fly ash and other CCBs.

Clearly, there is a need to determine the most appropriate leaching test for evaluating the potential environmental impacts of CCBs when beneficially used, such as in highway construction applications. The experimental conditions of the selected leaching test must realistically predict leaching, thereby helping regulators and power plant companies minimize risk. The selected method must also be cost-effective and timely, and avoid misleading results, which would hinder efforts to promote increased reuse of CCBs. For example, Baba and Kaya (2004) found that ASTM batch leach tests indicated a fly ash waste was non-toxic whereas TCLP results showed elevated leachate metal concentrations and a toxic classification. Therefore, the primary objective of this project was to compare the methodologies and leaching results of three leaching tests commonly used today: the ASTM water leaching test (WLT), the TCLP test, and the ASTM flow-through column leaching test (CLT). Both batch and column tests were run to understand how the testing conditions influence the leaching results. In addition, the tests were conducted on different mixtures of soils and fly ashes, and the concentrations measured in each test were compared with those obtained by other researchers as well to the state and federal regulatory limits. The effect of pH on leaching was also examined through a series of batch-scale leaching tests. The results of these tests were used to provide recommendations on how to select leaching tests that give consistent leachate concentrations most representative of the field leaching conditions.

An initial survey of the metals present in the tested fly ashes was used to select the metals monitored in the three types of leach tests. The criteria for selection were that the metal must: (1) be present in relatively high levels in the fly ash, (2) be a concern from an environmental or human health perspective, and (3) be accurately measured on available instrumentation. Based on these criteria, chromium, copper, and arsenic were selected for study in this project. Chromium and arsenic are hazardous to human health which is reflected in their inclusion in the U.S. EPA's Safe Drinking Water Act as Maximum Contaminant Levels (MCLs). Copper was chosen because of its known toxicity to fish and other aquatic life (Horne and Dunson 1995). Although arsenic is a metalloid, it is referred to as a metal through this study. These metals also allowed anionic and cationic species to be examined across a wide pH range.

The work is presented in the following chapters. Chapter 2 outlines the materials used in this study and the procedures followed in performing the preliminary work and leaching tests. The results from the different leaching tests on the soil-fly ash mixtures are presented and discussed in Chapter 3. Chapter 4 provides some practical implications of the leaching test results, including an integrated protocol for the testing of fly ash-soil mixtures. Lastly, Chapter 5 contains a summary of the results and the main conclusions from this study.

2 Materials and Methods

2.1 Materials

Mixtures of two fly ashes and two soils were used to evaluate the effect of a range of chemical and physical properties on metal leaching. Fly ashes were added to the soils at 10% and 20% by weight to bracket the range most commonly applied in on-site embankment construction. Both soils underwent testing to determine several basic geotechnical properties, including specific gravity (ASTM D859), pH (ASTM D4972), loss on ignition (LOI) (ASTM D7848-08), and Atterberg limits (ASTM D318). Sieve analyses were also performed on the soils to classify them according to the Unified Soil Classification System. Total elemental analyses (TEA) were performed on soils and fly ashes at the University of Wisconsin Soil Testing and Plant Analysis Laboratories by using a Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometer. The results from the TEA are provided in Table 2.1. Table 2.2 provides a summary of physical and chemical properties of the materials used in this study. The classification of the soils showed that they are sandy soils, with varying percentages of clay particles. The first soil, designated as Soil C, has a higher fines (clayey) content while the sandy soil (Soil S) is more uniformly graded.

The fly ashes used in this study, Brandon Shores (BS) and Columbia (C), were provided by power plants in Maryland and Wisconsin, respectively. These represent a non-cementitious (low calcium oxide) fly ash (BS) and self-cementitious (high calcium oxide) fly ash (C). The higher calcium content reported in the TEA (14.4%) for the Columbia fly ash provides its self-cementitious property upon hydration. Specifically, a higher calcium level is indicative of higher levels of calcium oxide, which reacts with water to form hydroxide ions. This is reflected in the more alkaline pH of 11.9 of the C fly ash compared to the BS fly ash pH of 8.8

Two extraction fluids were used in the leaching tests described below. In the batch water leach tests (WLTs) and column leach tests (CLTs), the leaching solution was a 0.02 M NaCl solution. The ionic strength of the solution was selected to simulate the ionic strength of groundwater that would be flowing through a constructed embankment (Morar et al. 2010). Sodium chloride was expected to have minimal effect on the leaching process and the molarity was selected to be consistent with that of similar studies (Bin Shafique et al. 2007 and Morar et al. 2010). Extraction fluid #1, an acetate buffer solution, was used as the extraction solution in the TCLP tests. The solution was selected as outlined in EPA Method 1311 (U.S. EPA SW-846) on the basis of the pH of the soil-fly ash mixture after heating and addition of HCl. A detailed description of the preparation and selection of these extraction solutions is provided in Appendix B.

2.2 Sample Preparation

As part of the specimen preparation, the soils were oven dried at 120 °C for a minimum of 24 hours to remove all moisture. This was necessary to accurately assess the water content during preliminary compaction tests and achieve proper moisture content in the final compacted mixtures. For the column tests, the soils were sieved using a No. 4 sieve (4.76 mm). A total of 12 different mixtures were prepared for testing. For the batch tests, additional sieving through a No. 12 (2.00 mm) sieve was done to account for the smaller size of the testing equipment. No sieving of fly ashes upon shipment was necessary due to their relatively fine grain sizes. To maximize the degree of homogeneity, the soil-fly ash mixtures were mixed by hand and using metal spoons in five-gallon buckets. Mixing was carried on for a minimum of 5 minutes or until the mixture appeared well mixed. Mixture samples were labeled using the following format: soil (C for clayey or S for sandy) – fly ash used (C for Columbia or BS for Brandon Shores) – percent fly ash by mass (10 or 20). For example, sample S-BS-10 contained a mixture of sandy soil plus 10% (by mass) BS fly ash. Table 2.3 provides a complete list of mixtures used in this study.

2.3 Leaching Test Procedures

2.3.1 Water Leach Test (WLT)

WLTs were performed on 12 mixtures according to ASTM D3987 with two modifications. One, the size of the extraction vessel was downsized from 2 L to a 60 mL centrifuge tube to fit the equipment available in the laboratory as previously done by Morar et al. (2010). Two, a 0.02 M NaCl leaching solution was used instead of the deionized water specified by the standard method. This background electrolyte produced conductivities more representative of actual embankment situations. To initiate the test, a 2.5-gram aliquot of the sample mixture was transferred to an acid-washed centrifuge tube, and 50 mL of leaching solution were added, corresponding to a 20:1 liquid-to-solid ratio. The tubes were rotated at 29 rpm for 18 hours ± 2 hours using an end-over-end tumbling mixer (ATR Corporation) to allow for equilibration.

After rotation, the WLT samples were then placed in a centrifuge (Beckman Allegra) at 2000 rpm for 10 minutes to separate the liquid leachate and solid phases. Additional solids separation was achieved by filtering the resulting leachate through a 0.2 μm membrane filter (Pall Corporation) using a 60-mL LuerLock syringe fitted with a 25-mm Easy Pressure filter holder. Electric conductivity and pH measurements were taken for all samples immediately after filtration. The samples were then acidified to pH < 2 by adding roughly 0.5 mL of concentrated trace metal grade HNO_3. All samples were refrigerated at 4 ° C until metal analysis could occur.

A second series of WLTs were performed to examine the effect of pH on the leaching behavior of the fly ash-soil mixtures. These tests followed the WLT procedures described above, except the 0.02 M sodium chloride extraction solution was buffered at target pHs of 7 and 9. The biological buffers, BES and CAPSO (> 99% Sigma Aldrich) were used to maintain a pH of 7 and 9, respectively, due to their minimal interference with metals. The buffered solutions were prepared by dissolving 2.13 grams of BES and 2.47 grams of CAPSO in 100 mL of the original WLT extraction fluid. The pH was measured and adjusted to the target value by the addition of 4 N NaOH during constant mixing by magnetic stirrer. Preliminary tests were conducted to confirm that the addition of the buffers provided adequate buffering capacity. Specifically, pH measurements were performed on WLT samples every two hours for the first 6 hours of the preliminary testing and then again after 24 hours to check for pH fluctuations.

2.3.2 Column Leach Test (CLT)

Columns were used to more realistically simulate field leaching conditions. All specimens were compacted at their 2% dry of optimum moisture contents (OMCs) in an acrylic tube having a 101.6 mm inside diameter and 305 mm height. By compacting to the dry of optimum water content, higher hydraulic conductivities could be achieved that helped allow enough sample to be collected in a reasonable amount of time. Standard Proctor effort (ASTM D 698) was used during compaction. Table 2.4 provides the optimum moisture content and maximum dry unit weights (γ_{dm}) of the mixtures based on compaction tests. The mixtures with the Brandon Shores fly ash were used directly after compaction, However, due to their high calcium content, the mixtures prepared with Columbia fly ash ash were cured for 7 days in a humidity chamber (95% relative humidity, 23 C°) following compaction. Additional information on the column compaction procedures can be found in Appendix B. Figure 2.1 presents a schematic diagram of the column setup. Acid-washed plastic centrifuge tubes were used to store the samples before metal analysis and were labeled using the same system as described above.

After compaction, the column reactors were fabricated by placing porous stones above and below the sample to prevent the compacted media from being washed out of the column and evenly distribute the influent solution. The columns were then capped with top and bottom latex plastic end plates that contained ports for influent and effluent tubing attached to plastic connectors. The plates were held in place using threaded rods, sealed with silicone sealant for a water-tight connection. Influent to the column was provided in a downflow flow direction via a peristaltic pump (Cole Palmer, Masterflex Model 7518-00) and 1/4 inch Masterflex plastic tubing (Cole Palmer) at a rate of 60 mL/hr as recommended by Gelhar et al. (1992) and Morar et al. (2010). The influent 0.02 M sodium chloride solution was stored in five-gallon buckets, and continuously mixed by magnetic stirrer.

A total of 10 CLTs were performed in two sets. In each test, sampling of the column effluent was conducted 4-5 times a day for the first 3 days to capture the initial fluctuations in metal leachate concentrations. Sampling frequency was then decreased to 3 times a day, followed by twice a day, daily, and once every two days as the testing duration increased. Acid-washed plastic bottles were used to collect between 30 to 50 mL of leachate samples at each sampling time. All samples were analyzed for pH and EC, and then preserved by acidification with trace metal grade HNO_3 to pH < 2 and refrigeration (4°) for later metals analysis. The pH of the influent solution was measured at least twice daily and adjusted using 1 N NaOH to ensure it remained within the designated pH range of 6.5-7. The CLTs were run until the EC and pH values appeared to be approaching equilibrium and at least 25 pore volumes of flow (typically 35-65) had occurred.

A tracer study using bromide as a conservative tracer was conducted at the conclusion of both sets of CLTs to provide a basis for comparison to the metal leachate concentrations. The procedure summarized by Morar et al. (2010) was followed. A stock solution of 1000 mg/L bromide was prepared by dissolving 0.64 grams of NaBr (Sigma Aldrich) into 500 mL of the 0.02 M NaCl solution. The bromide stock solution was diluted with additional 0.02 M NaCl influent solution to prepare 100 and 250 mg/L bromide solutions for the first and second set of columns, respectively. Three or four samples were taken of column effluent prior to the influent tubing being switched to the bromide solution to create a step input. Sampling of effluent during the tracer study occurred every hour initially then decreased to every two hours, with a total elapsed study time of roughly 30 hours. The samples were then analyzed for bromide concentration as described in Section 2.4.2.

2.3.3 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP test was conducted on the 12 soil-fly ash mixtures as outlined in EPA method 1311 (U.S. EPA SW-846), except that the size of the extraction vessel was downsized as described for the WLT (George et al. 2007). Based on the TCLP test, extraction fluid #1, an acetate buffered solution, was used as the leaching solution. Sample preparation, mixing, and post-mixing handling followed the steps described above for the WLT except that the leachate collected after centrifugation was vacuum filtered through TCLP glass fiber filters (Fisher Scientific) instead of membrane filters. Electric conductivity and pH measurements were taken for all samples immediately after filtration. The filtered leachate was then acidified to pH < 2 using trace metal grade HNO_3 and refrigerated until analyzed for metal concentrations.

2.4 Analytical Methods

2.4.1 pH and electrical conductivity (EC) measurements

Measurements of pH were performed using a combination pH probe (Orion, Model 91560) and meter (Orion, Model 520A). The meter was calibrated before each use using standard buffer solutions at pH 4, 7, and 10. The probe tip was thoroughly rinsed with deionized water between each standard and sample measured. Calibrations were performed roughly every 4 hours during the CLTs and two hours for the WLTs. A conductance meter (YSI, Model 35) was used to measure electrical conductivity. The tip of the probe was repeatedly submerged a minimum of three times into the solution being tested to allow the EC meter to stabilize. Once the same EC value was measured three times successively, it was recorded. Again, thorough rinsing of the probe was carried out to prevent contamination.

2.4.2 Bromide Measurements

Bromide concentrations were measured using a voltmeter (Orion, Model 520A) equipped with a Br selective membrane probe (Cole Palmer, Model 27506-00), which was used according to the manufacturer's instructions. Five standards (1, 10, 50, 100, and 500 mg/L bromide) were made by serial dilution of the stock solution described in Section 2.3.2. An ionic strength adjuster (ISA), 5 N $NaNO_3$, was added to both standards and samples in a ratio of 1 mL ISA to 50 mL standard or sample. Standards were thoroughly mixed and a calibration was performed every two hours during the tracer studies, with duplicate measurements. The average voltage values were used to construct a calibration curve relating meter voltage to bromide concentration. Linear regression was performed and only calibration curves with R^2 values of greater than 0.995 were used to convert sample voltage readings to Br concentration.

2.4.3 Leachate Metal Concentrations

The samples from all of the leaching tests were analyzed for heavy metals using an atomic absorption spectrophotometer (Perkin Elmer, Model 5100ZL) equipped with a graphite tube furnace module. A separate FIAS-400 hydride generator was used to determine concentrations of arsenic. AS-90 and AS-71 autosamplers were used to assist in sample analysis for the furnace and hydride generator apparatuses, respectively. Hollow cathode lamps were used for chromium and copper, while an electrodeless discharge lamp with a Perkin Elmer EDL System 2 power source was required for arsenic. The lamps were set at the following wavelengths specific to the metal being analyzed for: 193.7 nm for As, 357.9 nm for Cr, and 324.8 nm for Cu.

Certified stocks solutions of 1000 mg/L (Fisher Scientific) were used to prepare sets of standards for each metal. Five to six standards were created, ranging from 2 to 40 μg/L for chromium and copper and 0.5 to 10 μg/L for arsenic based on the range where a linear relationship between absorbance and concentration was found. The standards were made using the same background matrix as the samples. Calibration curves with an R^2 value of greater than 0.99 were used. Two standards were measured as samples before and after sample analysis to check the accuracy of calibration and precision of instrument. An approximately 1 mL aliquot of each sample was placed in plastic cups, transferred to the autosampler rack, and analyzed. Estimated metal concentrations in the leachate were calculated from calibration curves produced internally by the AA instrument software. Metal concentrations and sample absorbance values were recorded for each sample duplicate. Dilutions were made when necessary to ensure a sample's absorbance was within the range of standards used. A new calibration curve was constructed every 20-25 samples. The detection limits of the equipment based on the 0.02 M NaCl leaching solution for As, Cr, and Cu as determined by the EPA Method Detection Limit procedure (Standard Method 1030C) were 0.22, 0.35, and 1.00 μg/L, respectively. Method detection limits were higher for the TCLP Extraction Fluid #1 matrix, and were determined to be 0.49, 1.8, and 1.4 μg/L for As, Cr, and Cu, respectively.

3 Results and Discussion

WLT, TCLP, and CLT leaching tests were performed on the same 8 different fly ash-soil mixtures to evaluate the metal leaching behavior as a function of the characteristics of the different testing protocols and the soil/fly ash properties. In addition, pure fly ash and pure soil samples were tested to provide a basis for comparison in terms of expected upper and lower bounds for metal leaching. A series of WLTs were conducted at variable pH values to observe the effect of pH on leaching. Leachate pH and Cu, As, and Cr concentrations were monitored in the three tests and compared to the Maryland State Aquatic Toxicity limits (MDE COMAR) and EPA Drinking Water MCLs (EPA Drinking Water Contaminants). In the following paragraphs, the Cu, As, and Cr concentrations observed in the three tests are discussed sequentially, specifically as a function of the fly ash content and the solution pH. Subsequently, the CLTs are examined in more detail, focusing on the reproducibility of the tests, and interpretation of the tracer study results. Finally, the results of the three test methods are compared.

3.1 Leaching Test Results: Copper

3.1.1 General Trends

Cu concentrations in the WLT leachate (Table 3.1) were below the strict Maryland chronic Cu Aquatic Toxicity limit of 9 μg/L in 75% of the fly ash-soil mixture samples, with the exception of the C-C-10 and C-C-20 samples at 12 and 14 μg/L, respectively. These differences in leaching behavior are likely the combined result of the fly ash and soil composition (e.g., metal content and alkalinity) and other factors, such as pH, which are discussed further below (Bin Shafique et al. 2002, Palumbo et al. 2007). For example, based on the TEA (Table 2.1), soil C (27.16 mg/kg) and C fly ash (188.56 mg/kg) had a higher Cu content compared to soil S (1.28 mg/kg) and the BS fly ash (59.63 mg/kg). Correspondingly, mixtures containing C fly ash generally had higher leachate Cu concentrations (up to 6 times) than similar mixtures with the BS fly ash. The exception to this was the 100% fly ash samples, where both fly ashes had WLT Cu leachate concentrations below 3 μg/L.

The TCLP results (Table 3.2) showed Cu leaching increased in all soil S mixtures compared to the WLT, especially for fly ash BS, while soil C mixtures had TCLP Cu concentrations that were approximately the same as the WLT for the BS fly ash and about 40-50% lower for the C fly ash. TCLP Cu concentrations in the soil C mixtures were all below the Maryland Cu Aquatic Toxicity chronic limit, but three out of the four soil S mixtures (S-C-10, S-BS-10, and S-BS-20) had Cu concentrations exceeding that criterion.

Based on the replicate CLTs for the S-BS mixtures (Figure 3.1), Cu leaching exhibited a first flush behavior, with concentrations decreasing from 12-20 μg/L to < 5 μg/L after the first 1-2 PV. Interestingly, the S-BS column with the higher fly ash content (i.e., 20% vis-à-vis 10%) did not always have the higher Cu concentration in the leachate. The replicate C-BS CLTs also exhibited a first flush behavior (Figure 3.2); however, lower initial peak Cu concentrations (~ 7 μg/L) were measured in the C-BS-20 columns compared to the initial peak Cu concentrations in the S-BS columns (~ 20 μg/L) despite soil C having approximately 21 times the copper content as soil S based on the TEA. One possible explanation for the difference in leaching between the soils is that adsorption of aqueous Cu onto the mineral surface may have occurred at the pH range of 4-6 for the BS fly ash CLTs and contributed to the reduced leaching found from soil C. For example, in column studies under acidic conditions, Ariese et al. (2002) observed a large portion of the leached metals were retained by the soils, reducing aqueous concentrations by different adsorption or binding mechanisms. Soil C, with a higher percentage of fines (silts and clays), is likely to have increased surface area and surface charge compared to soil S, which are important factors in determining soil adsorption capacity.

Both the S-C-10 and S-C-20 columns had initial Cu concentrations above 20 μg/L (Figure 3.3). These concentrations decreased dramatically with continued leaching, and after 5 PV concentrations were below the Cu Aquatic Toxicity limit. The C-C-20 column exhibited similar leaching behavior as the S-C columns (Figure 3.4). The initial peak Cu concentration was measured at 110 μg/L, or about 12 times the Maryland aquatic toxicity chronic limit for Cu, but concentrations stabilized around 12 μg/L after 20 PV.

CLT leaching of Cu from the soil S-fly ash mixtures was comparable both in behavior and magnitude to that of the 100% soil S column (Figure 3.5). This indicates that the soil can act as a source of metal ions, especially given that 80-90% of the mixture mass is soil and if the soil contains metals in more easily solubilized forms compared to fly ash. The contribution of soil to leaching would vary with its composition and fluctuations in pH. Soils can play a large role in metal leaching because of their effect on processes that govern leaching mechanisms as well as serving as a “compartment” for the storage and/or release of metals. Since soils can comprise a large portion (greater than 80% by mass) of the total mixture, soil buffering capacity can influence leachate pH which directly affects metal concentrations. Depending on soil properties, soils can be highly adsorptive and remove dissolved metals or release additional metal ions into solution (Bin Shafique et al. 2007). The effect of the fly ash content and pH on Cu leaching are examined further below.

3.1.2 Effect of fly ash content on copper leaching

Increased fly ash content had less effect on the WLT Cu concentrations in the BS fly ash mixtures than the C fly ash mixtures, with aqueous copper for all BS fly ash mixtures measured at < 5 μg/L (Figures 3.6 and 3.7). For the BS fly ash mixtures, the largest increase in Cu concentration was observed going from 10% to 20% fly ash. In comparison, the C fly ash mixtures showed the largest increase (9.4 μg/L for soil C and 6.2 μg/L for soil S) in leachate Cu when fly ash content was raised from 0 to 10% as shown in Figures 3.8 and 3.9; however, the Cu concentrations decreased as the fly ash content increased further, from 10% to 20% and/or 100%.

The trends in TCLP Cu concentrations as a function of fly ash content were also different between the BS and C fly ashes. BS fly ash mixtures exhibited a positive, nonlinear relationship between fly ash content and leachate metal concentration, with higher levels of leaching observed in the soil S compared to soil C (Figures 3.10 and 3.11). This difference could be attributed to the larger surface area of soil C due to a higher clay content, which would facilitate adsorption onto soil particles, including iron and aluminum oxide surface deposits (Evans 1989). On the other hand, C fly ash mixtures had a large increase in TCLP leachate Cu concentrations upon the initial addition of fly ash to the soils (from 0 to 10% fly ash by mass), followed by a decrease in Cu concentrations in mixtures with 20 and 100% fly ash (Figures 3.12 and 3.13).

This nonlinear relationship between the leaching of metals from fly ash mixtures with variable fly ash contents has been observed by others (Bin Shafique et al. 2007, Morar et al. 2010) and illustrates the difficultly in predicting leaching behavior. The low metal content in both soils compared to the fly ashes is likely a factor in the nonlinear relationship, especially under the more acidic conditions in the TCLP in which fly ash can serve as the source of the majority of the leached metal. However, as the fly ash content is increased, the percent of soil by mass decreases, thereby reducing the ability of the dissolved metal ions to interact with substances found in the soil. This is particularly relevant to copper because of its high affinity for complexation with humic and fulvic acid portions of soil organic matter, which can cause increased detection of soluble copper (Evans 1989). The difference in TCLP leaching between soils is supported by the higher LOI measured for soil S (8.6%) compared to soil C (7.1%), which would provide more organic matter for Cu complexation.

3.1.3 Effect of pH on copper leaching

Changes in pH can affect the speciation, and therefore the solubility, of metals in the leachate. The distribution of common Cu(II) species as determined by the Visual Minteq chemical equilibrium software is shown in Figure 3.14. In the case of copper, the Cu^{2+} cation is the dominant species at $pH < 8$ (Evans 1989). Above this pH, hydroxide precipitation of Cu is expected, which would lead to lower measured aqueous levels. However, the presence of inorganic and organic compounds can cause the formation of soluble complexes that can increase leachate metal concentrations (Rigol et al. 2009). For example, comparing the two fly ashes studied, it is clear the approximate 5 unit difference in leachate pH is a major contributor to the increased WLT Cu leaching seen from the C fly ash (Table 3.1). Calcium in fly ash in the form of calcium oxide reacts with water to form calcium hydroxide,

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat} \qquad (3.1)$$

which dissociates to give 1 mole of Ca^{2+} and two moles of OH^-,

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad (3.2)$$

Thus, the higher calcium content in the C fly ash compared to the BS fly ash (14.43% vis-à-vis 0.22%), and correspondingly higher CaO content, result in more alkalinity and pH values around 11.5 as observed in the unbuffered WLTs and CLTs (Table 3.3). Calcium levels in the fly ash have been reported as a major factor in determining the leachate pH because of relatively high levels of calcium compared to other alkaline elements (Palumbo et al. 2007). Conversely, increased acidity can desorb Cu and release more Cu through the dissolution of minerals, as illustrated by all 4 TCLP soil S samples having higher leachate Cu than the WLT results for the same mixtures (Table 3.2).

To examine the effect of pH on Cu leaching more closely, all batch Cu data were compiled in Figure 3.15 for the S-C mixtures and Figure 3.16 for the C-C mixtures. No clear trends in Cu leaching were observed in the buffered WLTs from the BS fly ash mixtures due to the large scatter of data, so those data are not shown. For the mixtures with C fly ash (Figures 3.15 and 3.16), the Cu concentrations were higher in the samples buffered at pH 7 and 9 compared to those from the original WLTs (pH ~11.5) and the TCLP tests. Similar results were seen for both soils and supported increased leaching of Cu as the pH is decreased from the unbuffered value. This is possibly attributed to higher levels of Cu release from increased dissolution of fly ash and soil particles under acidic conditions and complexation reactions with positively-charged Cu species and negatively-charged soil organic matter resulting in higher soluble Cu levels (Fytianos et al. 1998, Ram et al. 2007).

The pH also impacted the results of the CLTs. The BS fly ash columns exhibited more fluctuations in the CLT pH measurements, sometimes changing 1-2 pH units within several pore volumes. In contrast, columns containing C fly ash had stable pH measurements throughout the test duration. There were certain CLTs, such as the S-BS-20 (Figure 3.1) and C-BS-20 (Figure 3.2) columns, where in some portions of the leaching curves there appears to be a correlation between decreases in pH and increased Cu concentrations. This confirms the importance of pH in determining leachate metal concentrations, and how simple pH measurements can aid in predicting metal speciation and leaching behavior.

