

**LEACHING OF TRACE ELEMENTS FROM ROADWAY  
MATERIALS STABILIZED WITH HIGH CARBON FLY ASH  
AT THE MINNESOTA DEPARTMENT OF  
TRANSPORTATION MNROAD FACILITY**

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## **ABSTRACT**

- Percolation rates and concentrations of trace elements are presented from leachate collected in pan lysimeters installed beneath roadway sections where high-carbon fly ash was used to stabilize recycled pavement material (RPM) base course. Data from control sections are also presented. Additionally, laboratory column leach (CLT) and water leach (WLT) tests were performed on all materials. Percolation rates from the base of a pavement profile vary seasonally in response to seasonal variations in meteorological conditions. Flux discharged from the stabilized roadway layers is expected to be 2% to 8% of precipitation for stabilized RPM base course. Occasionally the flux from the stabilized materials approaches 15% of precipitation for a period of several months, but the long-term average is never more than 7.8% of precipitation. All field cells had pH near 7 and predominantly oxidizing Eh of approximately +150 to +300 mV. Among elements that were tested for during the entire operation of the site and that were detected at the site, 61% of elements had the peak concentration occur during the first two PVF. B, Mo, and V concentrations in leachate from the fly-ash-stabilized materials were elevated relative to concentrations from the control sections, have peak concentrations above the MCL,

and exceed the MCL for many PVF. Both As and Pb have concentrations that remain near the MCL and were observed to periodically exceed the MCL over many PVF. The concentrations of As and Pb are only slightly statistically elevated relative to the control concentrations. At sites where Cd and Cr exceeded the MCL, they only exceeded the MCL during the first sampling event (PVF at Peak  $\leq 0.26$ ) and were below in all subsequent PVF. When using lab tests to predict field leaching concentrations, an analytical method with minimum detection limits equal to or less than the lowest MCL should be used. Peak concentrations of many elements in leachate from the CLTs and WLTs are likely to be less than peak concentrations from the field leachate. Elements that are not detected in the lab tests may be present in field leachate, and may exceed the MCL in the field. The method detection limits should be determined before testing of samples begins. The pH of leachate from CLT and WLT on stabilized materials (generally 10 to 11) is higher than from the same materials in the field (6 to 8). Eh of leachate from CLT and WLT on stabilized materials is lower (-5 to +40 mV) than from the same materials in the field (mostly between +150 to +300 mV), where leachate was generally oxidizing. CLT average peak concentration was within one order of magnitude of the average peak field concentration 77% of the time. Of the four liquid to solid ratios tested, the 3:1 WLT provides the best prediction of field peak concentrations. All elements with peak field concentrations of 500  $\mu\text{g/L}$  or greater were detected in the WLT. If the WLT leachates were analyzed with lower detection limits, the 3:1 WLT may have detected more or all of the elements detected in the field. When CLT and WLT results are compared using the same detection limits the ability of both tests to predict peak field concentrations is similar. Both have peak or average peak within one order of magnitude of the field for B, Mo, and V, which have peak concentrations above the MCL for many PVF.



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## SECTION 1

### 1. INTRODUCTION

This report describes field and laboratory experiments conducted to analyze leaching of trace elements from roadway base course stabilized with fly ash at the Minnesota Department of Transportation (MNDOT) MnROAD Facility. The MnROAD Facility is a full scale highway testing laboratory. Particularly of interest in this study were the type, concentration, and pattern of elemental leaching. The report also evaluates the use of laboratory water leach tests and column leach tests to predict field leaching of elements from fly ash stabilized materials.

Fly ash is a coal combustion product (CCP) captured from hot flu gases and trace metals present in the coal, including As, B, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Sr, Tl, V, and Zn (NRC, 2006) (US EPA 2008). In 2007 the US produced approximately 131 million tons (119 million Mg) of fly ash, of which 43% was used in beneficial applications, primarily in Portland cement concrete (ACAA 2009). Cementitious fly ash can be mixed with soils or granular materials in roadway construction to increase the strength and stiffness of the materials (Edil *et al.* 2002; Bin-Shafique *et al.* 2004; Li *et al.* 2007; Hatipoglu *et al.* 2008; Li *et al.* 2009), as well as to reduce the swelling of expansive soils (Cokca, 2001; Buhler and Cerato 2007). Use of fly ash as a stabilizer in road construction has also been found to reduce construction costs and energy use (Kumar and Patil 2006; US EPA 2008; Lee *et al.* 2010) depending on the scale of the project and the local availability of fly ash and other construction materials (Kumar and Patil 2006).

The primary limitation to greater use of fly ash in road construction is concern about environmental impacts to soil and groundwater from potentially toxic metals present in the ash. Limitations placed by states on the use of fly ash focus on the

potential toxicity of the ash (US DOE NETL 2009). A summary of state regulation of coal byproducts is included as Appendix D.