3.2 Leaching Test Results: Arsenic

3.2.1 General Trends

Aqueous WLT arsenic concentrations were measured below the EPA MCL of 10 µg/L for all fly ash-soil mixtures (Table 3.1). In fact, leachate As concentrations were generally < 1 µg/L with little variation between mixtures of different soils or fly ashes in the WLTs, except for the 100% BS fly ash at 23 µg/L. This suggests that the same leaching mechanisms are occurring in mixtures of the different soil and fly ashes. The low (generally < 1 µg/L) levels of As detected also suggest that soluble arsenic is either being strongly adsorbed or precipitated out of solution.

Similarly, the aqueous TCLP arsenic concentrations were also measured at below the EPA MCL for all soil-fly ash mixtures (Table 3.2). However, both 100% fly ash samples exceeded the MCL with concentrations of 30 and 85 µg/L for C and BS fly ashes, respectively. The TEA results (Table 2.1) indicate that the arsenic content of the BS fly ash is higher than that of the C fly ash (24.2 mg/kg versus 15.0 mg/kg), consistent with the higher leaching in the 100% BS fly ash samples. The S-BS-20 mixture had the highest TCLP As concentration of the soil-fly ash mixtures, but the arsenic leachate concentrations for all fly ash-soil mixtures exhibited a very tight range compared to the other metals, with all ranging from < 0.49 to 3.0 µg/L. Thus, the presence of the soils dramatically influenced the As concentrations in the leachate. The addition of fly ash to soil C appeared to have a less pronounced effect on As leaching as the 100% C soil samples had a slightly greater concentration for leachate arsenic (1.7 µg/L) than the fly ash-soil mixtures (<0.49 to 1.1 µg/L).

Peak leachate As concentrations did not exceed 40% of the EPA MCL for any of the CLT specimens, but the patterns varied depending on the soil and fly ash properties. S-BS As leaching in the CLTs followed first flush behavior with a maximum initial concentration around 3 μg/L (Figure 3.17). Arsenic leaching was higher in the S-BS-20 mixture, illustrating that increasing the fly ash content can result in larger leachate concentrations under some conditions. A very different pattern was observed for the As concentrations in the S-C-10 and S-C-20 columns, in which case As increased with time, albeit still remaining below the EPA MCL (Figure 3.18). Further testing is needed to better characterize leaching in relation to regulatory limits under a longer leaching period. Arsenic can become more solubilized under alkaline conditions, such as observed in the S-C mixtures, and leach in greater quantities because of electrostatic repulsion between anionic As species and negatively-charged soil particles (Palumbo et al. 2007, Jegadeesan et al. 2008). As concentrations in the C-C-20 column also remained below the EPA MCL throughout the test duration, but showed a slight increase to approximately 2.0 μg/L (Figure 3.4). Leaching of arsenic in the C-BS-20 columns (Figure 3.19) peaked after several PV and then rapidly decreased. The generally low levels of As leaching (< 5 μg/L) could be the result of the strong attraction of As species to soil particles (increased adsorption of dissolved As) and possible precipitation of As as some type of iron-lead oxide. High levels of As retention by soils were found in both highly organic and highly mineral soils, which may have contributed to lower aqueous levels detected (Balasoiu et al. 2001).

3.2.2 Effect of fly ash on arsenic leaching

BS fly ash mixtures generally had increasing WLT As concentrations as the fly ash content was raised from 0 to 100% fly ash (Figures 3.6-3.7) , although the relationship was nonlinear. The soil C mixture actually had a small decrease in As concentrations increasing from 10 to 20% fly ash content, but the increase from 20 to 100% fly ash produced the largest increase in concentration up to 22 µg/L. This fly ash content increment corresponded to the largest change in leachate WLT pH (2.8 pH unit increase for S-BS and 2.2 pH unit increase for C-BS) (Table 3.1), supporting the connection between changes in pH from fly ash addition and the amount of leached metalloid or metal, as discussed further below. The C fly ash mixtures for both soils showed an increase in WLT As concentration from 0 to 10% but decreased as the fly ash content was raised further (Figures 3.8-3.9). This initial increase in As concentration also corresponded to the largest pH change in the WLT samples, an increase of 5.8 units for soil S mixtures and 2.6 units for soil C mixtures. Higher leaching from the 100% BS fly ash compared to 100% C fly ash (Table 3.1) is likely to be related to the higher As content of this fly ash by roughly 10 mg/kg based on the TEA (Table 2.1).

In the TCLP test, increasing the fly ash content from 10 to 20% resulted in 1-2 µg/L higher As concentration in the leachate for soil S samples with both fly ashes (Figures 3.10 and 3.12), but this trend was not seen with soil C (Figures 3.11 and 3.13). The largest increase in As concentration in all of the TCLP tests occurred with the increase from the 20 to 100% fly ash content, and could be the result of the absence of soil particles that enhance adsorption or release precipitating agents from the fly ash which such as lead or sulfide.

3.2.3 Effect of pH on arsenic leaching

Previous studies have found that As is found in fly ash primarily as As(V), possibly due to the highly oxidizing environment of coal combustion, which would convert arsenite (As(III)) species to As(V) species (Cullen and Reimer 1989, Shah et al. 2008). A distribution of As(V) species produced by Visual Minteq software is provided in Figure 3.20. Alkaline pH conditions favor increasingly negatively-charged As species, such as $HAsO_4^{2-}$ and AsO_4^{3-} for As(V), to dominate in solution, with the latter present in appreciable quantities at $pH > 11$. However, if As(III) is the main form of As present in the fly ash, then leaching could produce arsenous acid (H_3AsO_3) or $H_2AsO_3^-$. Arsenite can become more significant at higher pH values and in reducing environments, such as may have occurred in the closed, saturated CLT system. This is important because retention of As(III) by soils is less than that of As(V) (Balasoiu et al. 2001). If dissolved concentrations exceed the adsorption capacity of the soil, increased leaching of arsenic can be observed because of repulsion between the metal ion and the soil particle surface. Therefore, at very alkaline pH values above 11, As species can exhibit reduced adsorption to negatively-charge surfaces and therefore leach in higher concentrations under conditions such as those seen with the C fly ash (Wang et al. 2006, Morar et al. 2010). A more in-depth speciation study would be helpful in confirming the As species present and providing evidence of the observed leaching behavior.

Consistent with the discussion above, the S-BS mixtures showed relatively constant As levels from pH 5-7, but increasing As concentrations in the batch leach tests as the pH rose from 7 to 9 (Figure 3.21) , although this was not clearly observed in the C-BS samples (data not shown). In the latter case, the finer particles of soil C may have promoted more adsorption via the increased surface area of iron and manganese oxides. In contrast, arsenic leaching for C fly ash mixtures with soil S increased from pH 5 to 7-9, then decreased with an additional pH increase to 11 (Figure 3.22) except for C-C-10 which had a slight increase (data not shown). The large, roughly 5 unit difference in pH is likely a major factor in the different observed leaching results. The different As species dominant at the slightly acidic pH (BS fly ash mixtures) and basic pH (C fly ash mixtures) would have different adsorption, complexation, and precipitation capacities. At TCLP As leaching from both fly ashes mixtures all had concentrations < 3 μg/L, reflecting the similar pH conditions.

3.3 Leaching Test Results: Chromium

3.3.1 General Trends

Except for the 100 μg/L of aqueous Cr measured in the C-C-20 mixture, all other WLT Cr levels were below the 100 μg/L EPA MCL (Table 3.1). WLT Cr concentrations ranged from 57-100 μg/L for C fly ash mixtures compared to <0.35 to 1.4 μg/L for BS mixtures. Thus, Cr leached from S-C mixtures at concentrations ranging from 160-190 times the concentration for the corresponding S-BS mixture, and C-C mixtures at concentrations approximately 50-80 times more than from the corresponding C-BS mixture. All of the C fly ash samples with elevated Cr levels had pH values > 10, similar to the results obtained by Fytianos et al. (1998) and Palumbo et al. (2007).

TCLP Cr concentrations were measured below the EPA MCL for Cr in all soil-fly ash mixtures (Table 3.2). Only the 100% C fly ash exceeded the MCL, consistent with the relatively high Cr content of this fly ash based on the TEA (64.6 mg/kg). With the exception of the S-C and C-C mixtures, all of the TCLP Cr concentrations exceeded the WLT Cr concentrations. This is probably due at least in part to the lower pH of the TCLP (average pH of 6.3 for 100% C fly ash samples). Zandi and Russell (2007) describe how certain metals such as Cr are typically found in the glassy, exterior coating of the fly ash particles resulting from condensation following coal combustion. More acidic conditions degrade this surface Cr and release it into solution, leading to more dissolved Cr as seen in the BS fly ash mixtures. In addition, the lower pH range (4.8 to 6.3) of the TCLP favors the dominance of cationic species of Cr such as $CrOH^{2+}$ and $Cr(OH)_2^+$ that would adsorb less to soils under acidic conditions because of the dominance of positively-charged surfaces.

Several of the CLT tests exhibited a lagged leaching response for Cr, and had portions of the leaching curves that showed decreases in pH resulting in increased Cr concentrations. For example, Cr concentrations from the first set of CLTs with S-BS (Figure 3.23) had the most variation and showed a lagged leaching response with two periods of elevated chromium levels above 50 µg/L. A lagged Cr leaching response could be caused by Cr being located in less easily solubilized fractions of the soil and fly ash particles. Thus, as time progresses, leaching solution is able to reach these Cr sources and dissolution reactions reach the point where the Cr is released into solution. Edil et al. (1992) also observed that while the majority of CLTs exhibited first flush leaching, Cr had a different leaching response. A sharp spike in Cr to 250 μg/L in the first set S-BS-20 column around 10 PV was the only time the CLT leachate concentrations exceeded the Cr MCL limit. Similar lagged spikes in Cr concentration to 35 μg/L and 20 μg/L were observed in the second set S-BS-20 column (Figure 3.23), and first C-BS-20 column (Figure 3.24), respectively, which corresponded to the first major drop in pH. In contrast, both the S-C-10 and S-C-20 columns had initial Cr concentrations that exceeded the EPA MCL (Figure 3.25), but quickly dropped within 5 PV to below regulatory limits. The C-C-20 column also had initial Cr concentrations (238 μg/L) over two times the 100 μg/L regulation limit (Figure 3.4), similar in order of magnitude to leaching from other columns containing C fly ash, followed by declining Cr levels.

3.3.2 Effect of fly ash content on chromium leaching

Fly ash content appeared to have minimal effect on WLT Cr leachate concentrations in the BS fly ash mixtures, with a range of Cr concentration of < 0.35 to 2.8 μg/L in the 100% BS fly ash sample (Figures 3.6-3.7). Mixtures of both soils and C fly ash show an increase in WLT Cr concentration initially with a peak at 20% fly ash before decreasing with 100% fly ash sample (Figure 3.8-3.9). The higher leachate Cr from soil-fly ash mixtures is possibly due to the increased repulsion of Cr species with charged surfaces more abundant in the presence of the soil particles. The presence of soluble soil organic matter could also play an important role in causing increased Cr in the leachate. Mixtures of fly ash with soil C displayed higher Cr concentrations than the corresponding mixtures with soil S, which may be partially due to this soil having the highest levels of Cr present (65.9 mg/kg) of all 4 materials, although soil C itself had lower leachate levels than soil S (Table 2.1). The relatively sharp increase in metal concentration from 0 to 10% C fly ash can be attributed to the pH change of approximately 6 for soil S and 3 for soil C that occurred from the increase of 0 to 10% fly ash, which may have led to an increased attack on the mineral structure of the soils and dissolution of the exterior coating on fly ash particles.

The TCLP leaching results indicated an approximately linear relationship between leachate Cr concentrations and fly ash content for all soil and fly ash mixtures (Figures 3.10-3.13), with a minimum coefficient of determination determined to be 0.9655 (trendlines not shown). The slope of this relationship is similar for the BS fly ash mixtures, as it is for the C fly ash mixtures, suggesting that the fly ash metal content was determining the results. The more uniform leaching pattern observed corresponds to the more consistent pH in the TCLP samples compared to those from the WLT. The smaller fluctuations in pH with varying fly ash content seen in the TCLP (Table 3.2) could produce a more consistent release of Cr into solution as the acidity with different fly ash contents remains relatively constant.

3.3.3 Effect of pH on chromium leaching

Cr can be present in fly ash as Cr(VI) in low percentages (< 5%) that vary with the coal source and combustion conditions (Shah et al. 2008). The dominance of either the Cr(III) or Cr(VI) form is strongly linked to pH and other conditions such as the pE of the system, which indicates the thermodynamic driving force for reduction and oxidation of Cr species. Cr(III) typically forms increasingly negative species with minimum solubility around pH 6-7, and eventually precipitates out as $Cr(OH)_3$ (Rai et al. 1987). At very alkaline pH values greater than 10, Cr(III) can form species like $Cr(OH)_4^-$, which behaves like other anions with decreased adsorption under alkaline conditions (Shah et al. 2008). This change in Cr(III) speciation is shown in Figure 3.26 which has the relative distribution of Cr(III) species as a function of pH. This anionic behavior is probably a main contributor to the higher unbuffered WLT Cr concentrations from the C fly ash mixtures, which have higher pH values of roughly 11.5 compared to around 6.5 for BS fly ash mixtures (Table 3.3, Figures 3.27-3.28). TCLP Cr concentrations were higher than for the unbuffered WLT as the pH was decreased for the BS fly ash, but the opposite effect was observed for the C fly ash mixtures. The leaching of Cr is generally magnified at acidic pH values compared to negligible leaching occurring in neutral or alkaline conditions as the acidic conditions aggressively attack the Cr-containing compounds in the materials, releasing Cr into solution (Fytianos et al. 1998, Jo et al. 2008). These findings are consistent with the increased leaching of Cr under acidic TCLP conditions observed in the current study for the BS fly ash mixtures.

Consistent with the discussion above, the Cr concentrations in the buffered WLT with the BS fly ash mixtures increased from pH 7 to pH 9, with a similar but less dramatic effect in the C fly ash samples (see Figure 3.27-3.28). The weaker trend with the C fly ash can be explained if a majority of the Cr present in this fly ash was Cr(VI), which has high solubilities over a pH range of 2-12 and, thus, aqueous concentrations would be similar at different pHs (Rai et al. 1989). A single colorimetric determination of Cr(VI) with diphenylcarbazide reagent performed on one set of CLT samples showed levels of Cr(VI) in the BS fly ash column leachate to be below 1.0 μg/L, while C fly ash had 114 μg/L, which represented approximately 50% of the total leached Cr. Thus, if the BS fly ash mixtures have predominantly Cr(III), then the combined TCLP and buffered WLT test results from this study agree well with the expected bowl-shaped solubility of Cr(III) across the pH scale: at acidic pH values (~ 5.5 for TCLP), solubility of Cr(III) is raised and higher leachate concentrations are observed; similarly, at alkaline pH values (9 for buffered WLT), solubility and therefore leaching of Cr(III) is again enhanced after reaching a minimal around neutral pH (Rai et al. 1987). In comparison, the relatively consistent magnitude of the Cr concentration in the leachate from the C fly ash mixtures across the pH values tested is consistent with Cr(VI) being dominant in C fly ash, whose distribution of species as a function of pH is shown in Figure 3.29. Interestingly, at the high pH values (> 10) where increased leaching of As was found, Balasoiu et al. (2001) found that the presence of arsenate significantly decreased Cr(VI) adsorption on an iron oxide surface deposits due to competition for adsorption sites and electrostatic effects. This potential for interactions between metal ions illustrates another aspect of the complexity of natural leaching mechanisms, especially when dealing with several metals of interest at once.

3.4 CLT Reproducibility

The duplicate columns prepared with soil C and fly ash BS at 20% all exhibited a similar leaching behavior for all of the metals, which could be described as a first flush response pattern (Figures 3.2, 3.19, and 3.24). In addition, with the exception of a spike in Cr concentration in the C-BS-20 #1 column, the magnitude of the leachate concentrations also exhibited good reproducibility, with effluent concentrations that differed by less than 3 μg/L throughout the test. The highly variable pH in the BS fly ash mixtures could explain the difference in leaching behavior in the duplicated columns because sudden fluctuations in pH could affect the solubilization processes occurring in a specific portion of the column.

Duplicate S-BS-10 and S-BS-20 columns showed similar first flush leaching behavior for Cu and As (Figures 3.1, 3.17, and 3.23). Differences in leachate concentration between duplicate CLTs were small at < 5 μg/L for Cu and < 1 μg/L for As throughout the test duration. Cr leached from the S-BS column exhibiting first a lagged and then a first flush leaching response, with the lagged response CLTs have higher measured leachate Cr. Again, differences in the flow through the column media and natural heterogeneity could be the cause of discrepancies in leaching from columns composed using the same mixture.

In addition to pH, another factor that could contribute to variability between replicate columns is the formation of preferential flow paths, which could facilitate the solubilization of portions of the column having varying amounts of metals present. This is supported by the difference in breakthrough times between the first and second set of CLTs. In addition, due to the heterogeneous nature of the soils and fly ash, differences within materials could contribute to fluctuations in both metal concentration and effluent pH. Nonetheless, although differences exist in leaching between columns composed of the same mixture, the results show that CLTs can be reproduced and similar estimates of leaching potential obtained.

3.5 Tracer Study Results

Bromide breakthrough curves showing C/Co as function of pore volumes of flow for both sets of CLTs are shown in Figures 3.30-3.31. All of the tests were performed in the same manner, although there was less variation in influent solution bromide measurements from the second set of CLTs. Breakthrough curves are useful tools in assessing the transport parameters of mixtures and evaluating the presence of flow anomalies such as preferential flow paths that could impact the leaching of heavy metals as the leaching solution flows through the column media. Despite some inconsistency in the influent bromide concentrations, the breakthrough curves for all 10 columns were similar, with all exhibiting the typical "S" curve response to the step input of bromide. However, there was some variability in the timing of the breakthrough point, which was reported as reached when the C/Co ratio approximately equaled 1. For example, the tracer studies for the first set of CLTs (Figure 3.30) had earlier breakthrough points compared to the second set of columns (Figure 3.31). In addition, within the first set, the type of fly ash appeared to have a strong impact on the point of breakthrough, with the C fly ash mixtures having breakthrough occur earlier than the BS fly ash mixtures, at approximately 0.25 and 0.75 PV, respectively. In comparison, all columns from the second set of CLTs had breakthroughs occur at roughly the same time around 1 PV as expected for a conservative tracer.

One possible explanation for the observation of an earlier breakthrough in the first set of C fly ash columns compared to other columns could be the increased porosity that results from combining the soils with a smaller particle size fly ash. However, this phenomenon should have affected the BS fly ash columns as well. Therefore, it is more likely that these results suggest that there was either short circuiting along the column walls or preferential flow paths could have developed within the fly ash columns that would allow leaching solution to pass through the columns more rapidly than expected, thereby changing the extraction time and metal leaching behavior.

3.6 Comparison of Different Leaching Test Results

There were significant differences in the leachate metal concentrations obtained in the three leaching tests performed, as shown in Table 3.4 and Figures 3.32-3.34. When comparing results from leaching test methodologies, it is important to consider the impact of chemical factors, such as pH differences, and hydrologic conditions (flow-through or static). For example, critics of the use of the TCLP for evaluating the leaching potential of fly ash point out that the more acidic test conditions characteristic of landfill leachate often result in higher leaching and can overestimate the leaching potential of fly ash mixtures when placed in other environments (Baba and Kaya 2004). This is demonstrated by the results of a study by Jegadeesan et al. (2008) comparing the synthetic precipitation leaching procedure (SPLP), which uses a sulfuric and nitric acid mixture as the leaching solution for fly ash, and the TCLP test. They found that aqueous As and Cr concentrations were three times higher in the TCLP tests, while Cu concentrations were <0.006 mg/L for the SPLP compared to 0.81 mg/L for the TCLP (Jegadeesan et al. 2008).

In comparing the batch results from this research, pH was the major factor contributing to the different observed metal leachate concentrations. Leachate concentrations from the TCLP were generally higher compared to those from the WLT for both Cu and As (Figures 3.35 and 3.36), with the exception of C-BS-10 and five of the C fly ash mixtures, for which the WLT concentrations were higher. Increased Cr concentrations were also seen in the WLTs for all of the C fly ash mixtures (Figure 3.37). TCLP As concentrations were higher than the WLT results for the 100% fly ash samples by approximately 30 μg/L for C fly ash and 60 μg/L for the BS fly ash (Tables 3.1 and 3.2). In comparison, the increases in the TCLP As concentration observed in BS fly ash mixtures were small (< 2 μg/L) compared to the WLT results. Jo et al. (2008) also reported leaching of As and Cu concentrations similar in magnitude from bottom and lagoon coal ash. The magnitude of the difference in pH between the TCLP (~5.3) and WLT (~6.5 for BS fly ash and ~11.5 for C fly ash) is largely responsible for explaining the different leaching trends. The difference between the TCLP and WLT concentrations were lower for the BS fly ash mixtures because of the smaller differences in pH (~1 pH unit) compared to the C fly ash mixtures (~7 pH units) which had Cr concentrations roughly double from the TCLP to the WLT.

When comparing the batch and CLT results, both pH and contact time become important. In this regard, the work by Ariese et al. (2002) is helpful in explaining some of the findings in this study. Ariese et al. (2002) concluded from pH-stat experiments on several different fly ashes at pH 3 and 5 that extraction time (7 vis-à-vis 24 hrs) had little effect on leachate concentrations, indicating equilibrium was possibly reached early on. This observation is consistent with the first flush leaching behavior seen in the majority of the CLT results, with highest transformation and transport of metal ions occurring in the beginning of the leaching test. Furthermore, sequential extraction tests performed by Ariese et al. (2002) showed that the readily exchangeable fractions of Cu comprised 60% of the total extractable amount. Thus, the high Cu concentrations leaching from the C fly ash in some of the CLTs in this study could result from increased solubilization from cation exchange reactions and steady-state being achieved early on. Ariese et al. (2002) also found that leachate Cu concentrations were higher under more acidic conditions. This confirms that changing the testing conditions, including lowering the pH, can affect metal leachate concentrations and yield higher or lower estimates of leaching potential. For example, elevated levels of Cr were measured at alkaline pHs in this study, and leachate Cu and Cr concentrations at pH 5 from the same pH-state tests by Ariese et al. (2002) were similar to the TCLP results from the current study. The different leaching behavior seen for the three metals studied reflect their different speciation and adsorption/precipitation mechanisms.

Performing a reasonable comparison of the batch leach tests to the CLTs also requires careful consideration of the point of comparison. For this work, two different comparisons were made. First, the peak column effluent concentrations were determined, which correspond typically to the initial first flush or concentrations measured with the first or second PV. Caution should be used, however, when comparing peak values as sole spikes in metal concentration could misrepresent the overall leaching behavior of the column. Second, a volume-weighted mean concentration (MC) was calculated using the highest L:S ratio common to all 10 columns. Calculated L:S ratios for the columns ranged from 4.8 and 5.1 because of differences in the sampling schedules between columns. The target L:S ratio was 5, which corresponds approximately to 25 years of leaching conditions (Ram et al. 2007) assuming typical dilution factors from normal groundwater flow. By examining the temporal change in leachate metal concentrations over longer time periods (weeks to months), CLTs allow estimations of leaching to be made that reflect both conditions more similar to the field and time frames that simulate prolonged leaching from a highway embankment with dozens of PV passing through the column representing many sequential rain events that could cause metal leaching.

Previous studies (Bin Shafique et al. 2007, Ram et al. 2007) report that peak leachate metal concentrations were higher in the CLT compared to WLT as was observed in the current study (Figures 3.32-3.34). Peak Cu, Cr and As CLT concentrations were higher than those from the WLT for all sample mixtures, except S-BS-10 and C-C-10. The peak Cu, Cr, and As CLT concentrations were also higher than the TCLP except for Cu in the S-BS-10, C-BS-10, and C-C-10 mixtures, As in the S-BS-10, C-BS-10, and C-C-10 mixtures, and Cr for the C-BS-10 mixture. Again this was possibly due to the increased acidity and favorable conditions for dissolution in the TCLP. The higher fixed L:S ratios (20:1 in the TCLP and WLT) found in batch leach tests can explain the lower concentrations generally found in the leachate of those tests. High initial concentrations of metals are also commonly found in the first few PV from CLTs because of the lower L:S ratio at the beginning of the CLT. However, as the saturation increases, the L:S ratio increases and concentrations generally decrease (Jo et al. 2008). Thus, the CLT MC concentrations are generally reduced for all metals compared to the peak concentrations, as expected given the typical exponential decrease in leaching observed in CLTs. Based on these results, it is expected that both test duration and L:S ratio are important parameters in comparing the results of CLTs and batch tests, while the pH of the TCLP distinguishes its leaching results from other testing methods.

Work done by Bin Shafique et al. (2006) and Ram et al. (2007) compared WLT and CLT results to estimate conservative scaling factors (e.g., 10 for Cr) for converting estimations of leachate metal concentration between WLT and CLT. Relative leaching of the three tests performed in this research was consistent with these other studies comparing different leaching protocols, with the fly ash and soil composition accounting for any differences. From this work, the ratio of CLT peak concentration to WLT concentration ranged from 3.1-5.5 for As, 1.9-12.4 for Cu, and 2.4-714 for Cr. These ratios, however, are noticeably reduced when the CLT mean concentrations are used: 0.9-2.5 for As, 0.3-1.9 for Cu, and 0.5-60 for Cr (see Table 3.5). Figures 3.32-3.34 show that in the C fly ash and BS fly ash mixtures, the peak CLT concentrations were 2-8 and 1-15 times the highest TCLP or WLT leachate metal concentration, respectively. Clearly, the batch tests confirm the importance of pH in metal leaching and the CLTs show how much leachate metal concentrations can vary with time.

Table 3.6 provides estimations of leachate metal concentrations for a theoretical 100% leaching scenario, where all metal present in the soil-fly ash mixture is solubilized and released into the leachate. Though very unlikely to happen in the field, the leaching predictions provide a useful frame of reference. For example, the highest predicted As concentration for 100% leaching is 9.87 mg/kg, which is orders of magnitude greater than the highest concentrations reported from the leach tests. A comparison between Table 3.4 and Tables 3.6 indicate that even the highest leaching observed is resulting from only a small portion (<10%) of the total metal present in the mixture becoming dissolved in solution.

The effect of extraction time and solution pH are connected to the distribution of metals in different fractions, such as exchangeable, attached to Fe oxides, or contained in carbonate compounds. Ram et al. (2007) describe two phases or "compartments" where metals can accumulate within the materials: the magnetic (Cu) phase and the non-magnetic (Cr and As) phase, which primarily involves the fly ash particle surfaces with high dissolution capacity and is similar between both batch and column leach tests. For example, Cr leaching was shown by Zandi and Russell (2007) to be controlled by the amount of the metal present in the fly ash; therefore, estimations of aqueous Cr could be made from knowledge of concentrations of metals in the soils and fly ashes. This agrees with the near linear relationship between fly ash content and leachate concentration in the TCLP tests of this study. As stated before, the properties of the materials used in fly ash-soil mixtures can have a major effect on the processes that contribute to overall leaching behavior, such as precipitation, sorption, and dissolution. Wang et al. (2004) states that surface characteristics such as surface charge, specific surface area, and metal binding capacities govern the metal partitioning in fly ash. While some of these properties (e.g., effective surface area) have been extensively studied, others such as metal binding site densities and acidity constants have not been quantified. Continued research into examining these mechanisms and properties would be useful, especially in the development and verification of leaching models.

4 Practical Implications

Obviously two of the most important parameters to consider when selecting a protocol for assessing metal leaching from fly ash are pH and the L:S ratio. While sorption processes play an integral role in determining metal concentrations in the leachate, large fluctuations in pH can facilitate the dissolution of metal-containing minerals, especially under acidic conditions (Bin Shafique et al. 2007). Changes in pH over time affect the amount of metals released into solution, but also what precipitates and complexes are formed that affect the re-adsorption of dissolved metals and mobility of metals in the environment. In this study, the pH measurements in the WLTs and CLTs exhibited a larger pH range than in the TCLP that more clearly illustrates the effect of fly ash composition on leachate pH. A comparison of leaching protocols provided by this study highlights the importance of pH, as well as leaching time and the L:S ratio, for understanding the larger picture for a given fly ash mixture.

The higher L:S ratios seen in batch tests compared to CLTs can be viewed as representative of more dilute leaching, possibly related to potential groundwater contamination, while CLTs can simulate leaching behavior seen in the soil solution in areas immediately close to the fly ash-soil mixtures. Thus, different leaching tests can represent different scenarios, including the soil solution in the areas containing the fly ash-soil mixture or estimations of concentrations of metals that might migrate to groundwater supplies. For example, initial results from CLTs would likely overestimate risk of leaching if regulations compare leachate concentrations to federal drinking water standards (Jo et al. 2008).

While CLTs can provide more realistic leaching measurements given the more site-specific and flow-through conditions, WLTs, on the other hand, are viewed as a rapid method to gain reasonable estimation of metal leaching concentrations. Batch leach tests require less time to run and a simpler experimental setup, which is why they are typically included in regulations governing CCB disposal. These tests, however, can misrepresent actual field conditions by having pH values or L:S ratios not typically seen in the field. For example, the increased metal leaching found under TCLP conditions observed for some metals and fly ash mixtures in this study supports the statement that the TCLP leaching solution is too aggressive, while tests like the ASTM WLT provide more a reasonable simulation of natural leaching conditions (Baba and Kaya 2004). The WLT or CLT is preferred because their leaching solution is more similar to the natural water that would flow through an embankment compared to the acetic acid solution used in the TCLP to simulate landfill leachate conditions. Additionally, the hazardous waste criteria pertaining to heavy metal concentrations listed in the TCLP standard procedure are much less stringent compared to the Aquatic Toxicity limits or the EPA MCLs (mg/L vis-à-vis µg/L). For this reason, the listed concentrations do not accurately reflect the hazards to environmental or human health.

Furthermore, the flow-through nature of CLTs compared to the static, contained system in the TCLP and WLT provides different contact times, soil-fly ash interactions, and L:S ratios that can alter the reactions and equilibration processes which affect final pH and aqueous metal concentrations. Clearly, leaching in an actual highway embankment is more accurately characterized by the downward infiltration of rain or movement of surface runoff than the end-over-end tumbling action used in the batch tests. Ram et al. (2007) states that column tests are preferred to evaluate long-term leaching and risks to the environment/humans, but batch tests should also be incorporated into guidelines. CLTs can be more easily adjusted to fit certain site-specific conditions, including changes to the influent flow rate and the physical properties of the fly ash medium such as unit weight, moisture content, and porosity. This would allow for leaching results to be obtained that better reflect environmental conditions in a certain area, and more accurately assess potential risks and alternatives for CCB disposal.

Based on the results of this study and the work of others (Baba and Kaya 2004, Bin Shafique et al. 2007, Zandi and Russell 2007), a leaching test protocol was developed, which combined batch and column tests aimed at characterizing different aspects of leaching behavior (Figure 4.1). The proposed protocol includes preliminary work aimed at characterizing the materials and using knowledge of field conditions to select the test parameters. Preliminary batch leaching tests can serve as an integral part of the testing framework to provide initial fly ash mixture characterization and pinpoint reasonable parameters for future testing. In the first step of the proposed protocol, the application scenario of interest is defined, and the pertaining regulatory constraints assembled. In addition, the fly ashes and soils are characterized in terms of their pH, total elemental analysis, and geotechnical properties. Then batch WLTs are performed with the soil-fly ash mixtures of interest to determine the system parameters, such as pH, and their effect on metal leaching.

Batch tests are used initially because they are advantageous when a large number of fly ashes mixtures are being screened for use in actual construction. Next, candidate fly ash-soil mixtures that result in increased leaching based on the WLTs are selected and subjected to CLTs to evaluate the spatial and temporal evolution of key system parameters and metal concentrations. CLTs would provide a more detailed evaluation of long-term leaching potential for the selected mixtures. By comparing the WLT and CLT leachate metal concentrations to applicable state and federal water quality criteria, risks from heavy metal leaching could be gauged. The goal of the proposed protocol is provide a flexible testing framework that attempts to most closely simulate field leaching conditions while allowing evaluation of fly ash mixtures under varying detail, cost, and time constraints. When a simpler approach is needed (there is neither the time nor resources to run CLTs), the quicker WLTs could be used and additional factors such as the L:S adjusted to be more consistent with field conditions.

It is important that the protocols developed for the testing of CCBs be sufficiently flexible that a variety of leaching conditions can be investigated in one study, including area-specific factors. The testing of fly ash and other CCBs should incorporate standardized leaching tests that provide regulators and other interested parties with a mechanism for encouraging CCB reuse and the development of disposal guidelines. Continued research in characterizing the leaching of fly ash-soil mixtures is needed to better understand the leaching behavior of these materials and the different factors that affect it. Selecting a leaching protocol that provides both consistent and realistic predictions of metal leaching has ramifications in both the protection of natural ecosystems and the costs and time required for proper fly ash waste management and disposal.

5 Summary and Conclusions

Three different leaching tests (WLT, CLT, TCLP) were performed on fly ashes, soils, and fly ash-soil mixtures to evaluate the As, Cu, and Cr leaching behavior of these materials and provide a comparison between the leaching test methodologies. Leachate metal concentrations were compared to federal and state regulatory water limits to evaluate the potential risks from heavy metal leaching. Consistent with similar leaching studies, key factors considered when comparing the relative leaching with the different tests, and the leaching behavior of the three metals, were the solution pH and the following testing parameters: leaching solution composition, L:S ratio, and extraction time.

The large difference in leachate pH values between the BS and C fly ashes led to noticeable effects in the leachate metal concentrations. C fly ash-soil mixtures showed higher levels of leaching for all metals in the WLT than the corresponding BS fly ash mixtures, consistent with the more alkaline conditions created by this fly ash compared to the BS fly ash. For example, the repulsion between anionic metal species and the negatively-charged soil surfaces at pH values > 10 probably contributed to the increased leaching seen with fly ash C. In addition, complexation with soluble organic matter is also a contributing factor to leaching, particularly for Cu, which is usually precipitated out at high pHs. Nevertheless, in 75% of fly ash-soil mixtures tested, none of the regulatory limits were exceeded by WLT leachate metal concentrations, as shown in Table 3.1.

TCLP leaching results between fly ashes were mixed, with more As and Cu leached from the S-BS mixtures compared to the S-C mixtures, and more Cu leached from the C-C mixtures than the C-BS mixtures, but with similar As levels. Elevated Cr concentrations were measured for the C fly ash mixtures compared to the BS fly ash mixtures. TCLP metal concentrations were observed to be higher than those from WLTs in the majority (about 60%) of mixtures. Leaching of Cr from the C fly ash mixtures was one of the exceptions to this trend, where WLT Cr concentrations were approximately two to three times the TCLP concentrations. Leaching of the 100% fly ashes was also magnified under TCLP conditions compared to those found in the WLT, with the exception of Cu for the C fly ash, consistent with increased dissolution of minerals and solubilization of metals at low pHs.

The results of the CLT showed that the fly ash-soil mixtures typically exhibited one of two different leaching behaviors as described by Edil et al. (1992): first flush or lagged response. Of the fly ash–soil mixtures exhibiting the first flush behavior, the general observed trend was an exponential decay curve, as commonly seen in other CLT studies (Bin Shafique et al. 2007, Ram et al. 2007, Morar et al. 2010). The one exception to that trend was the arsenic concentrations for the C fly ash mixtures, which followed the initial decrease in concentration with a recovery in concentration. As a result of the typical first flush pattern, peak concentrations were generally measured at the start of the test. Consequently, in 70% of the CLTs, at least one metal was measured at the beginning of the test in concentrations above the appropriate regulatory limit. Effluent metal concentrations, however, in 80% of the columns tests decreased with time and stabilized around detection limits generally after 10-20 PV. The C fly ash columns seemed to show a more prolonged release of metal, with higher concentrations of metals measured for a longer duration of the test.

C fly ash mixtures also exhibited relatively constant pH values around 11.5 which supports the smoother leaching curves obtained from the C fly ash mixtures compared to large spikes in metal concentration seen in the BS fly ash mixtures, which also experienced pH fluctuations. CLT pH values were slightly lower than those of the WLTs, possibly due to the difference of contact time between solid media and leaching solution (Bin Shafique et al. 2007). Increased contact time in the WLT between leaching solution and solid phase mixture could allow for equilibrium to be more closely approached, or reached.

Overall, Cu levels for the S-C and C-C mixtures and As levels for the S-C mixture were elevated at intermediate pH (pH 7-9), and reduced at lower (pH ≈ 5) and higher (pH ≈ 11) pH values. However, As and Cr levels with the S-BS mixture showed an opposite trend, with reduced concentrations in the leachate at pH 7 and elevated levels at pH ≈5 and pH ≈9. In contrast, Cr levels with the C-C mixture exhibited a relatively flat pattern, with a gradual increase in Cr leachate concentration as the pH increased from ≈ 5 to 11. The differences in leaching behavior for Cr as a function of pH for mixtures S-BS and C-C were largely a result of different Cr speciation (Cr(VI) in C fly ash and Cr(III) in BS fly ash) as well as the effect of higher clay content of the C soil that can lead to higher leaching through repulsion between metal ion and particle surface.

Clearly, the “leachability” of these elements is affected by many factors, including their solubility and adsorption capacity, the composition of coal ash, and the chemistry of the extracting water, including pH and ionic strength (Jo et al. 2008). More data from additional testing would be useful in confirming trends and predicting leaching behavior based on pH measurements. Nevertheless, these results illustrate the significant effect that leachate pH can have on the leaching of heavy metals from fly ash-soil mixtures. A comparison of test results across a pH range from approximately 5-11 indicates that while leaching behavior varies by metal, under smaller pH ranges metal concentrations from some mixtures were found to be inversely proportional to the leachate pH (e.g., Cr leached from S-BS mixtures) which has been concluded in other soil-fly ash leaching studies (Bin Shafique et al. 2007, Ram et al. 2007, Palumbo et al. 2007).

The L:S ratio is second most important parameter behind pH in determining leaching behavior of heavy metals from amended soil media (Zandi and Russell, 2007). As discussed above, the majority of the CLT leaching curves exhibited first flush behavior, with leachate metal concentrations started high and sharply decreasing after several PV. Peak (typically initial) concentrations from the CLTs were typically higher than those of the TCLP and WLT batch tests, which is expected given the low L:S ratio present at start of CLTs. These CLT results are consistent with previous studies (Bin Shafique et al. 2007, Morar et al. 2010) and indicate that although leachate concentrations can initially exceed regulatory limits, this is observed for a short period of the leaching test and concentrations quickly decrease. Thus, while leachate concentrations from an embankment constructed with fly ash-amended soil might initially be measured at or above the regulatory limits, these elevated metal concentrations might only exist in the environment for a short period of time (i.e., hours to days), thereby reducing the overall risk of endangerment to aquatic and human health.

Increased fly ash content generally resulted in more metal leaching, although the rate of increase was not always uniform, nor was this trend observed in all sample mixtures and tests. For example, for Cu in S-BS TCLP mixtures, the difference in leachate concentrations between 10 and 20% fly ash was less compared to the initial addition of fly ash to the 100% soils (i.e., 0 to 10% fly ash), and the increase in fly ash content from 20% to 100%. This non-linear relationship makes simple estimations based solely on fly ash contents difficult and likely to either over- or underestimate actual metal concentrations in the leachate.

The test data also suggest that soil type has an importance influence on leaching. For example, TCLP Cr and Cu metal concentrations from soil S mixtures were 3-10 and 5-15 times higher, respectively, than the same mixtures with soil C. Similarly, WLT concentrations of Cu and Cr sometimes measured 10-30 μg/L higher in the soil S mixtures compared those with soil C. Soil C mixtures in the CLTs showed similar results with lower peak levels of aqueous metals measured compared to soil S mixtures, except for Cu in C-C-20 column. This is partly the result of different soil properties controlling adsorption onto particles surfaces and dissolution of minerals. The higher content of all metals in soil C, combined with lower observed leaching suggests that adsorption onto the finer particles in soil C was likely occurring and having a strong influence on leachate metal concentrations. Soils can be a sink through metal adsorption or a source through dissolution depending on pH conditions and the composition (metal content) of the other materials in the mixture, further complicating the leaching evaluation.

In summary, the key conclusions based on these results are as follows:

1) There exists a nonlinear relationship between leachate pH and fly ash content. As pH is one of the most important factors in determining metal leaching behavior, this relationship helps to explain differences in leaching between soil materials (C versus BS fly ash mixtures) and leaching tests (TCLP versus WLT). Processes that determine the final leachate pH are complex and vary both temporally and spatially within a soil column. Simple pH and oxidation-reduction potential measurements can serve as tools for predicting leachate metal species and their mobility and toxicity in the environment.

2) Although increased fly ash content may produce higher leaching of metals, the results of this study suggest that there is often a nonlinear relationship between leachate metal concentrations and fly ash content. For this reason, predictions of leaching based on simple dilution factors correcting for fly ash content are often not accurate and can under-predict actual metal concentrations (Bin Shafique et al. 2007). This potential for error highlights the need for reliable leaching protocols that can provide reasonable information necessary to determine risks associated with heavy metal leaching.

3) The chemical composition of the soil and the fly ash were key factors in determining leaching behavior by dictating the amount of available metal ions, the dominant species, and the location of metal ions on the particles (i.e., on the surface or embedded in mineral matrix). The distribution of metal species depends on the type of coal burned and the conditions of

combustion. When comparing the results of leaching tests, it is important to factor in higher initial metal contents in materials that exhibit increased leaching. Materials containing high original metal contents can become sources for dissolved metals, while materials with high adsorption capacities can provide sinks for dissolved metals and reduced aqueous metal concentrations.

4) There were instances in both the batch and column tests where leachate metal concentrations exceeded the corresponding regulatory limits for all three metals. However, caution should be exercised when applying leach test results to the development of CCB regulations and disposal guidelines. Batch tests do not always represent realistic field conditions while the typically high peaks seen at the beginning of CLTs are not representative of the long-term leaching risks.

5) Conducting CLTs with numerous samples of different soils and fly ashes would be impractical due to the long testing time needed and high costs of laboratory work. However, they provide useful insight into prolonged leaching as it would more likely occur in the field. Therefore, these tests should be included as part of a thorough investigation into leaching potential of any fly ash mixture.

6) TCLP leaching from the 100% soil and 100% fly ash samples provided upper and lower boundary limits for the leaching of fly ash-soil mixtures, as observed metal concentrations typically fell between these two. This trend was not as clearly observed in the WLTs, where levels of copper in

the 100% BS and C fly ashes and As in the 100% C fly ash were lower than in the soil-fly ash mixtures. A possible explanation of this is that precipitation and dissolution reactions can control metal concentrations when soil is not present (i.e., 100% fly ash samples). Soils provide an abundance of organic and inorganic ligands for complexation and precipitation and can increase soluble metal fractions.

7) Batch leach tests have an important role in the characterization of leaching behavior due to their short test duration, simple procedure, and relatively low costs. Efforts, however, should be taken to adjust test parameters to more reasonable values that better simulate the field. These adjustments could include reducing the L:S ratio to more accurately reflect average porosity and hydraulic conductivities in the constructed embankment or highway or changing the leaching solution used. Depending on the composition of the soils used, pH values could be adjusted to simulate a large carbonate content or the ionic strength increased to model groundwaters with a high salt content.

Tables and Figures

Table 2.1: Total elemental analysis results conducted on soils and fly ashes by University of Wisconsin Soil Testing and Plant Analysis Laboratories. All concentrations are reported as mg/kg dry weight except when stated otherwise.

Material	P (%)	K (%)	Ca (%)	Mg (%)	S (%)	Zn	B	Mn	Fe	Cu	Al	Na
BS FA	0.04	0.37	0.22	0.10	0.08	53.9	21.3	33.9	6400	59.6	21300	539
C FA	0.16	0.25	14.4	2.41	0.81	92.2	600	91.6	24400	189	91800	11200
Soil C	0.04	0.27	0.06	0.19	0.01	58.2	3.25	220	42200	27.2	49400	75
Soil S	0.02	0.05	0.03	0.04	0.01	15.0	2.86	38.2	10800	1.28	28800	33

Material	Cd	Co	Cr	Mo	Ni	Pb	Li	As	V	Ag	Sb	Tl
BS FA	0.42	20.9	49.5	11.7	21.3	23.0	35.7	24.2	78.8	0.001	0.05	<0.001
C FA	1.14	19.5	64.6	4.54	2.31	15.8	38.7	15.0	187	<0.001	0.06	<0.001
Soil C	<0.4	13.1	65.9	0.79	13.1	10.1	19.3	6.30	116	<0.001	0.02	<0.001
Soil S	<0.4	4.62	15.5	<0.4	<0.3	<2	4.02	<3	16.5	<0.001	0.02	<0.001

Table 2.2: Select chemical and physical properties of soils and fly ashes

Material	pH	Loss on Ignition	Classification	Atterberg Limits	Specific Gravity
Soil S	7.99	8.6%	SP-SC (poorly graded sand with silt)[2]	N/A	2.6
Soil C	6.07	7.1%	SW-SC (well graded sand with clay & gravel)[2]	37/21[3]	2.8
BS Fly Ash	4.98	5.5%	Off-spec[1]	N/A	2.3
C Fly Ash	12.11	0.4%	Class C[1]	N/A	2.7

Notes: [1]ASTM C816 classification; [2]USCS classification; [3]liquid limit/plastic limit

Table 2.3: Soil-fly ash mixture labels used in this study

Mixture Label	Fly Ash	Soil	% Fly Ash by Weight
S-BS-10	Brandon Shores	Soil S	10
S-BS-20	Brandon Shores	Soil S	20
S-C-10	Columbia	Soil S	10
S-C-20	Columbia	Soil S	20
C-BS-10	Brandon Shores	Soil C	10
C-BS-20	Brandon Shores	Soil C	20
C-C-10	Columbia	Soil C	10
C-C-20	Columbia	Soil C	20
BS FA	Brandon Shores	None	100
C FA	Columbia	None	100
Soil S	None	Soil S	0
Soil C	None	Soil C	0

Table 2.4: Properties of soil-fly ash mixtures obtained from preliminary compaction testing. This information was used in the setup of column leach tests to select compaction specifications of specimens.

Mixture	Optimum Moisture Content (%)	Dry Unit Weight (kN/m^3)	Pore Volume (mL)
S-BS-10	9	19.33	577
S-BS-20	11	18.65	622
S-C-10	11	18.94	643
S-C-20	13	18.79	665
Soil S	11	13.42	1171
C-BS-20	16	16.27	953
C-C-20	11	18.65	622

Table 3.1: pH measurements and concentrations of leachate Cu, Cr, and As from Water Leach Tests on soils, fly ashes, and soil-fly ash mixtures. EPA MCLs and Maryland freshwater Aquatic Toxicity limits are provided for comparison. Concentrations are averages of 4 replicates for fly ash-soil mixtures, 3 replicates for fly ash, and 2 replicates for soil.

Soil	**Fly Ash**	**Fly Ash Content (%)**	**Leachate pH**	**Metal Concentration (µg/L)**		
				Cu	**Cr**	**As**
Soil S	Columbia	10	11.6	7.6	57	0.90
		20	11.6	4.4	66	0.64
	Brandon Shores	10	6.7	1.7	<0.35	0.29
		20	6.0	3.9	<0.35	0.72
Soil C	Columbia	10	11.3	12	69	1.2
		20	11.5	14	100	0.63
	Brandon Shores	10	6.2	1.9	1.4	0.40
		20	6.6	3.9	1.2	0.38
Soil S	None	0	5.8	1.4	0.90	<0.22
Soil C	None	0	8.7	2.6	0.36	<0.22
None	Columbia	100	11.9	2.0	45	0.35
	Brandon Shores	100	8.8	2.6	2.8	23
U.S. EPA Drinking Water MCL				1300	100	10
Maryland State Aquatic Toxicity Acute Limits				13	570/16*	340
Maryland State Aquatic Toxicity Chronic Limits				9	74/11*	150

*regulation limits for chromium given as [Cr III]/[Cr VI]

Table 3.2: pH measurements and concentrations of leachate Cu, Cr, and As from Toxicity Characteristic Leaching Procedure Tests on soils, fly ashes, and soil-fly ash mixtures. EPA MCLs and Maryland freshwater Aquatic Toxicity limits are provided for comparison. Concentrations are averages of 4 replicates for fly ash-soil mixtures, 3 replicates for fly ash, and 2 replicates for soil.

Soil	**Fly Ash**	**Fly Ash Content (%)**	**Leachate pH**	**Metal Concentration (µg/L)**		
				Cu	**Cr**	**As**
Sandy	Columbia	10	5.2	11	20	<.49
		20	5.5	5.3	30	1.3
	Brandon Shores	10	4.9	29	8.0	1.0
		20	4.8	26	17	3.0
Clayey	Columbia	10	5.2	7.6	25	<.49
		20	5.5	7.3	54	<.49
	Brandon Shores	10	4.8	1.8	2.5	1.1
		20	4.8	4.7	7.3	0.49
Sandy	None	0	4.8	<1.4	<1.8	<.49
Clayey	None	0	4.8	<1.4	<1.8	1.7
None	Columbia	100	6.3	<1.4	140	30
	Brandon Shores	100	4.9	93	45	85
U.S. EPA Drinking Water MCL				1300	100	10
Maryland State Aquatic Toxicity Acute Limits				13	570/16*	340
Maryland State Aquatic Toxicity Chronic Limits				9	74/11*	150

*regulation limits for chromium given as [Cr III]/[Cr VI]

Table 3.3: pH measurements and Cu, Cr, and As leachate concentrations for buffered water leach tests. The water leach test procedure was performed twice for each mixture using each of the two buffers used (BES and CAPSO). Concentrations are reported as µg/L. Concentrations below detection limit for Cr (0.35 µg/L) and As (0.22 µg/L) are reported as ½ of the detection limit.

Mixture	Buffer	pH	[Cu]	[Cr]	[As]
S-BS-10 1	BES	6.99	42.9	0.175	0.634
S-BS-10 2	BES	6.99	41.8	0.175	0.253
S-BS-10 3	CAPSO	9.01	1.23	1.74	4.79
S-BS-10 4	CAPSO	9.00	3.19	6.23	4.31
S-C-10 1	BES	7.23	66.5	22.3	2.66
S-C-10 2	BES	7.20	63.4	10.8	2.31
S-C-10 3	CAPSO	9.29	50.7	54.3	2.89
S-C-10 4	CAPSO	9.28	49.6	52.3	2.81
S-BS-20 1	BES	6.95	47.0	0.175	1.77
S-BS-20 2	BES	6.97	46.1	0.175	1.69
S-BS-20 3	CAPSO	9.09	2.50	3.43	8.94
S-BS-20 4	CAPSO	9.11	5.46	3.86	14.6
S-C-20 1	BES	7.34	78.9	29.0	8.84
S-C-20 2	BES	7.32	79.2	29.2	10.0
S-C-20 3	CAPSO	9.46	87.0	19.8	3.57
S-C-20 4	CAPSO	9.44	81.2	21.3	4.79
C-C-10 1	BES	7.24	55.2	33.8	0.438
C-C-10 2	BES	7.25	53.2	31.4	0.308
C-C-10 3	CAPSO	9.35	53.5	73.8	0.467
C-C-10 4	CAPSO	9.31	55.3	76.7	0.333
C-C-20 1	BES	7.44	28.0	54.0	0.789
C-C-20 2	BES	7.42	25.2	50.3	1.19
C-C-20 3	CAPSO	9.45	64.4	112	0.498
C-C-20 4	CAPSO	9.49	72.1	117	0.762
C-BS-10 1	BES	7.06	31.6	1.67	0.110
C-BS-10 2	BES	7.05	12.3	1.31	0.110
C-BS-10 3	CAPSO	8.77	2.00	4.68	0.359
C-BS-10 4	CAPSO	8.77	2.74	4.50	0.518
C-BS-20 1	BES	7.04	27.4	1.71	0.110
C-BS-20 2	BES	7.03	24.4	1.57	0.110
C-BS-20 3	CAPSO	8.81	2.61	6.05	0.756
C-BS-20 4	CAPSO	8.79	2.64	7.35	1.07

Table 3.4: Comparison of leaching results from all three leaching tests conducted. Column leach test peak concentration is the highest measured concentration throughout the testing period. Column leach test MC concentrations are calculated based on a liquid-to-solid ratio of 5 and represent a volume-weighted average concentration. Concentrations are all reported as µg/L. N/A listed for the column leach tests indicate that that specific mixture was not tested using the CLT methodology.