## SECTION 2

### 2. SITE DESCRIPTION

The Minnesota Department of Transportation (MNDOT) MnROAD Facility is a full scale highway testing laboratory located in east-central Minnesota adjacent to Interstate 94 between Albertville and Monticello, Minnesota. The facility contains a low traffic volume road loop that simulates traffic on rural roads as well as a high volume freeway section that carries live traffic from Interstate 94 when active. Test sections at MnROAD contain sensors that measure load response and environmental data (MNDOT 2009).

Three test sections were constructed in 2007 on the low volume loop at MnROAD to evaluate fly-ash-stabilized recycled pavement material (RPM) as base course. One test section contains fly-ash-stabilized RPM base course, another contains unstabilized RPM, and the third contains crushed stone (Class 5, as classified by MNDOT) as the base course. The RPM was reclaimed from to a depth of 305 mm from a HMA wearing course and MNDOT Class 4 aggregate base course at the MnROAD facility and stockpiled before use.

The base courses were initially constructed in early August 2007. Each is 203 mm thick and was compacted with a steel-drum vibratory roller (Fig. 2.1). The stabilized RPM base course was mixed with 14% fly ash and compacted and then was covered with plastic sheets and allowed to cure for one week. Both the RPM and crushed stone aggregate base courses failed under the compactor due to heavy rainfall. Both were excavated and air dried. The RPM and crushed stone aggregate sections were compacted in early October 2007, and all three sections were then paved with a 102 mm HMA wearing course was paved.

One pan lysimeter was installed in each of the three sections during construction directly beneath the base course layer to collect leachate discharged from the layers above (Fig. 2.1). The lysimeters are located beneath the HMA wearing course, off set to one side, approximately 600 mm. from the shoulder along the closest side. Photographs of lysimeter construction are included in Appendix A. Leachate has been monitored since October 2007.

## SECTION 3

### 3. METHODS AND MATERIALS

#### 3.1. FLY ASH

Fly ash is classified based on chemical composition by ASTM C 618 as either Class C or Class F. Fly ash that does not meet the requirements of Class C or F is often referred to as “off-specification”. The composition within a class can vary significantly (US EPA 2008). The majority of the fly ash that is recycled in the United States is Class C or F (US EPA, 2008).

Fly ash is in a highly oxidized state and chemically reacts and cements in the presence of water and lime (CaO and CaOH) at standard conditions. Lime may already be present in the ash, constituting a self-cementitious fly ash, or lime may be added to produce cementitious ash. This study employed Riverside 8 cementitious fly ashes for stabilization of base course or subgrade. Riverside 8 fly ashes are from Xcel Energy’s Riverside Power Plant. Chemical and physical properties of one sample of Riverside 8 fly ash are presented as Table 3.1.

Riverside 8 fly ash was captured using electrostatic precipitators. Fly ashes are classified for use as either Class C or Class F by ASTM C 618 and AASHTO M 295. Riverside 8 does not meet the requirement for Class C or F, and is considered an off-specification ash due to its high carbon content (>5%) (Table 3.1). Elemental composition of the Riverside 8 ash is presented in Table 3.2. The major components of the fly ash (in descending order) are Ca, Al, S, Fe, Mg, Na, Si, P, K, Ba, and V. All other elements comprised less than 0.1% of the fly ash mass (Table 3.2).

### **3.2. BASES COURSE MATERIALS**

Particle size distribution of the RPM used at the MnROAD site is presented in Figure 3.1. The RPM classifies as well graded silty gravel (GW-GM) in the USCS system and A-1-a in AASHTO.

### **3.3. FIELD LEACHATE MONITORING**

The pan lysimeters were employed in this study to monitor leachate transmitted from the overlying pavement layers. A profile of a pan lysimeter is shown in Fig. 3.2. A depression was excavated to the size of the desired lysimeter and the depression bottom was graded for drainage to a single point. A 120-L HDPE leachate collection tank was installed along the road shoulder, buried approx. 2 m deep. The tanks were connected to the lysimeter through a trench using PVC pipe with adequate drainage gradient from the pan to the tank, and were connected vertically to the surface for leachate collection. The depression was lined with 1.5 mm thick LDPE geomembrane which was connected and heat-sealed to the PVC drainage pipe. A drainage layer consisting of geonet between two layers of geotextile was installed in the lysimeter. The stabilized layers were then compacted above the lysimeter. Photographs of lysimeter construction are located in Appendix A.

Leachate in the 120-L tanks was pumped and sampled periodically. Volume of leachate discharged from the layer was recorded and total pore volumes of flow (PVF) were calculated from the porosity of the stabilized layer. Volumetric fluxes from the layers were compared to local precipitation data. A daily precipitation rate was averaged for each month of the study (mm/day), and flux from the layer (mm/day) was calculated from the volume of leachate collected, the time between tank pumping events, and the area of the lysimeter. Long term average fluxes were calculated from the total volume collected, lysimeter area, and total days of lysimeter operation.