	TCLP			**WLT**			**CLT - Peak Conc.**			**CLT - L:S Ratio MC**		
Mixture	Cu	As	Cr	Cu	As	Cr	Cu	As	Cr	Cu	As	Cr
Soil S	<1.4	<.49	<1.8	1.4	<.22	0.90	12	0.62	160	1.7	0.28	9.9
S-BS-10	29	1.0	8.0	1.7	0.29	<.35	21	0.89	67	1.6	0.26	8.4
S-BS-20	26	3.0	17	3.9	0.72	<.35	12	3.1	250	1.3	0.97	21
S-C-10	11	<.49	20	7.6	0.9	57	83	3.8	290	7.5	1.9	44
S-C-20	5.3	1.3	30	4.4	0.64	66	35	3.5	270	5.5	1.6	36
Soils C	<1.4	1.7	<1.8	2.6	<.22	0.36	N/A	N/A	N/A	N/A	N/A	N/A
C-BS-10	1.8	1.1	2.5	1.9	0.4	1.4	N/A	N/A	N/A	N/A	N/A	N/A
C-BS-20	4.7	0.49	7.3	3.9	0.38	1.2	7.6	1.7	20	1.5	0.45	1.1
C-C-10	7.6	<.49	25	12	1.2	69	N/A	N/A	N/A	N/A	N/A	N/A
C-C-20	7.6	<.49	54	14	0.63	100	110	2.0	240	26	1.4	88
C FA	<1.4	30	140	2	0.35	45	N/A	N/A	N/A	N/A	N/A	N/A
BS FA	93	85	45	2.6	23	2.8	N/A	N/A	N/A	N/A	N/A	N/A

Table 3.5: Estimated scaling factors based on ratio of column leach test metal concentrations to water leach test metal concentrations. Part (a) uses peak column leach test concentrations while part (b) uses the volume-weighted average concentration up to a liquid-to-solid ratio of 5:1. An asterisk indicates that the scaling factor for Cr is based on a water leach test concentration of 0.35 µg/L since measured concentrations for these mixtures were below this detection limit.

(a) Peak CLT

Mixture	**Cr**	**Cu**	**As**
S-BS-10*	191	12.4	3.1
S-BS-20*	714	3.1	4.3
S-C-10	5.1	10.9	4.2
S-C-20	4.1	8.0	5.5
C-BS-20	16.7	1.9	4.5
C-C-20	2.4	7.9	3.2

(b) Mean CLT

Mixture	**Cr**	**Cu**	**As**
S-BS-10*	24.0	0.9	0.9
S-BS-20*	60.0	0.3	1.3
S-C-10	0.8	1.0	2.1
S-C-20	0.5	1.3	2.5
C-BS-20	0.9	0.4	1.2
C-C-20	0.9	1.9	2.2

Table 3.6: Leachate metal concentrations representing a 100% leaching scenario based on a mass-weighted average of original material metal content. Concentrations are reported in mg/kg dry weight.

Mixture	Maximum [Cu]	Maximum [Cr]	Maximum [As]
S-BS-10	7.12	18.9	5.12
S-BS-20	13.0	22.3	7.23
S-C-10	20.0	20.4	4.20
S-C-20	38.7	25.3	5.40
C-BS-10	30.4	64.3	8.09
C-BS-20	33.7	62.7	9.87
C-C-10	43.3	65.8	7.17
C-C-20	59.4	65.7	8.04

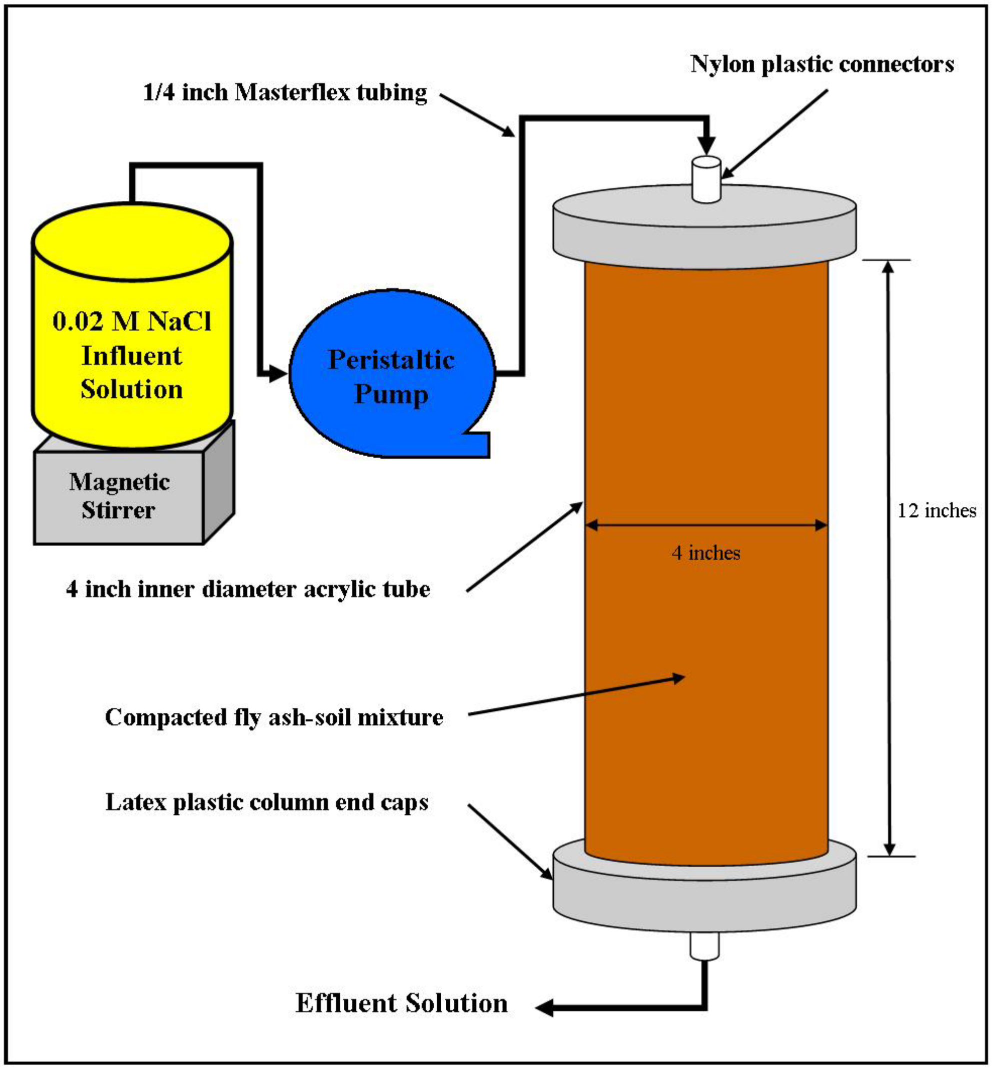


Figure 2.1: Schematic of experimental setup for column leach test.

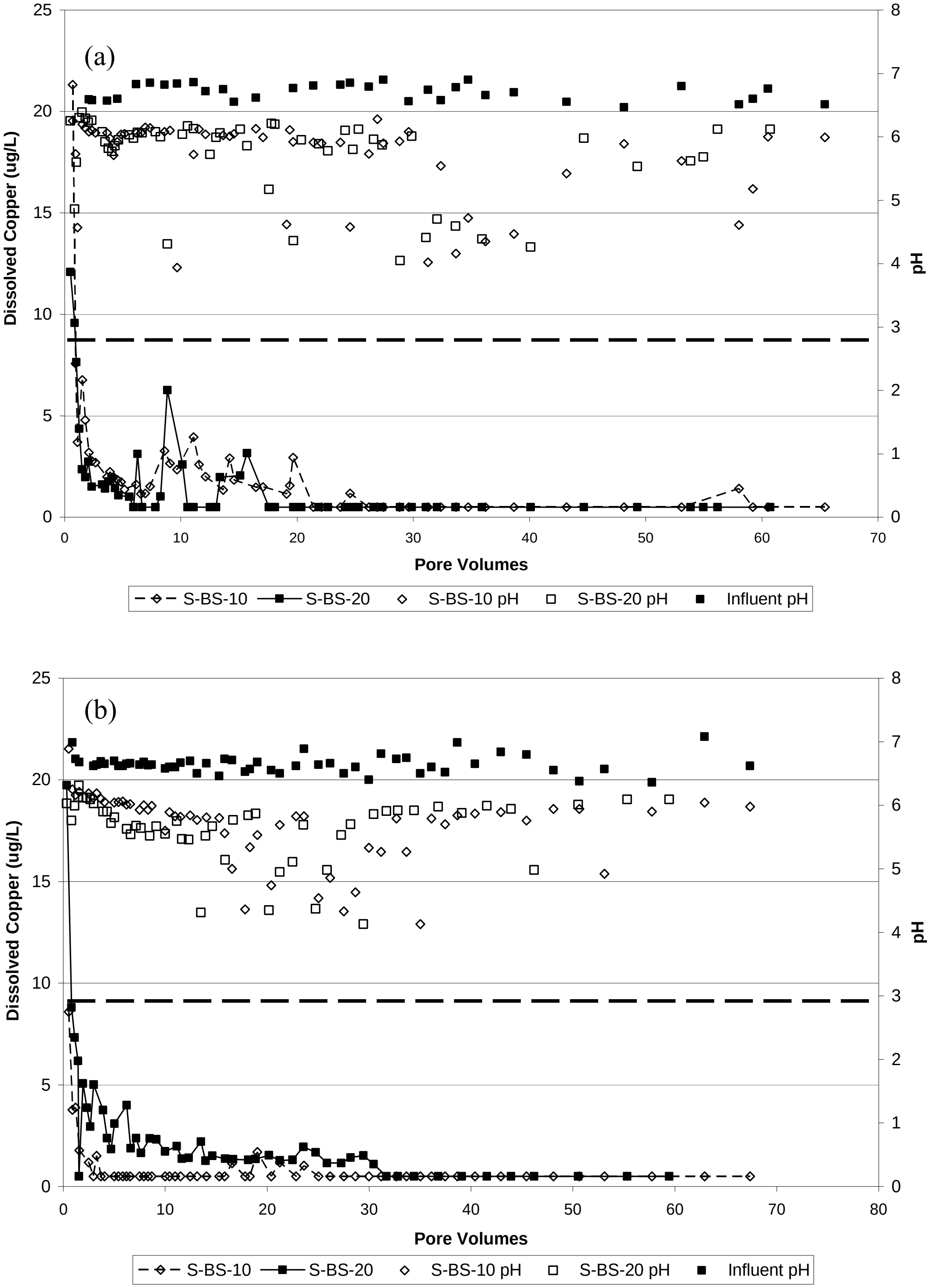


Figure 3.1: Copper leachate concentrations from: (a) the 1st set of column leach test S-BS mixtures, and (b) the 2nd set of column leach test S-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 1.0 µg/L were reported as ½ of the detection limit. Dashed lines represent Aquatic Toxicity limit of 9 µg/L.

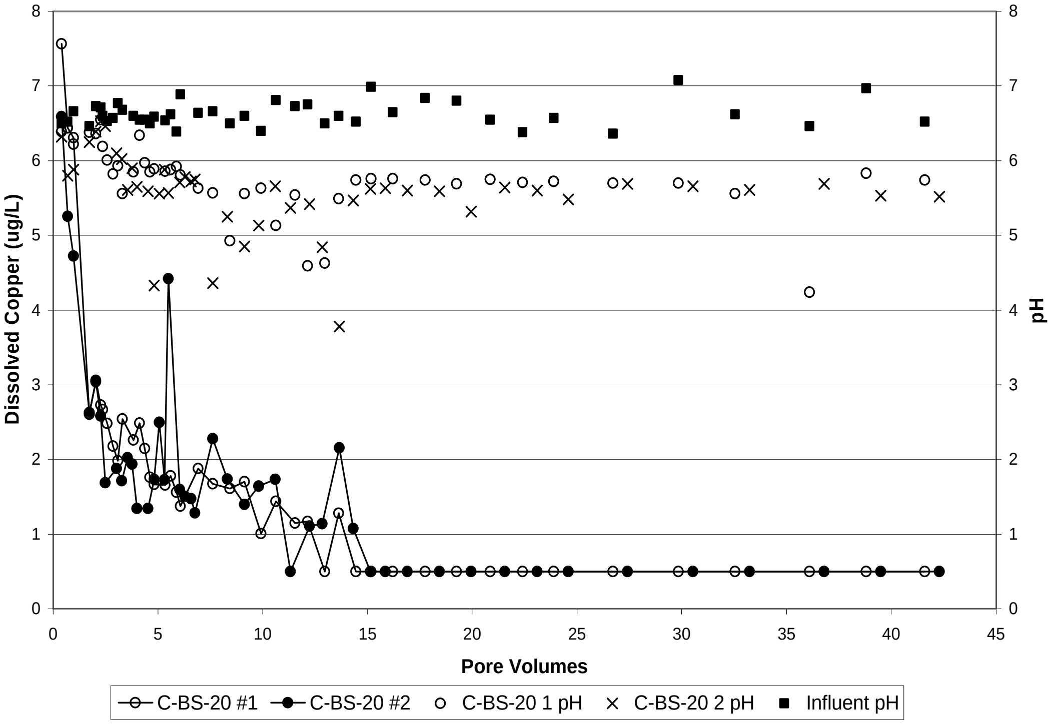


Figure 3.2: Copper leachate concentrations from column leach test C-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 1.0 µg/L were reported as ½ of the detection limit.

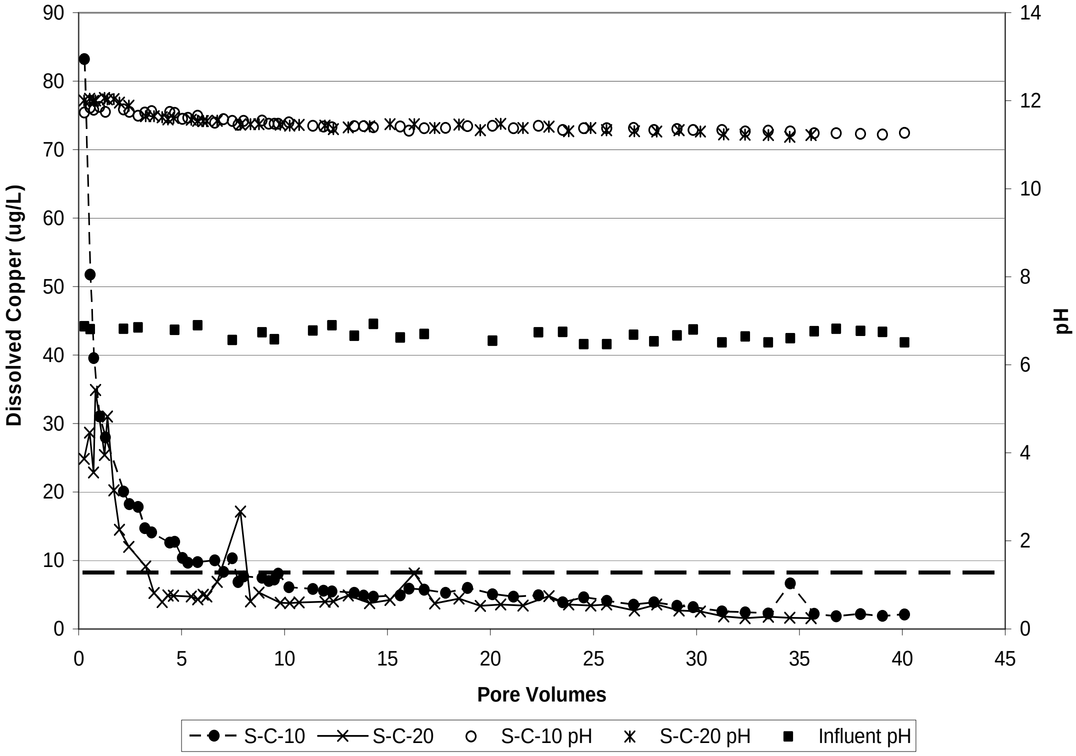


Figure 3.3: Copper leachate concentrations from the column leach test S-C mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 1.0 µg/L were reported as ½ of the detection limit. Dashed line represents Aquatic Toxicity limit of 9 µg/L.

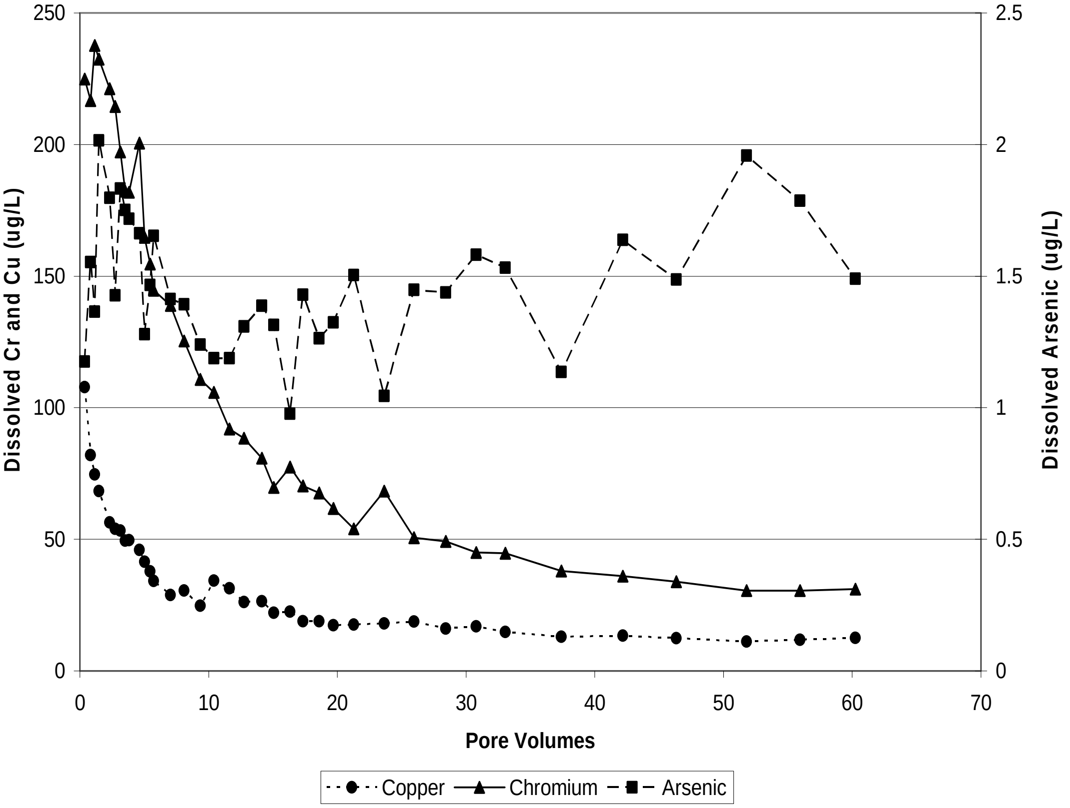


Figure 3.4: Copper, chromium, and arsenic leachate concentrations from column leach test C-C-20 mixture. Each symbol represents the average of two sample replicate metal measurements. The regulatory limits were 100 μg/L for Cr, 9 μg/L for Cu, and 10 μg/L for As.

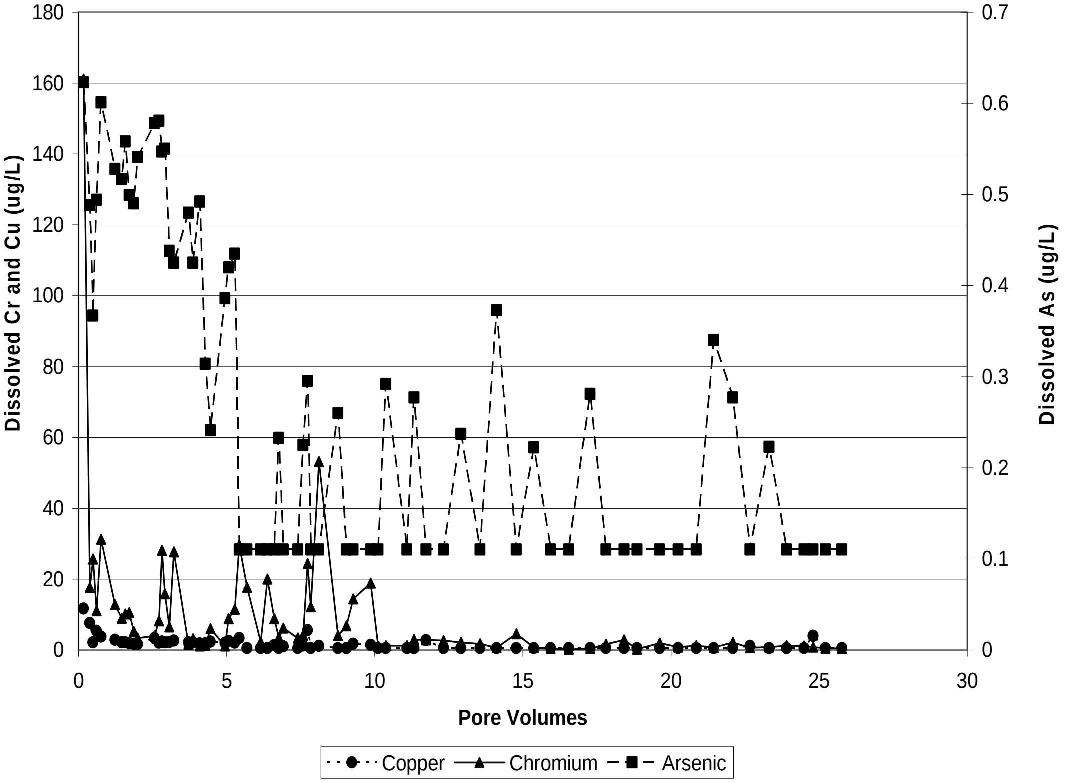


Figure 3.5: Copper, chromium, and arsenic leachate concentrations from column leach test 100% soil S mixture. Each symbol represents the average of two sample replicate metal measurements. The regulatory limits were 100 μg/L for Cr, 9 μg/L for Cu, and 10 μg/L for As.

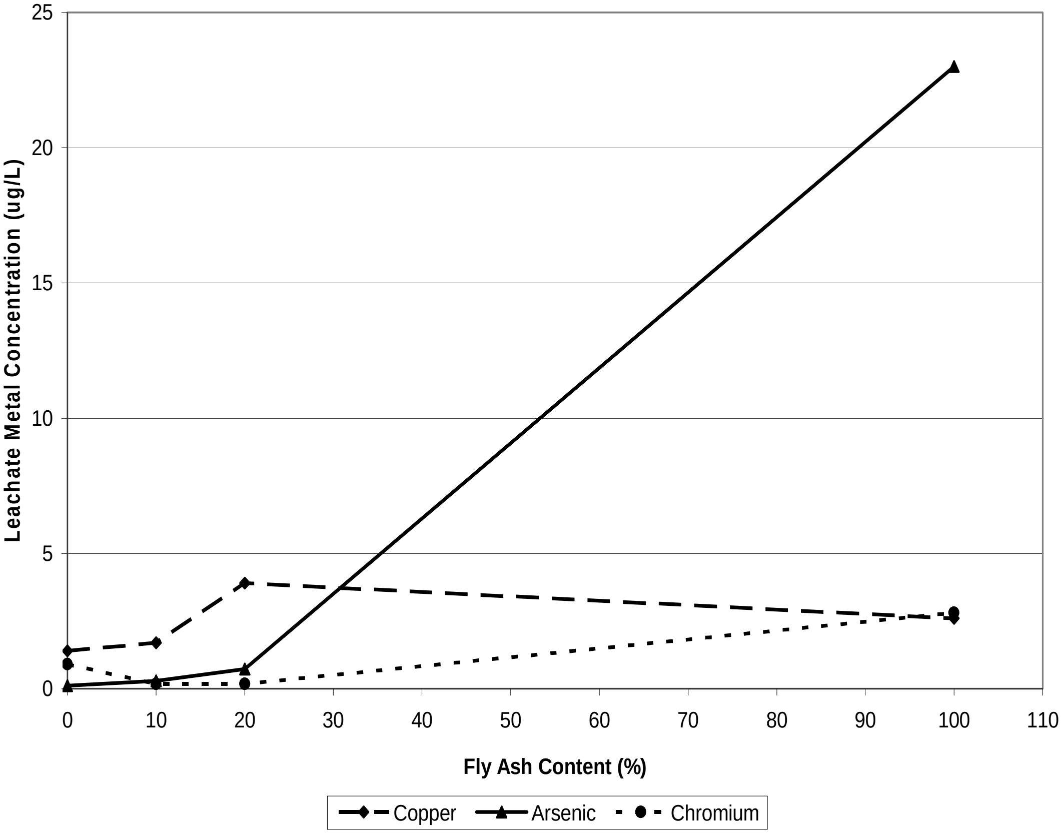


Figure 3.6: Effect of fly ash content on leachate metal concentrations for water leach test S-BS mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for S-BS-10 mixture are 7.12, 18.9, and 5.12 µg/L and for the S-BS-20 mixture are 13.0, 22.3, and 7.23 µg/L for Cu, Cr, and As, respectively.

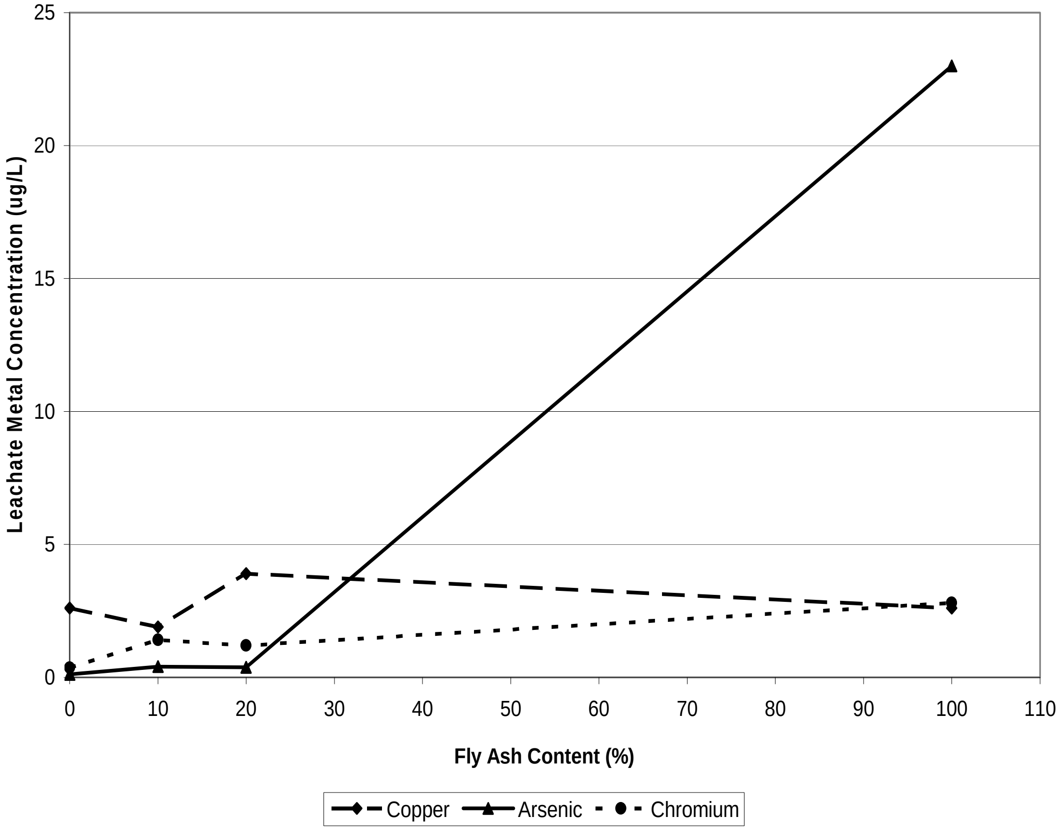


Figure 3.7: Effect of fly ash content on leachate metal concentrations for water leach test C-BS mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for C-BS-10 mixture are 30.4, 64.3, and 8.09 µg/L and for the C-BS-20 mixture are 33.7, 62.7, and 9.87 µg/L for Cu, Cr, and As, respectively.

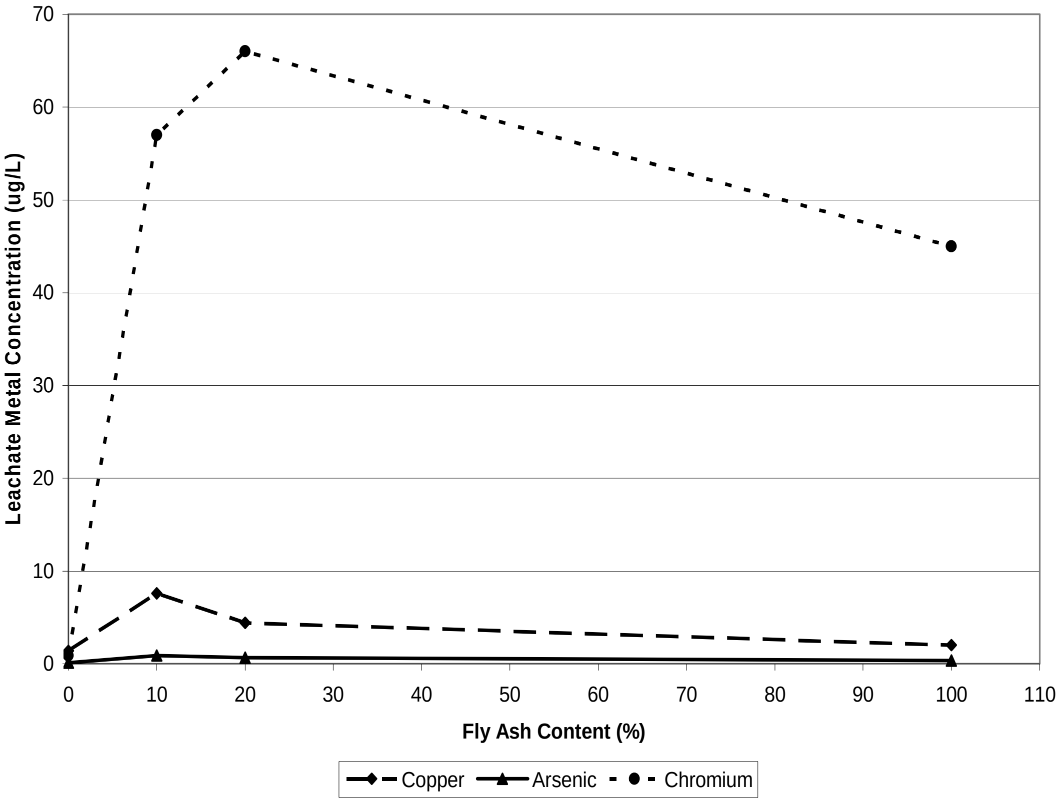


Figure 3.8: Effect of fly ash content on leachate metal concentrations for water leach test S-C mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for S-C-10 mixture are 20.0, 20.4, and 4.20 µg/L and for the S-C-20 mixture are 38.7, 25.3, and 5.40 µg/L for Cu, Cr, and As, respectively.

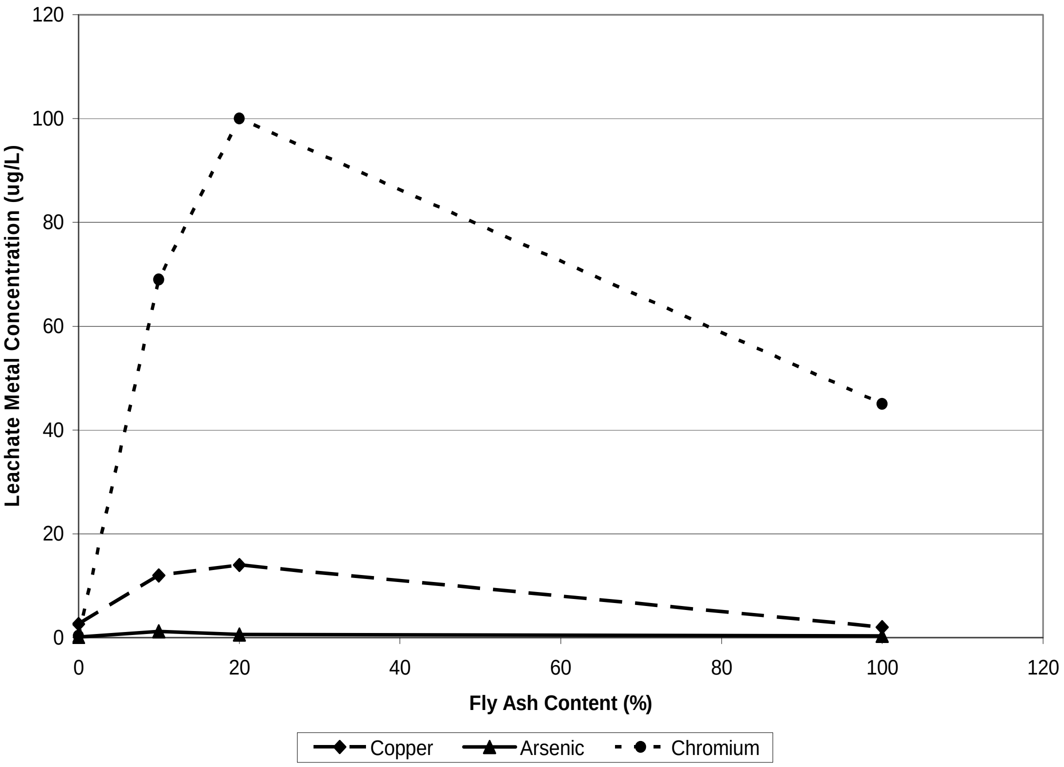


Figure 3.9: Effect of fly ash content on leachate metal concentrations for water leach test C-C mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for C-C-10 mixture are 43.3, 65.8, and 7.17 µg/L and for the C-C-20 mixture are 59.4, 65.7, and 8.04 µg/L for Cu, Cr, and As, respectively.

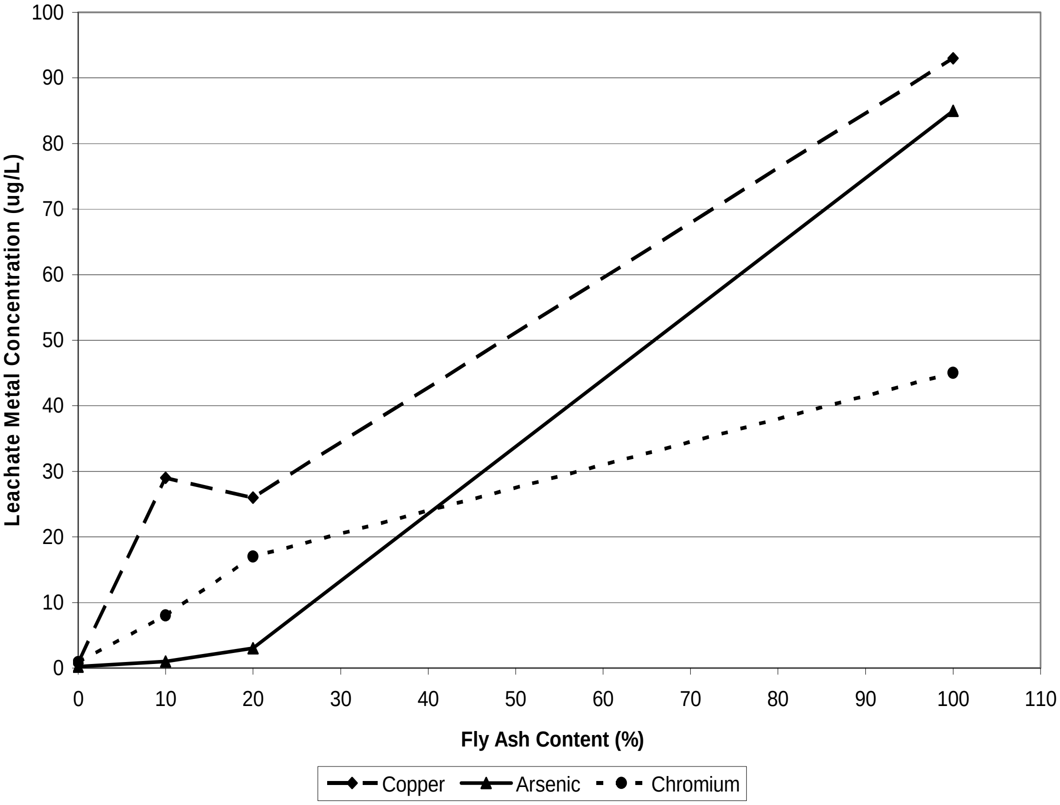


Figure 3.10: Effect of fly ash content on leachate metal concentrations for Toxicity Characteristic Leaching Procedure S-BS mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for S-BS-10 mixture are 7.12, 18.9, and 5.12 μg/L and for the S-BS-20 mixture are 13.0, 22.3, and 7.23 μg/L for Cu, Cr, and As, respectively.

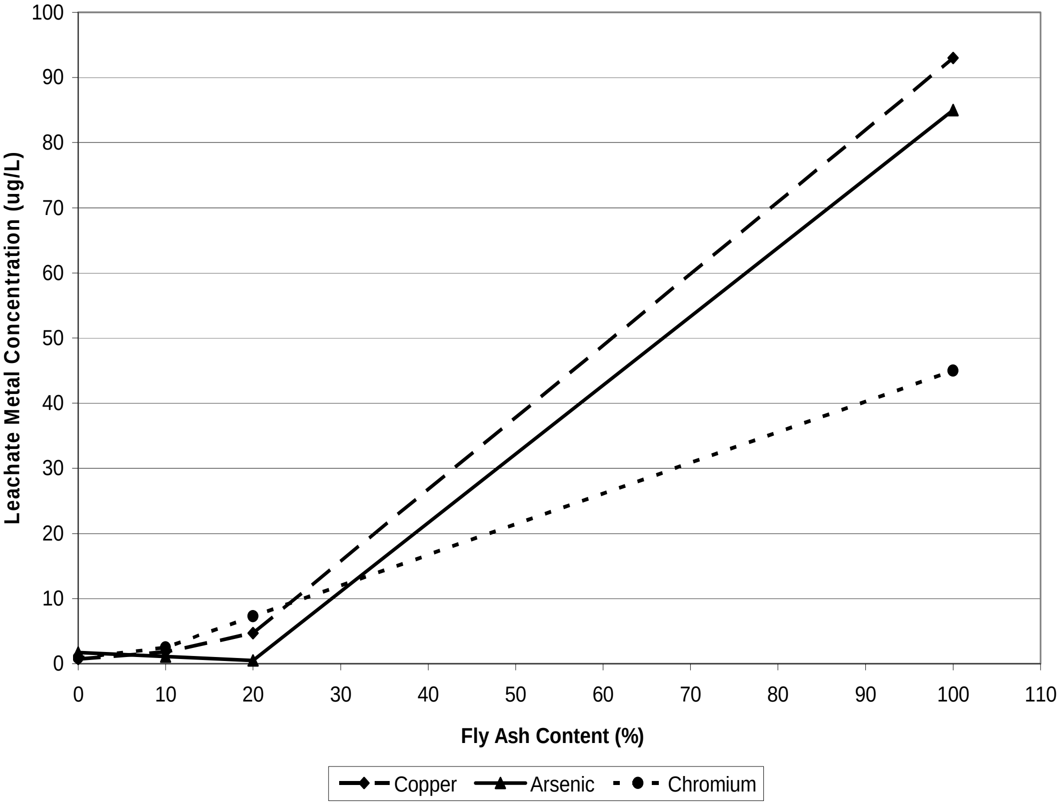


Figure 3.11: Effect of fly ash content on leachate metal concentrations for Toxicity Characteristic Leaching Procedure C-BS mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for C-BS-10 mixture are 30.4, 64.3, and 8.09 μg/L and for the C-BS-20 mixture are 33.7, 62.7, and 9.87 μg/L for Cu, Cr, and As, respectively.

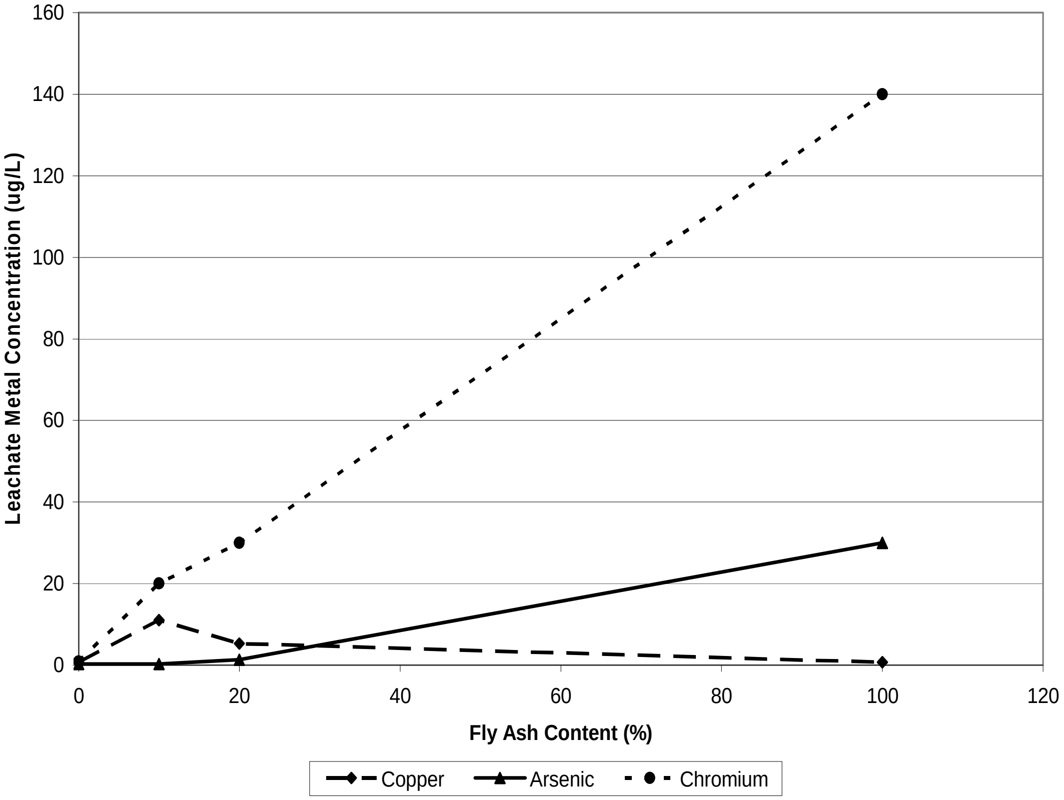


Figure 3.12: Effect of fly ash content on leachate metal concentrations for Toxicity Characteristic Leaching Procedure S-C mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for S-C-10 mixture are 20.0, 20.4, and 4.20 μg/L and for the S-C-20 mixture are 38.7, 25.3, and 5.40 μg/L for Cu, Cr, and As, respectively.

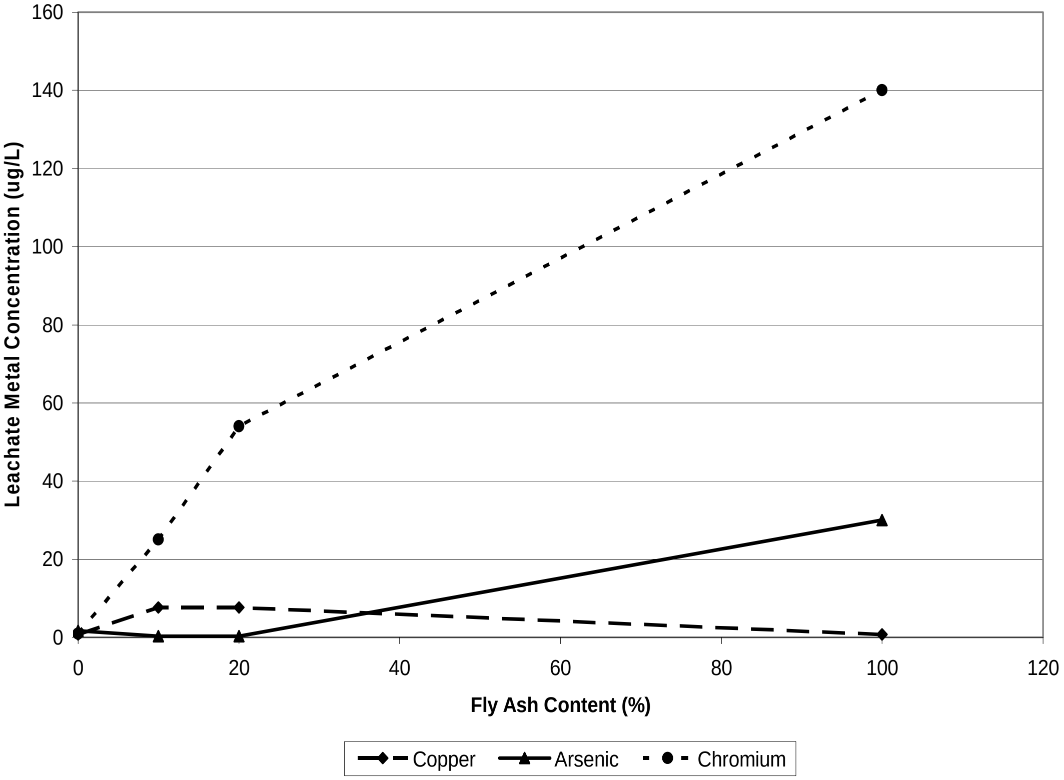


Figure 3.13: Effect of fly ash content on leachate metal concentrations for Toxicity Characteristic Leaching Procedure C-C mixtures. Total estimated metal concentrations from 100% leaching scenario based on original material metal contents for C-C-10 mixture are 43.3, 65.8, and 7.17 µg/L and for the C-C-20 mixture are 59.4, 65.7, and 8.04 µg/L for Cu, Cr, and As, respectively.

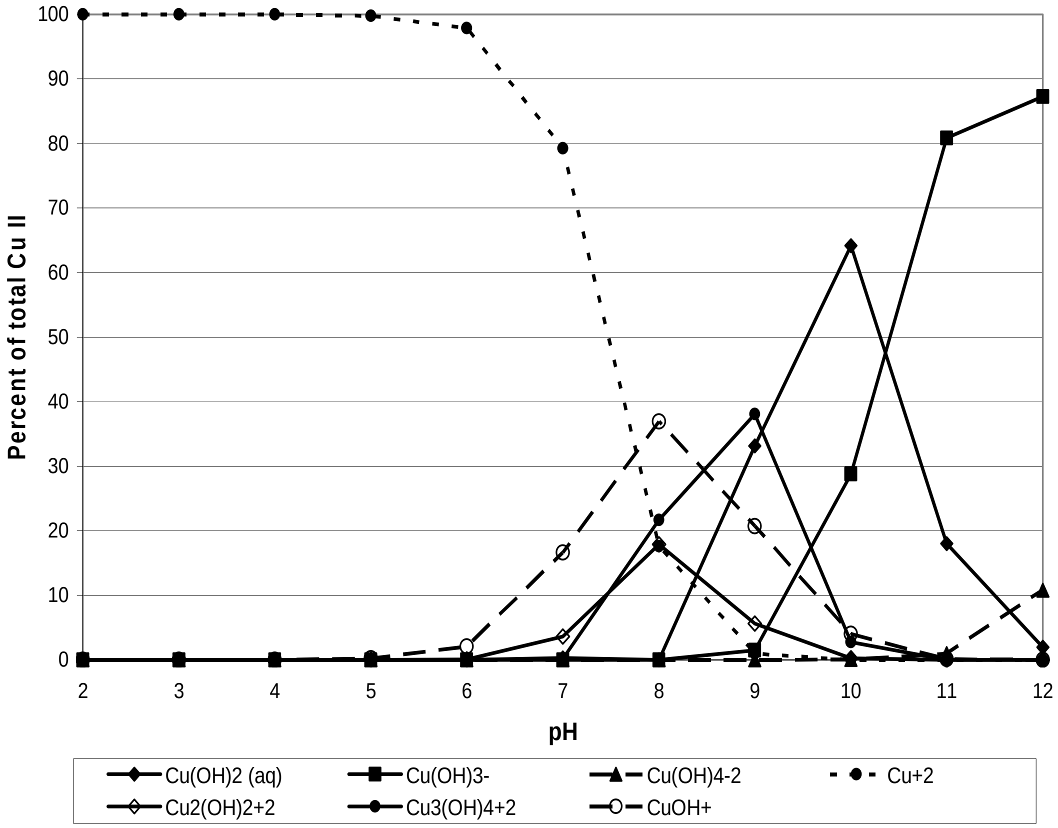


Figure 3.14: Effect of pH on Cu(II) species distribution. Relative distribution of species determined from Visual Minteq program with a fixed ionic strength of 0.02 and a total Cu(II) concentration of 1 mg/L. Notice the rise in dominance of the neutral and then anionic forms of Cu as the pH increases.

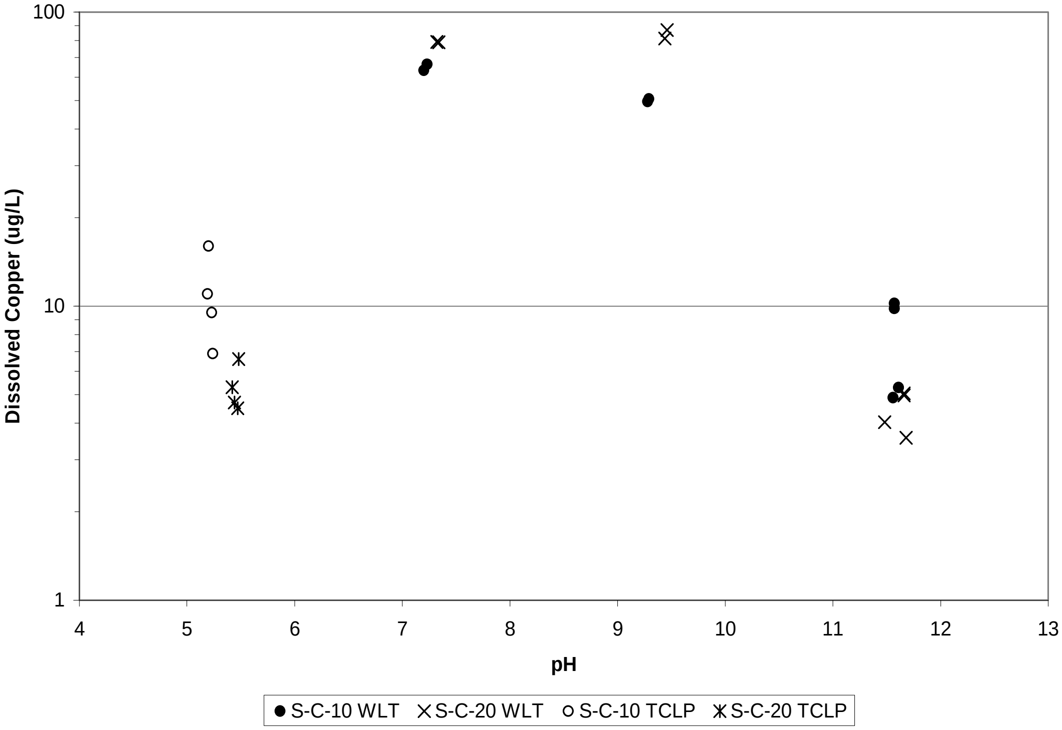


Figure 3.15: Effect of pH on leachate copper concentrations for S-C mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Lower concentrations around pH 11.5 could reflect precipitation likely under alkaline conditions, while higher concentrations measured around neutral pH suggest complexation with soil organic matter could maintain soluble metal in the leachate.

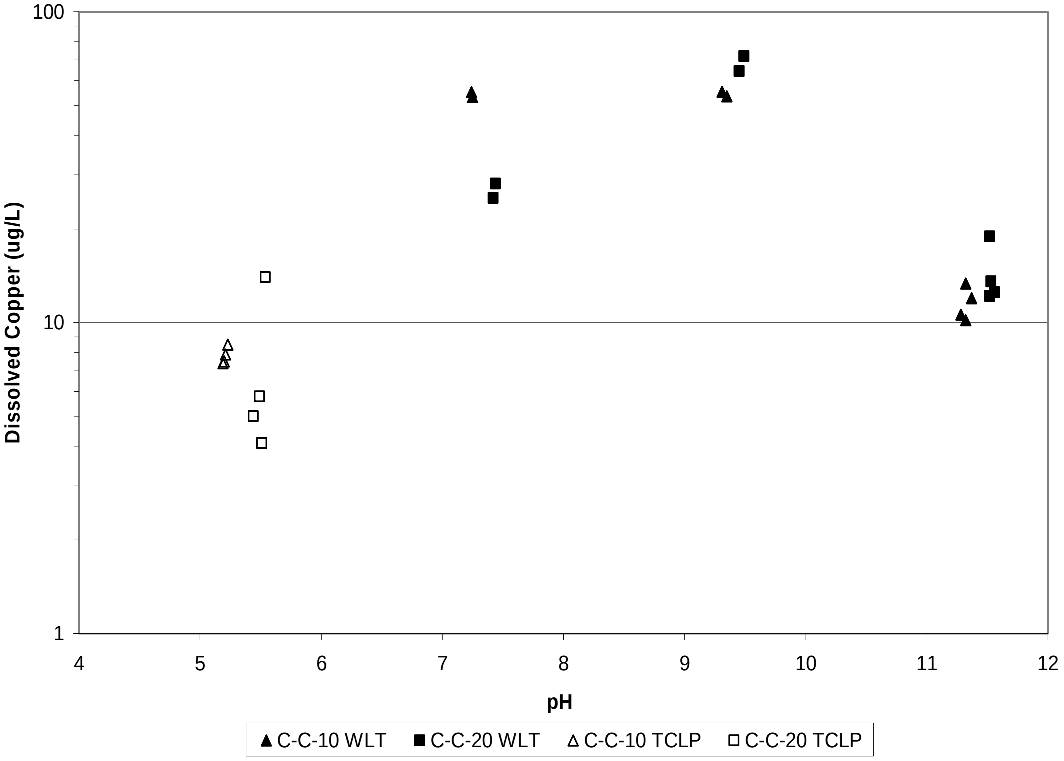


Figure 3.16: Effect of pH on leachate copper concentrations for C-C mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Soil organic matter is likely responsible for the higher leachate concentrations measured around pH 7-8 through complexation processes.

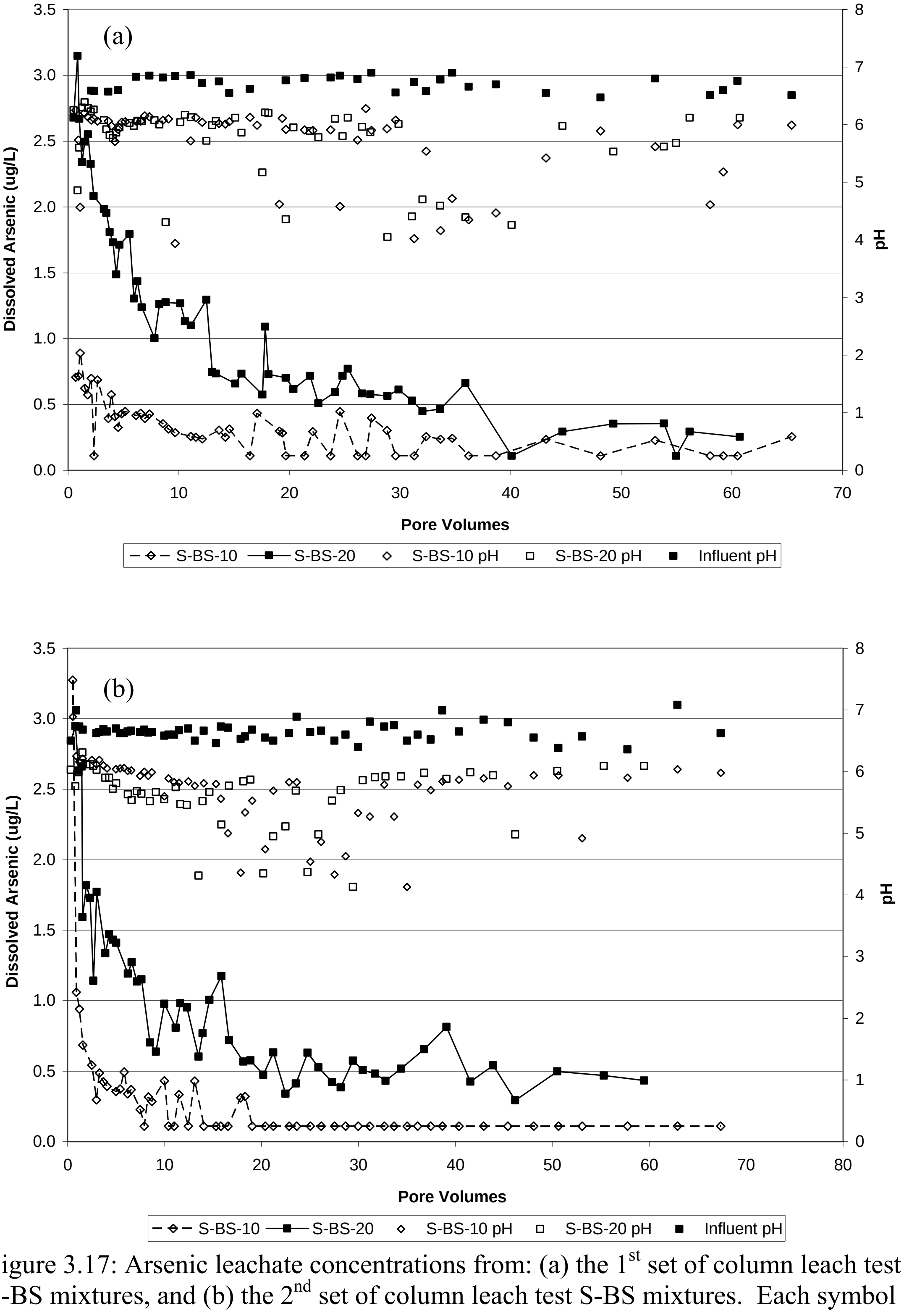


Figure 3.17: Arsenic leachate concentrations from: (a) the 1st set of column leach test S-BS mixtures, and (b) the 2nd set of column leach test S-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.22 ug/L were reported as ½ of the detection limit.

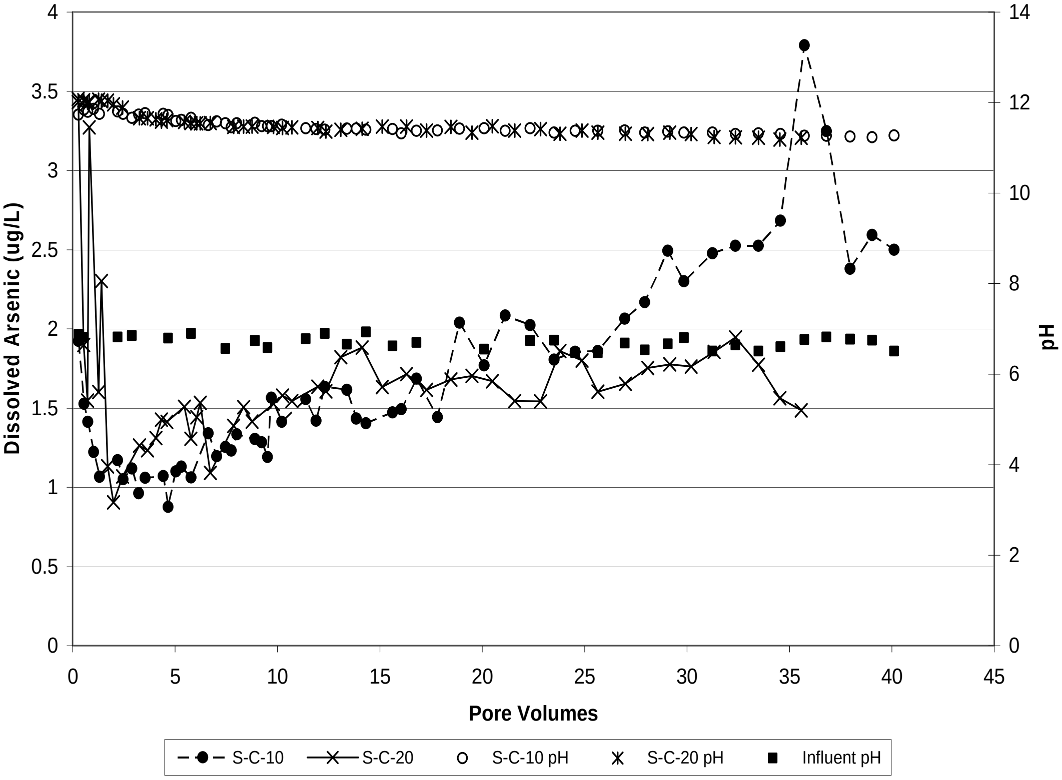


Figure 3.18: Arsenic leachate concentrations from column leach test S-C mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.22 μg/L were reported as ½ of the detection limit.

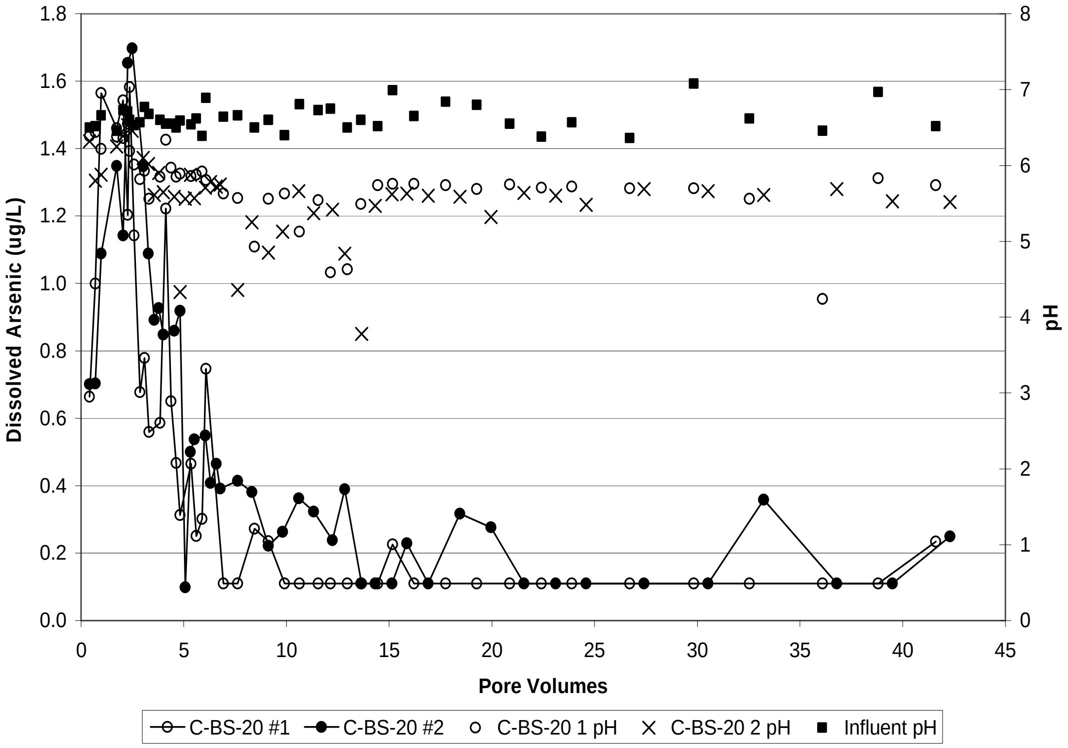


Figure 3.19: Arsenic leachate concentrations from column leach test C-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.22 μg/L were reported as ½ of the detection limit.

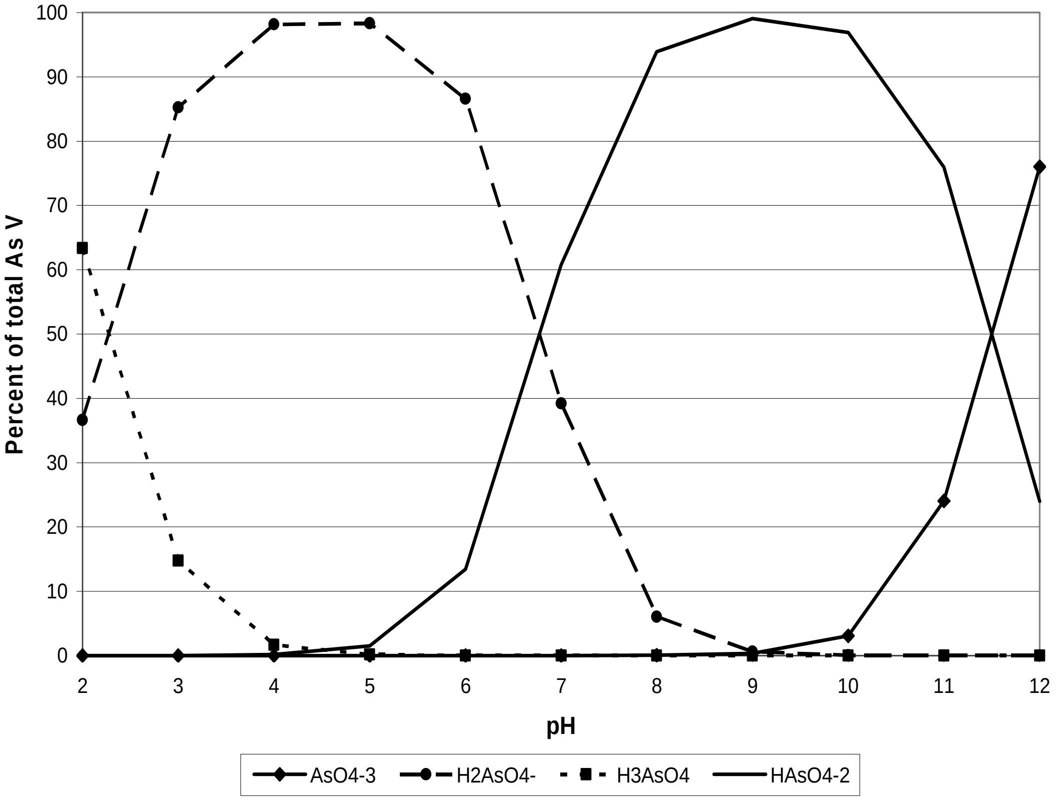


Figure 3.20: Effect of pH on As(V) species distribution. Relative distribution of species determined from Visual Minteq program with a fixed ionic strength of 0.02 and a total As(V) concentration of 1 mg/L.

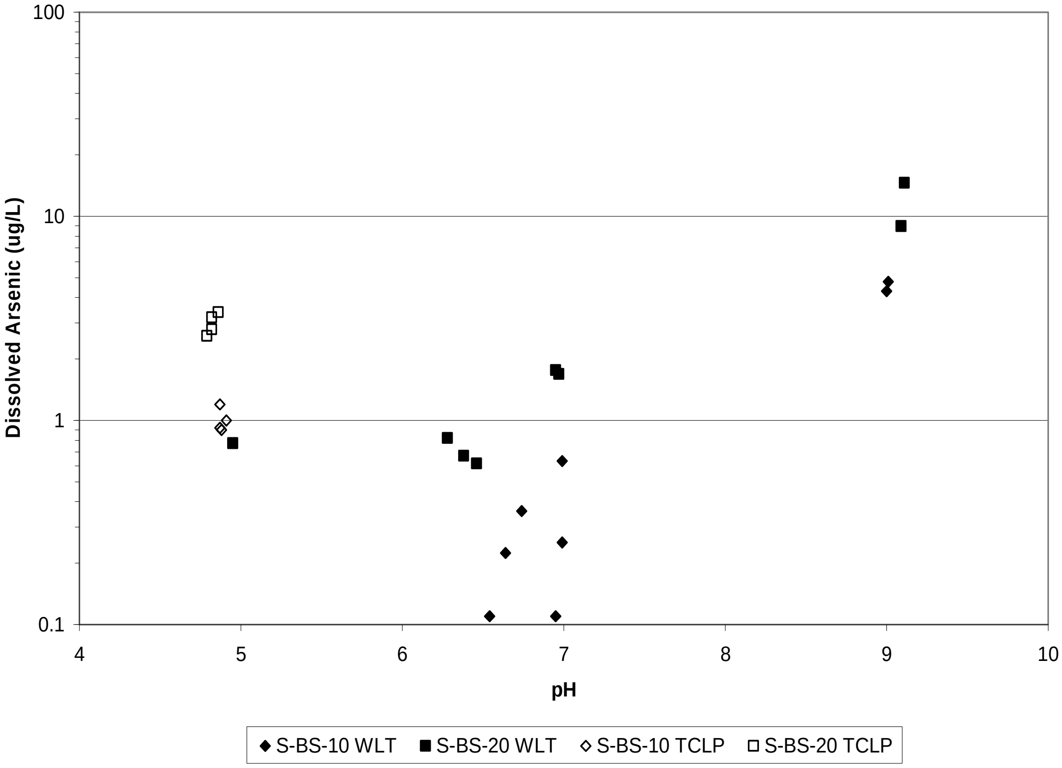


Figure 3.21: Effect of pH on leachate arsenic concentrations for S-BS mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Generally the As concentrations are below the EPA MCL of 10 µg/L except around pH 9, which could be due to repulsion of anionic As species under more basic conditions.

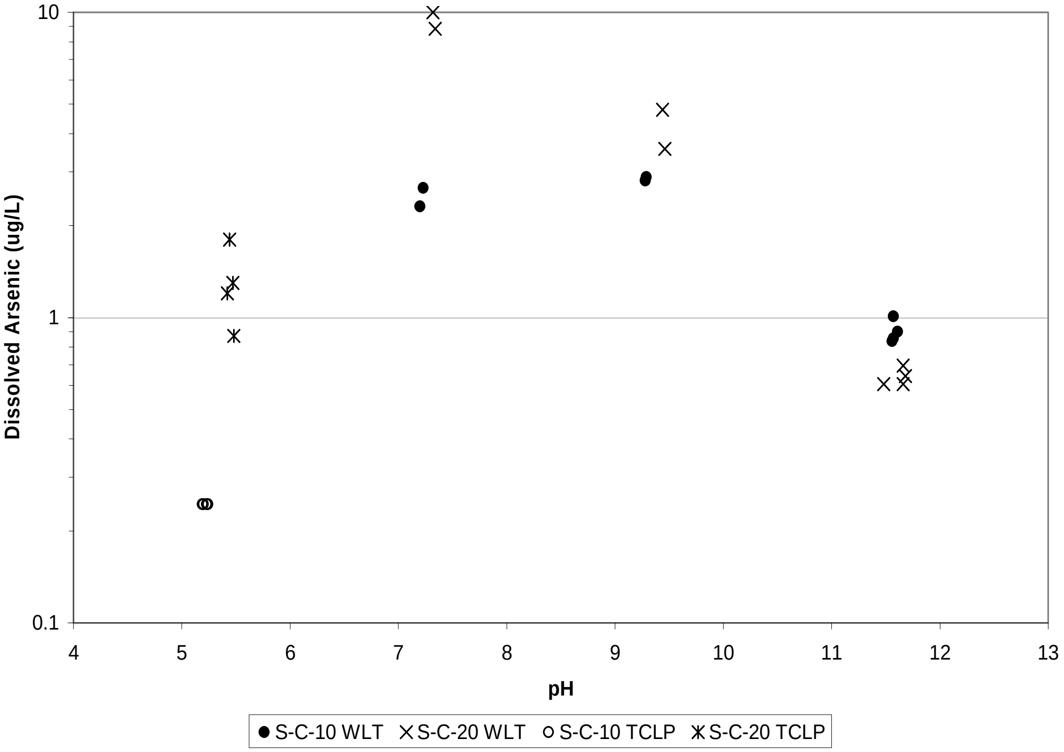


Figure 3.22: Effect of pH on arsenic concentrations for S-C mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Anionic repulsion could result in the higher concentrations seen in the pH range of 7-10. Highly alkaline conditions could cause the precipitation of As, leading to lower levels in the leachate as seen on the right side of the figure.

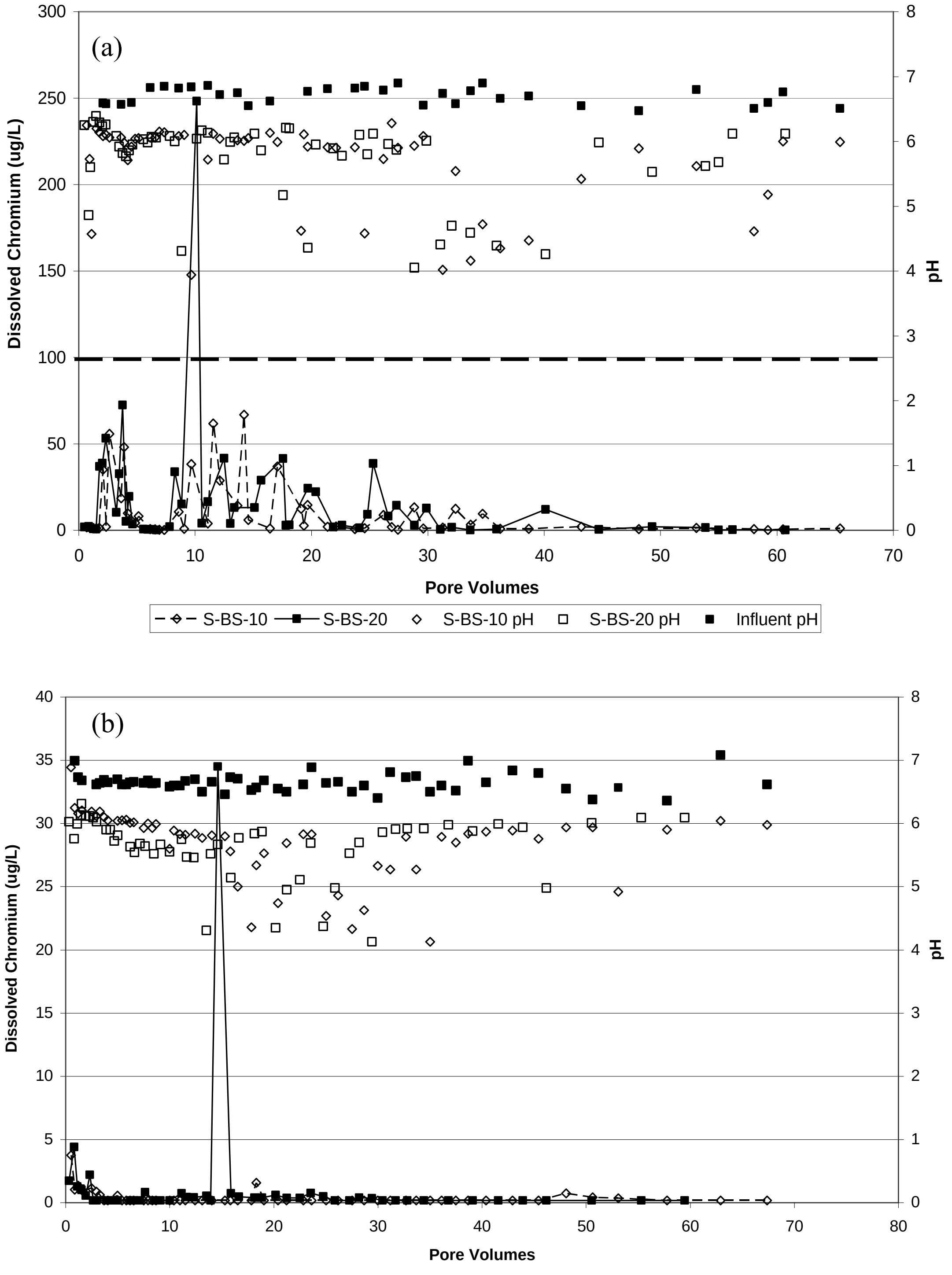


Figure 3.23: Chromium leachate concentrations from: (a) the 1st set of column leach test S-BS mixtures, and (b) the 2nd set of column leach test S-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.35 µg/L were reported as ½ of the detection limit. Dashed line represents EPA MCL of 100 µg/L.

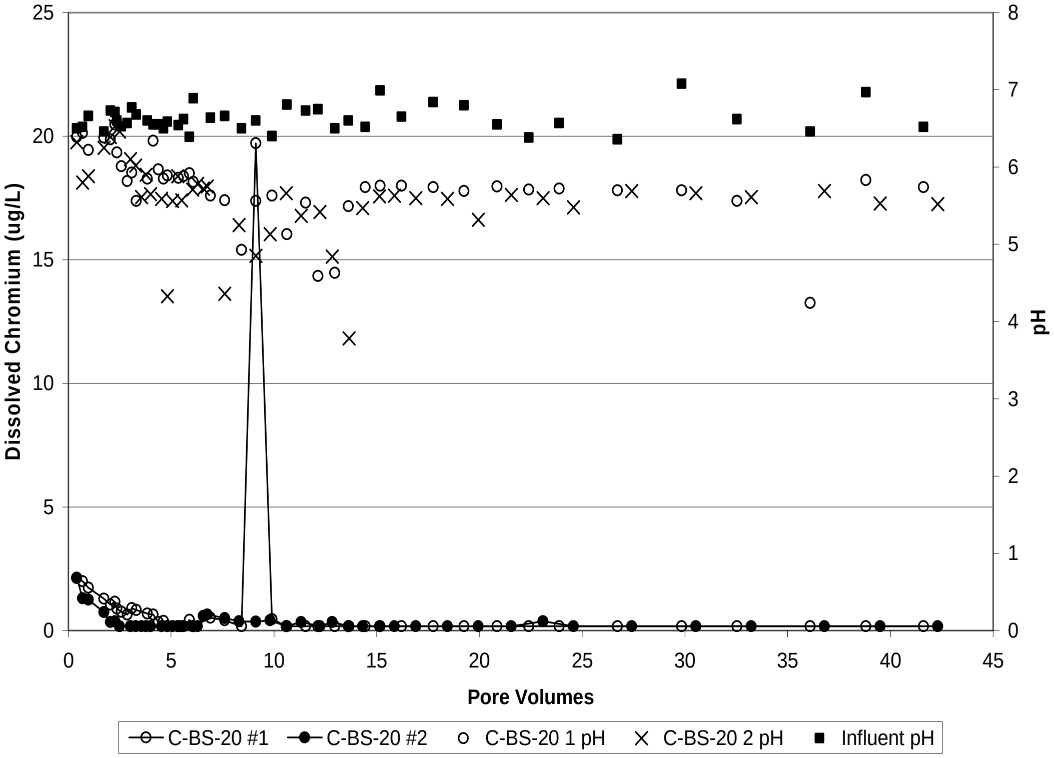


Figure 3.24: Chromium leachate concentrations from column leach test C-BS mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.35 µg/L were reported as ½ of the detection limit.

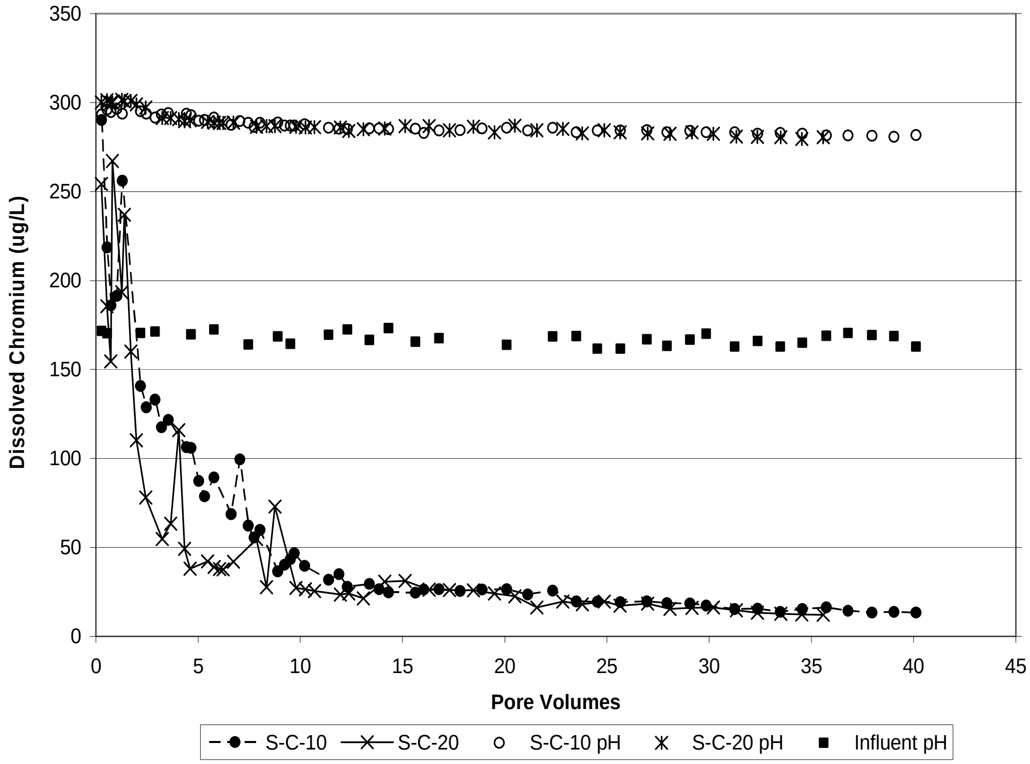


Figure 3.25: Chromium leachate concentrations from the column leach test S-C mixtures. Each symbol represents the average of two sample replicate metal measurements. Concentrations < 0.35 µg/L were reported as ½ of the detection limit.

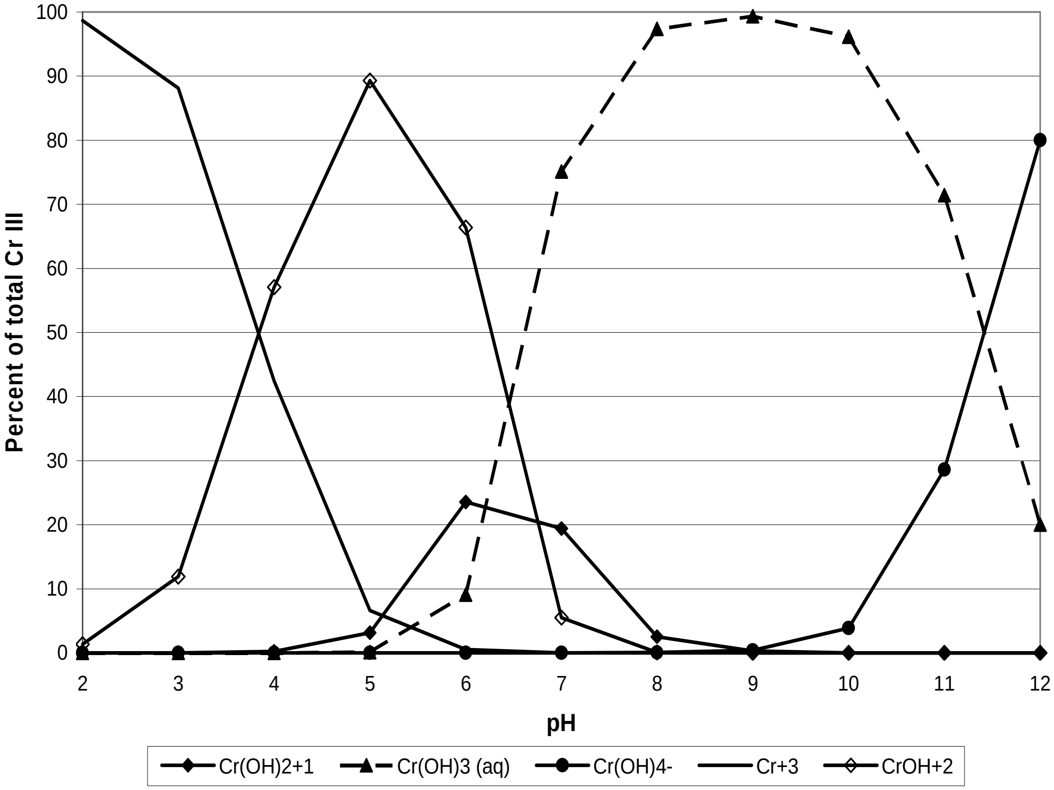


Figure 3.26: Effect of pH on Cr(III) species distribution. Relative distribution of species determined from Visual Minteq program with a fixed ionic strength of 0.02 and a total Cr(III) concentration of 1 mg/L. As the pH increased from 2 to 12, the dominant Cr(III) species changes from Cr+3 to Cr(OH)4-.

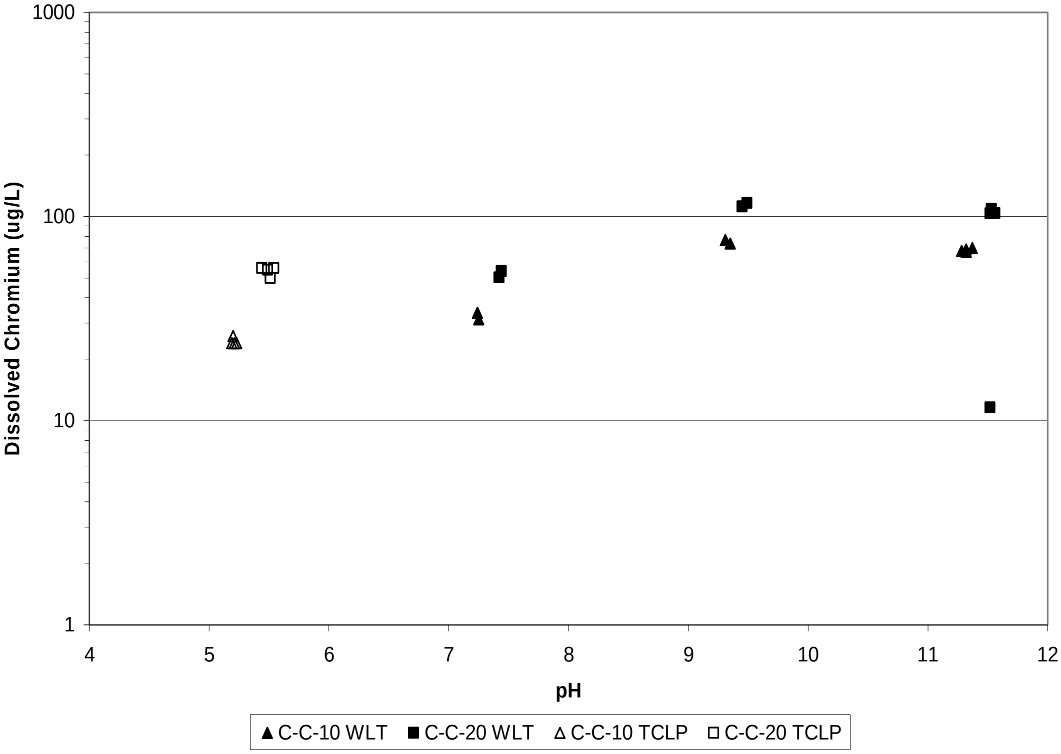


Figure 3.27: Effect of pH on leachate chromium concentrations for C-C mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. Note the concentrations are within the same order of magnitude over a wide pH range from 5-10 and begin to approach and exceed the EPA MCL of 100 μg/L at pH values above 9.

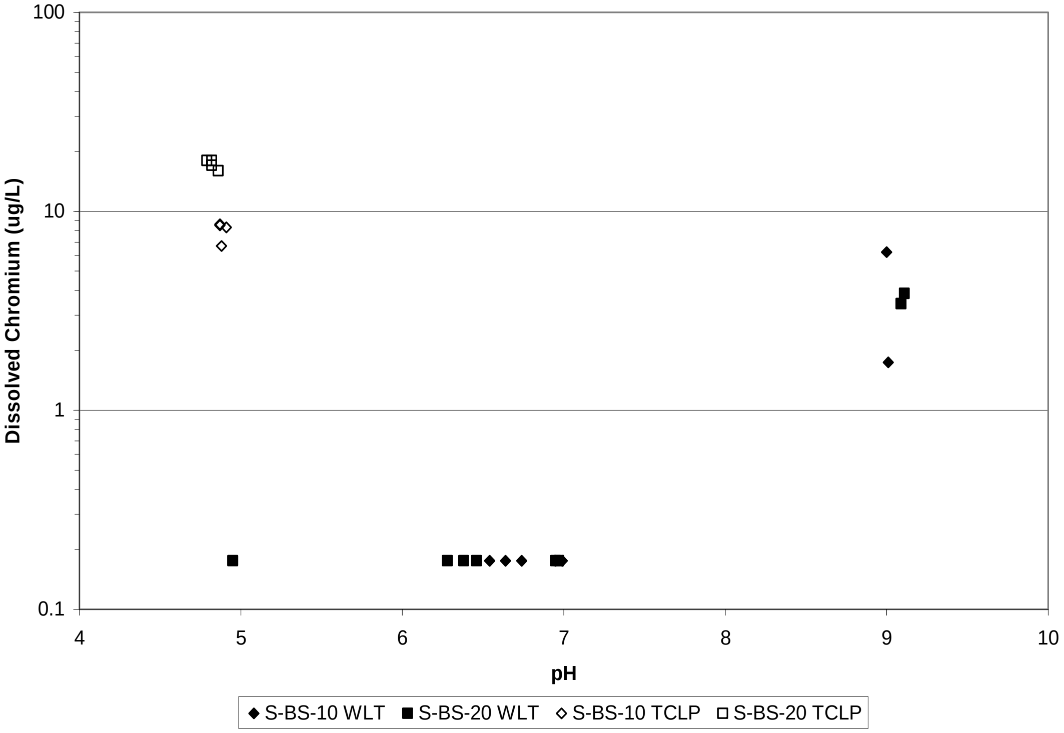


Figure 3.28: Effect of pH on leachate chromium concentrations for S-BS mixtures. Both water leach test and Toxicity Characteristic Leaching Procedure data are presented. The increased leaching of Cr at more acidic pH values (~5) and more alkaline pH values (~9) is similar to the solubility of Cr(III).

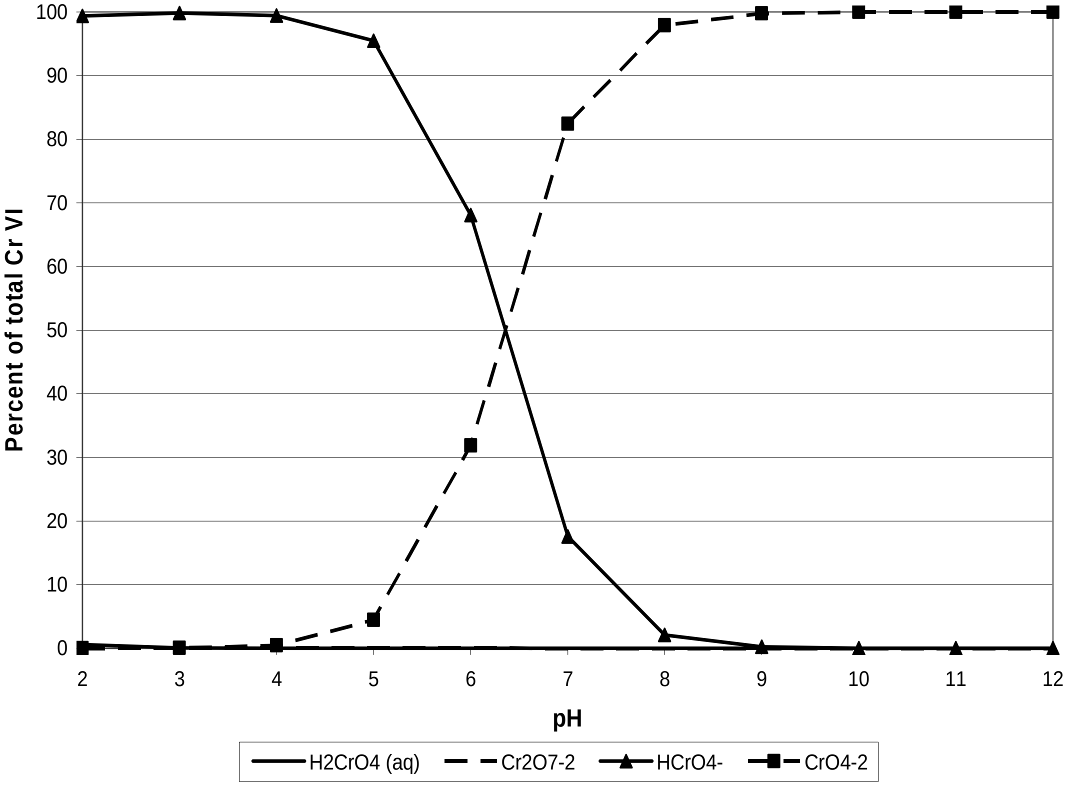


Figure 3.29: Effect of pH on Cr(VI) species distribution. Relative distribution of species determined from Visual Minteq program with a fixed ionic strength of 0.02 and a total Cr(VI) concentration of 1 mg/L. In the pH range of 2-12, the dominant Cr(VI) species are anionic, which contributes to high solubility of Cr(VI) over a wide pH range.

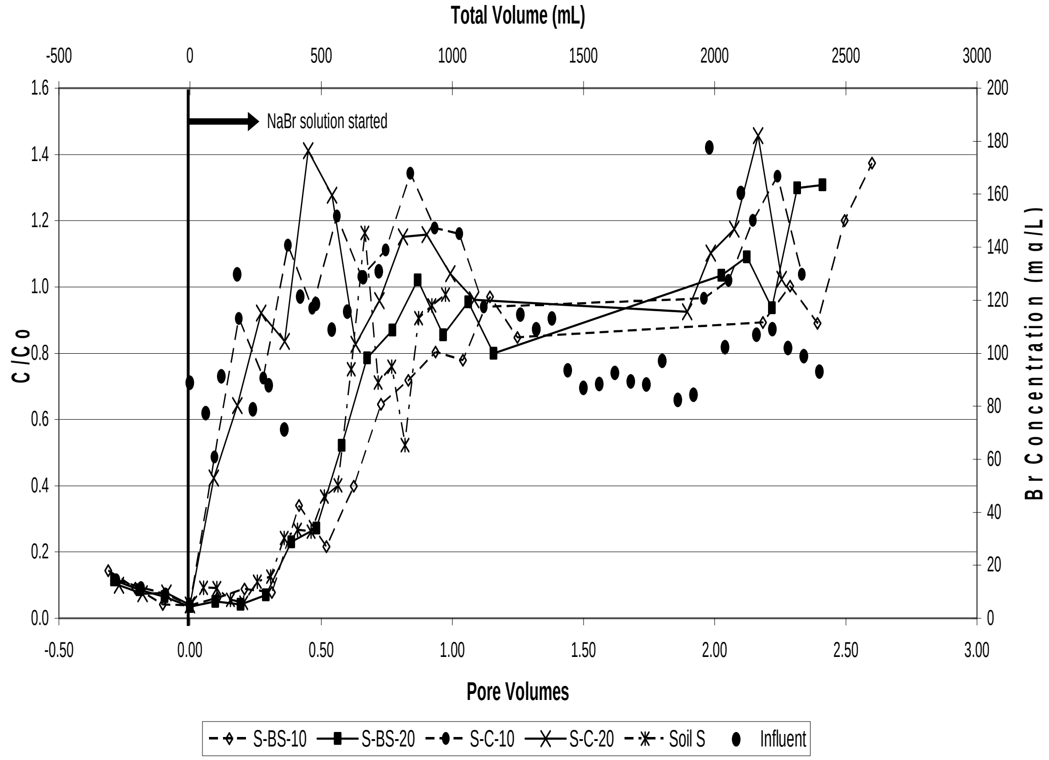


Figure 3.30: Breakthrough Curves from Tracer Study for 1st Set of Column Leach Tests. Influent bromide solution was 100 mg/L using NaBr. Negative numbers indicate conditions before switch to bromide step input.

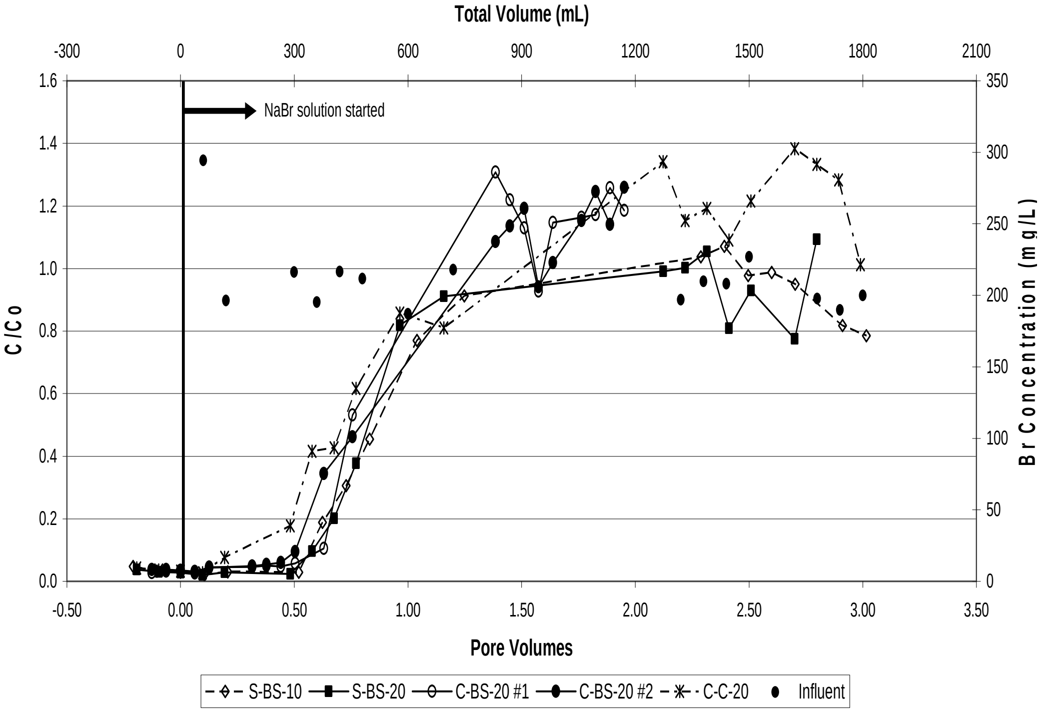


Figure 3.31: Breakthrough Curves from Tracer Study for 2nd Set of Column Leach Tests. Influent bromide solution was 250 mg/L using NaBr. Negative numbers indicate conditions before switch to bromide step input.

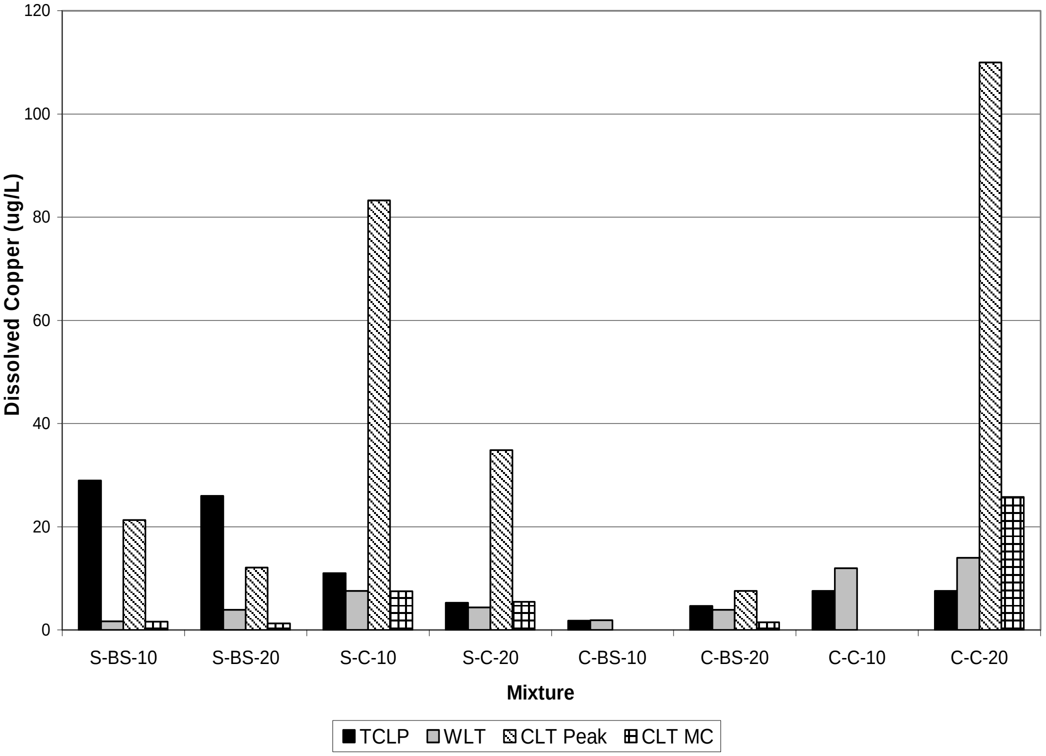


Figure 3.32: Comparison of copper leaching from water leach test, column leach test, and Toxicity Characteristic Leaching Procedure samples. C-BS-10 and C-C-10 mixtures were not tested using CLT methodology so no CLT data are reported in figure. Concentrations below detection limit are displayed as 0.

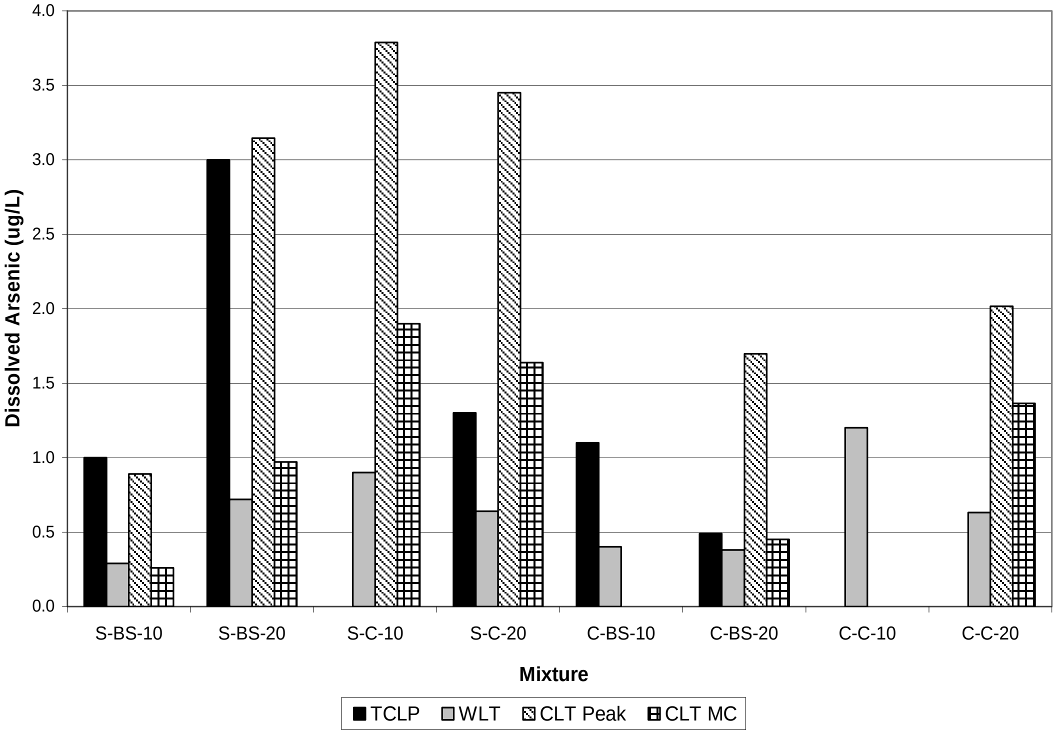


Figure 3.33: Comparison of arsenic leaching from water leach test, column leach test, and Toxicity Characteristic Leaching Procedure samples. C-BS-10 and C-C-10 mixtures were not tested using CLT methodology so no CLT data are reported in figure. Concentrations below detection limit are displayed as 0.

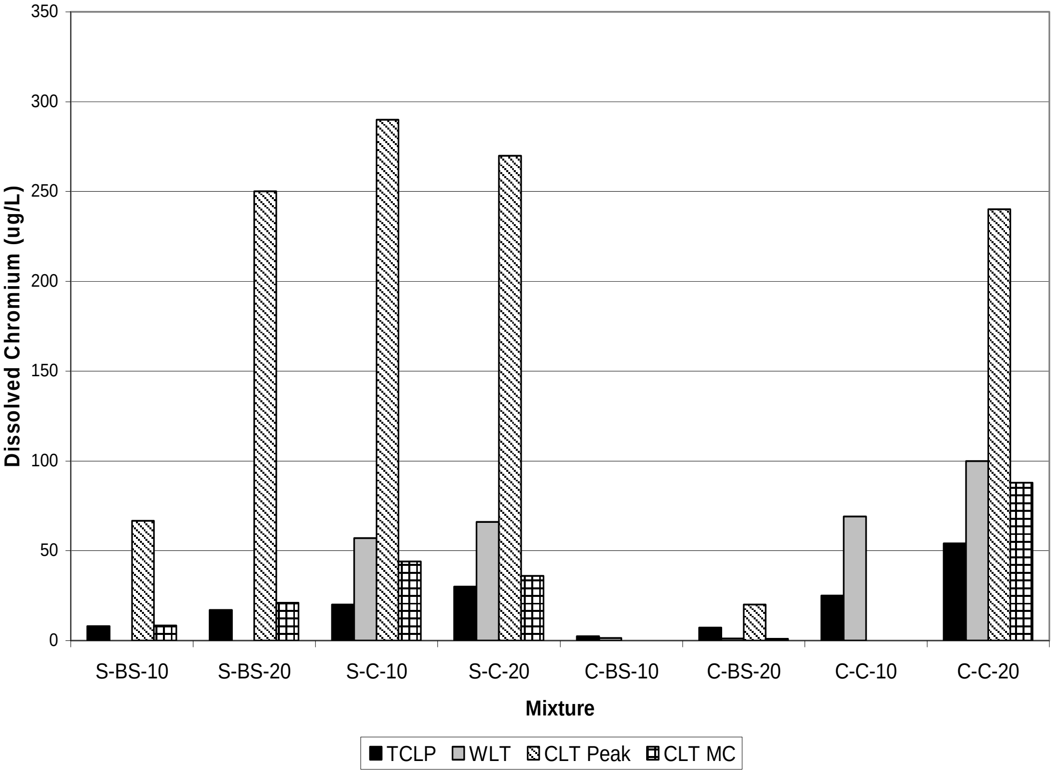


Figure 3.34: Comparison of chromium leaching from water leach test, column leach test, and Toxicity Characteristic Leaching Procedure samples. C-BS-10 and C-C-10 mixtures were not tested using CLT methodology so no CLT data are reported in figure. Concentrations below detection limit are displayed as 0.

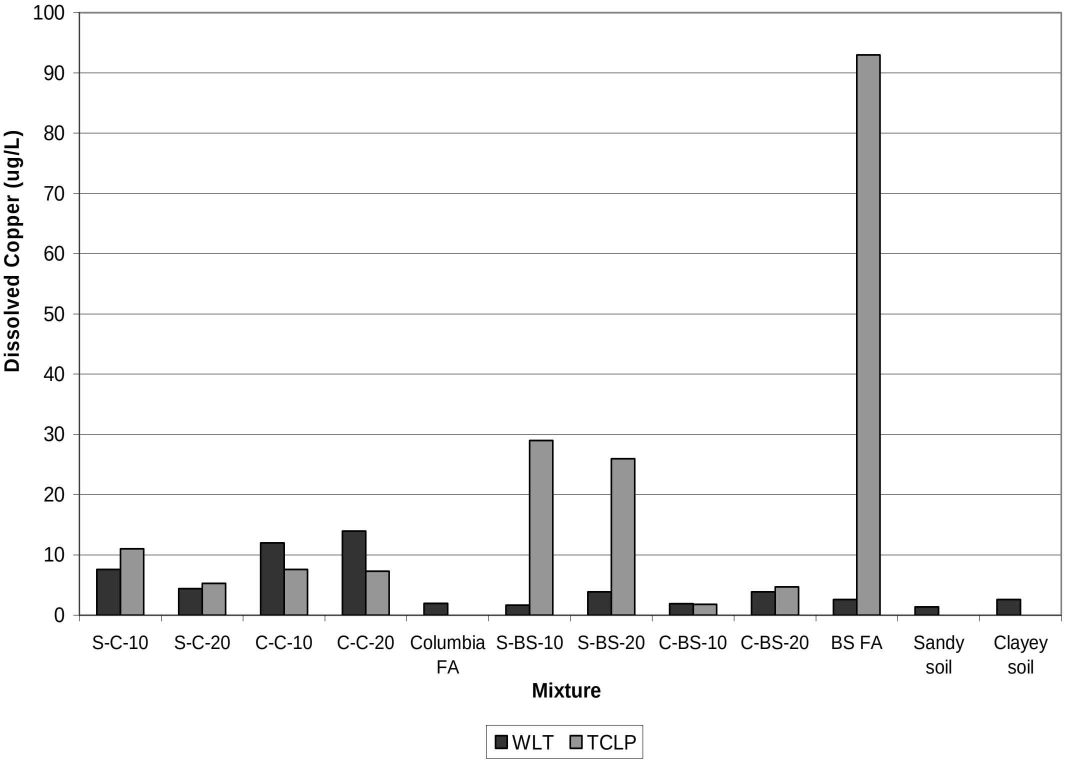


Figure 3.35: Comparison of water leach test and Toxicity Characteristic Leaching Procedure leachate copper concentrations. Concentrations below detection limit are displayed as 0.

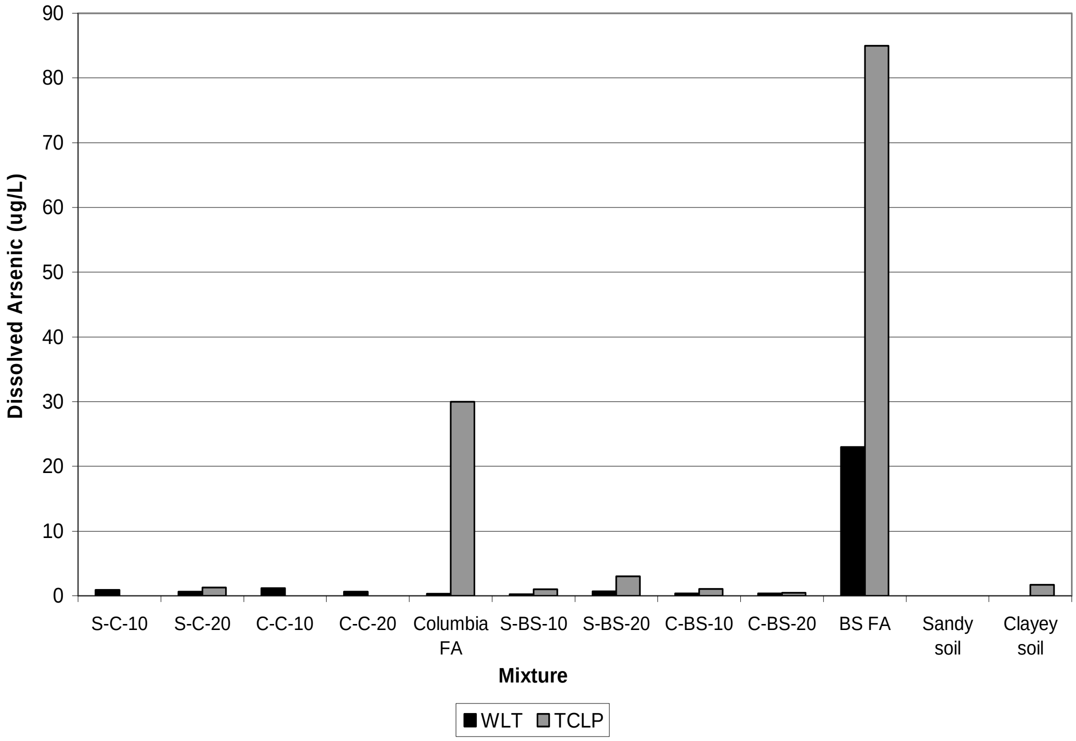


Figure 3.36: Comparison of water leach test and Toxicity Characteristic Leaching Procedure leachate arsenic concentrations. Concentrations below detection limit are displayed as 0. Note that no soil-fly ash mixture has arsenic concentrations that exceed the 10 μg/L EPA MCL.

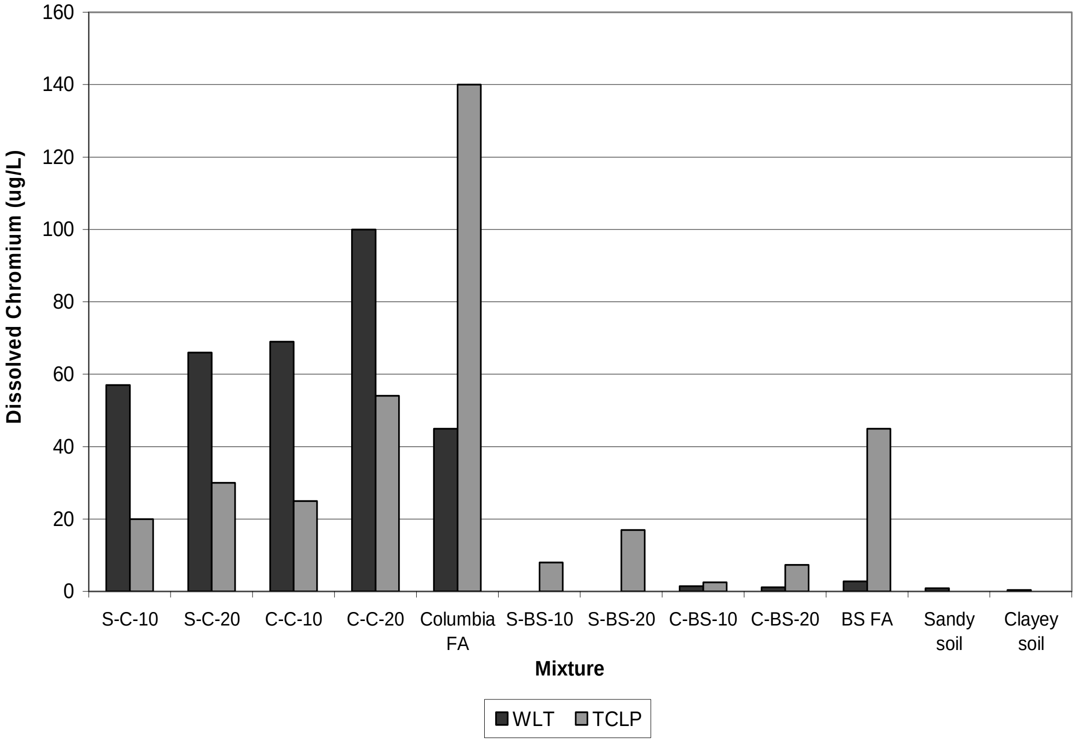


Figure 3.37: Comparison of water leach test and Toxicity Characteristic Leaching Procedure leachate chromium concentrations. Concentrations below detection limit are displayed as 0. As shown, the C fly ash mixtures on the left side have higher leachate chromium compared to the BS fly ash mixtures for both leaching tests, mainly a result of the highly alkaline pH conditions (~11.5) of the C fly ash.

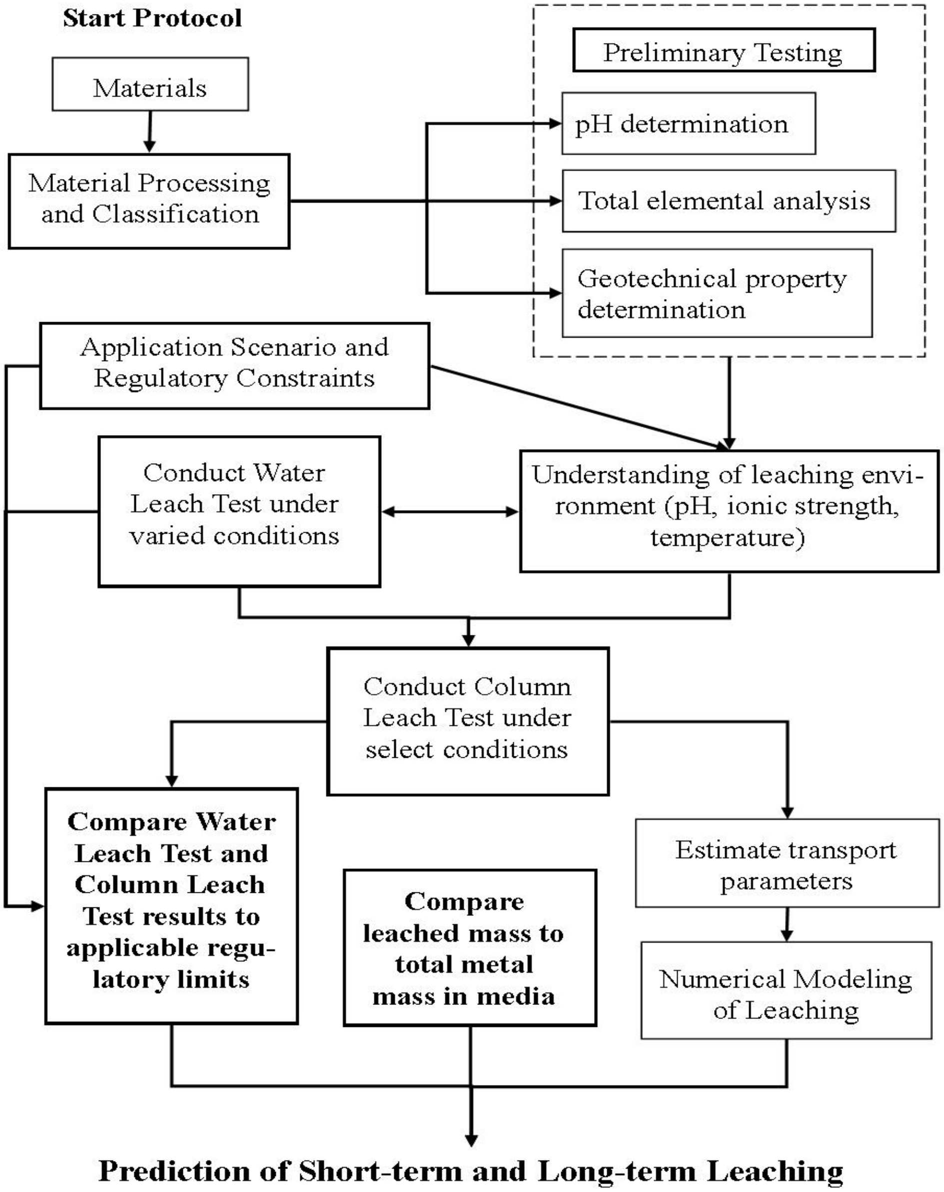


Figure 4.1: Summary of proposed leaching protocol. Preliminary testing provides foundation for conducting the water leach tests and column leach tests. Synthesis of different leaching test results provide evaluation of risks associated with heavy metal leaching. Additional preliminary testing, including L:S and contact time experiments, as well as numerical modeling, could be performed and incorporated depending on required level of detail and time frame.

Appendix A: Detailed Materials and Methods

A.1 Preparation and Determination of Extraction Fluids

The leaching solution for the CLT and WLT was prepared by dissolving 2.3376 grams sodium chloride (Fisher Scientific) in 2 liters of deionized water and mixing by magnetic stirrer for 5 minutes. The pH of each new batch was immediately measured, and adjusted to between 6.5 and 7 using 0.1 M NaOH prior to use in leaching tests.

Two different extraction fluids can be used in the TCLP test, depending on the sample properties. To determine which TCLP extraction fluid to use, 96.5 mL of deionized water were added to a beaker containing 5.0 grams of sample material, vigorously stirring for 5 minutes, and then measuring the pH. A measured pH of < 5 indicates that extraction fluid #1 should be used, whereas if the pH was > 5, 3.5 mL of 1 N HCL are added and the mixture heated to 50 ° C for 10 minutes. If at this point the pH is < 5, extraction fluid #1 is used, but if the pH is > 5, extraction fluid #2 is used. In this work, extraction fluid #1 was appropriate in all cases. Extraction fluid #1 was prepared in large batches (5 liters) to maximize solution homogeneity. To create the solution, first 5.7 mL of glacial acetic acid (Fisher Scientific) was added to 500 mL of deionized water. Then 64.3 mL of 1N NaOH was added to the original solution, which was diluted to a final volume of 1 L with deionized water before mixing for 10 minutes. The pH of the solution was immediately measured and compared to the specified value of 4.93 ± .05 units. Generally, there was very close agreement between the observed and required pH. In the case of discrepancies, 1 N NaOH was used to adjust the solution to the correct pH.

A.2 Preliminary Compaction Tests

The goal of these compaction tests was to determine the maximum dry unit weight and corresponding optimum water content. These values were needed in calculating the pore volume of each specific mixture for the CLTs. Compaction tests were performed on all soils and fly ash-soil mixtures according to ASTM D698. The compaction was done in three layers with 25 blows per layer from a standard compaction hammer in a circular motion. The dry unit weight of each mixture was calculated and plotted against water content to determine the water content that corresponded to the maximum unit weight. Two series of tests were performed: no delay and a 2 hour delay between the wetting of the mixture and compaction. Based on the compaction test results, the 2 hour delay had no significant impact on the maximum dry unit weights, and therefore was selected for use in the actual column specimen preparation. This delay simulated the delay often seen in actual compaction processes used on construction sites between the time the soil is moistened and mechanical compaction is applied.

A.3 Column Compaction Procedure

To prepare the compacted specimens for the CLTs, 10 kilograms batches of fly ash-soil mixture were mixed in five-gallon plastic buckets. The acrylic tubes were acid washed and then coated with a layer of silicone lubricant. The 100% silicone product was not expected to influence the leaching results and would aid in the release of the compacted mixtures from the columns. After thorough mixing, sufficient water was added to the material to give a moisture content equal to 2% less than the OMC. Compaction of soil mixtures in the field typically is carried out dry of the OMC to account for additional wetting that occurs from precipitation. Subsequent mixing was done by hand and with a metal spoon to ensure the water was evenly distributed. After a period of two hours, the wetted fly ash-soil mixture was compacted in 8 equal layers, with 28 blows from a standard compaction hammer per layer in a circular motion. The procedure for compacting each column was determined from calculation of total energy (13750 ft-lbf/ft3) delivered to the compacted media adjusted for the taller column height compared to the standard 4 inch tall Proctor compaction mold.

References

Ahmed, A., Khalid, H., Ahmed, A.,Chen, D., 2010. A lysimeter experimental study and numerical characterisation of the leaching of incinerator bottom ash waste. Waste Manag. 30, 1536-1543.

Ariese, F., Swart, K., Morabito, R., Brunori, C., Balzamo, S., Slobodnik, J., Korenokova, E., Janos, P., Wilderova, M., Hlavay, J., Polya'k, K., Fodor, P., Muntau, H., 2002. Leaching studies of inorganic and organic compounds from fly ash. Intn. J. Environ. Anal. Chem., 82, 751–770.

Balasoiu, C., Zagury, G., Deschenes, L., 2001. Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: influence of soil composition. Sci. Total Environ. 280, 239-255.

Bin Shafique, S., Benson, C., Edil, T., 2002. Leaching of heavy metals from fly ash stabilized soils used in highway pavements. Geo Engineering Report 02-14, University of Wisconsin.

Bin Shafique, S., Benson, C., Edil, T., Hwang, K., 2007. Leachate concentrations from water leach and column leach tests on fly ash-stabilized soils. Environ. Eng. Sci. 23, 53-67.

Cetin, B., 2009. Stabilization of recycled base materials with high carbon fly ash. Web. Digital Repository at the University of Maryland. <http://hdl.handle.net/1903/9573>

Chichester, D. L. and Landsberger, S. (1996). Determination of Leaching Dynamics of metals from Municipal Solid Waste Incinerator Fly Ash Using a Column Test. J. Air and Waste Manage. Assoc., 46, 643-649.

Creek, D. N. and Shackelford, C. D. (1992). Permeability and Leaching Characteristics of Fly Ash Liner Materials. Transp. Res. Rec., 1345. Transportation Research Board.

Cullen, W. and Reimer, K., 1989. Arsenic Speciation in the Environment. Chem. Rev. 89, 713-764.

Edil, T., Benson, C., Bin Shafique, S., Tanyu, B., Kim, W., Senol, A., 2002. Field evaluation of construction alternatives for roadway over soft subgrade. Transport. Res. Rec. 36, 1786.

Edil, T. B. (1998). Geotechnics of Industrial By-Products. Recycled Materials in Geotechnical Applications, Geotechnical Special Publication, ASCE New York, N.Y., 1-18.

EPA Drinking Water Contaminants. Updated July 1, 2010. United States Environmental Protection Agency <www.epa.gov/safewater/contaminants/index.html>

EPA Test Method 1311: Toxicity Characteristic Leaching Procedure. Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-864), 3rd edition. United States Environmental Protection Agency <www.epa.gov/osw/hazard/testmethods/sw846/online/index.htm>

Evans, L.J., 1989. Chemistry of metal retention by soils. Environ. Sci. and Technol. 23, 1046-1056.

Fytianos, K., Tsaniklidi, B., Voudrias, E., 1998. Leachability of heavy metals in Greek fly ash from coal combustion. Environ. Int., 24, 477-486.

Gelhar, L.W., Welty, C., and Rehfeldt, K.R. (1992). A critical review of data on field-scale dispersion in aquifers. Water Resour. Res., Vol. 28, No. 7, 1955-1974.

Ghosh, A. and Subbarao, C. 1998. Hydaulic conductivity and leachate characteristics of stabilized fly ash. J. of Environ. Eng. 124, 812-820.

Horne, M. T. and Dunson, W. A., 1995. Effects of low pH, metals, and water hardness on larval amphibians. Arch. Environ. Contam. Toxicol. 29, 500-505.

Jegadeesan, G., Al-Abed S., Pinto, P., 2008. Influence of trace metal distribution on its leachability from coal fly ash. Fuel. 87, 1887-1893.

Jo, H., Minb, S., Lee, T., Ahna, H., Lee, S., Honga, J., 2008. Environmental feasibility of using coal ash as a fill material to raise the ground level. J. Hazard Mater. 154, 933-945.

Kim, A., 2006. The effect of alkalinity of Class F PC fly ash on metal release. Fuel. 85, 1403-1410.

Kyper, T.N. (1992). “Institutional Constraints to the Use of Coal Fly Ash in Civil Engineering Construction”. Utilization of Waste Materials in Civil Engineering Construction, Published by ASCE, New York, N.Y., 32-43.

MDE COMAR. Numerical Criteria for Toxic Substances in Surface Waters. Code of Maryland Regulations 26.08.02.03-2.03-2 (Toxic Substance Water Quality Criteria). Maryland Department of the Environment <www.dsd.state.md.us/comar/SubtitleSearch.aspx?search=26.08.02.*>

Morar, D., Aydilek, A.H., Seagren, E.A., and Demirkan, M.M., 2010. Metal Leaching from Fly Ash-Sand Reactive Barriers. Journal of Contam. Hydrol., in review.

Palumbo, A., Tarver, J., Fagan, L., McNeilly, M., Ruther, R., Fisher, L., Amonette, J., 2007. Comparing metal leaching and toxicity from high pH, low pH, and high ammonia fly ash. Fuel. 86, 1623-1630.

Qiao X.C., Poon C.S, and Cheeseman, C. (2006). "Use of Flue Gas Desulphurisation (FGD) Waste and Rejected Fly ash in Waste Stabilization/Solidification Systems". Waste Manag, Vol. 26, 141-149.

Ram, L., Srivastava, N., Tripathi, R., Thakur, S., Sinha, A., Jha, S., Masto, R., Mitra, S., 2007. Leaching behavior of lignite fly ash with shake and column tests. Environ. Geol. 51, 1119-1132.

Rigol, A., Mateu, J., González-Nú˜nez, R., Rauret, G., Vidal, M., 2009. pHstat vs. single extraction tests to evaluate heavy metals and arsenic leachability in environmental samples. Anal. Chem. Acta. 632, 69-79.

Shackelford, C.D. and Glade, M.J.(1997). "Analytical Leaching Model for Contaminated Soil and Stabilized Waste". Groundwater, Vol. 35, No. 2, 233-242.

Shah, P., Strezov, V., Prince, K., Nelson, P., 2008. Speciation of As, Cr, Se and Hg under coal fired power station conditions. Fuel. 87, 1859-1869.

Standard Method 1030C: Data Quality. American Public Health Association; American Water Works Association; Water Environment Federation, 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. American Public Health Association: Washington, D.C.; American Water Works Association: Denver, Colorado; Water Environment Federation: Alexandria, Virginia.

Wang, J., Ban, H., Teng, X., Wang, H., Ladwig, K., 2006. Impacts of pH and ammonia on the leaching of Cu(II) and Cd(II) from coal fly ash. Chemosphere. 64, 1892-1898.

Wang, J., Teng, X., Wang, H., Ban, H., 2004. Characterizing the Metal Adsorption Capability of a Class F Coal Fly Ash. Environ. Sci. and Technol. 38, 6710-6715.

Zandi, M. and Russell, N. V., 2007. Design of a Leaching Test Framework for Coal Fly Ash Accounting for Environmental Conditions. Environ. Monit Assess. 131, 509-526.