Aqueous samples were collected for chemical analysis during pumping events. All samples were collected in HDPE sample bottles with zero head space. Within 24 hr of sampling pH and oxidation-reduction potential (Eh) were measured in the laboratory. The equipment used to test pH and Eh varied over the course of the study. The leachate was then filtered with a 0.2  $\mu\text{m}$  micropore filter and preserved to pH<2 using trace-metal-grade  $\text{HNO}_3$ .

### **3.4. LABORATORY LEACH TESTS**

#### **3.4.1. Column Leach Tests (CLTs)**

Column leach tests (CLT) were conducted on materials from MnROAD. The column testing conditions are summarized in Table 3.3. The CLTs were used to evaluate leaching under saturated steady-flow conditions.

Specimens were prepared from each material by compaction to field dry unit weight and water content (Table 3.3). Material was mixed to field water content using deionized water in a spray bottle, and compacted in rigid wall permeameters by mallet and tamp in several lifts. After compaction the stabilized specimens were cured for one week at constant temperature and 100% humidity.

All specimens were permeated from bottom to top with 0.1 M LiBr solution using peristaltic pumps. This solution was chosen to simulate percolate in regions where salt is used to manage ice and snow (Bin-Shafique *et al.* 2006). Neither lithium nor bromide have drinking water maximum contaminant levels (MCLs), and therefore would not be chemicals of interest in the leachate analysis. Effluent was collected in sealed Teflon bags to minimize chemical interaction with the atmosphere. Volume of leachate was measured by weighing the bag afterwards, and total pore volumes of flow (PVF) were calculated using weight-volume computations based on layer compaction and material properties. A sample was collected for chemical analysis and filtered with 0.2  $\mu\text{m}$

micropore filters and preserved with trace-metals-grade nitric acid to  $\text{pH} < 2$ . The Teflon bags were rinsed with deionized water between sampling events.

#### **3.4.2. Water Leach Tests (WLTs)**

Water leach tests (WLTs) were conducted on the three materials from MnROAD according to ASTM D3987-85. The stabilized materials were compacted to average field dry unit weight and water content, and then were cured for 7-d at constant temperature and 100% humidity. After curing, the stabilized materials were crushed by hand until the grain size gradation appeared similar to the unstabilized RPM.

WLTs were conducted on all the materials using a 20:1 liquid:solid (L:S) ratio (by mass) with deionized water as the eluent as described in the ASTM D3987-85. The materials were also tested with deionized water at 3:1, 5:1, and 10:1 L:S ratios. Only the 20:1 ratio is described in the standard.

Leaching was conducted in 2-L HDPE bottles rotated for eighteen hours. Afterwards the solids were allowed to settle 5 min., and then a sample was collected from the supernatant using a wide mouth syringe. The sample was filtered with 0.2- $\mu\text{m}$  micropore filters, and preserved to  $< \text{pH}$  of 2 using trace-metal-grade  $\text{HNO}_3$ . Pictures of the WLTs are in Appendix A.

### **3.5. LEACHATE ANALYSIS**

#### **3.5.1. Chemical Indicator Parameters**

The  $\text{pH}$  and oxidation-reduction potential (Eh) of all field and laboratory leachate samples were measured in the laboratory within 24 hours of sampling. The water quality instruments used for leachate testing varied between sites and over the years of testing.

### 3.5.2. Major and Minor Elements

The methods used for chemical analysis were inductively coupled plasma (ICP) and cold vapor atomic fluorescence spectrometry (CVAFS). These methods with the dates of use, chemicals analyzed for, and minimum detection limits are summarized in Table 3.4.

Field and laboratory leachates for were analyzed by inductively coupled plasma - optical emission spectrometry (ICP-OES) using a Varian Vista-MPX CCD Simultaneous ICP-OES instrument for 23 elements. The analytes tested for using ICO-OES are presented with MDLs in Table 3.4.

Beginning in 2008 leachate from field lysimeters was sampled and analyzed for mercury (Hg) using USEPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (CVASF). All sampling equipment that contacted the leachate samples was acid cleaned, dried, and double bagged in cleaned and sealed bags. Samples were collected using two people following the procedure in USEPA Method 1669. In this method, one person only touched the sample bottle and the inner of the two bags containing the bottle. Handling of the outer of the two bags containing the sample bottle and all other equipment and was conducted by the other person. A field blank and duplicate sample were collected for every 10 to 15 lysimeters sampled. Samples were collected in LDPE bottles with zero head space All Samples were maintained at 4° C, and were preserved and analyzed according to USEPA Method 1631.

Minimum detection limits (MDL) for ICP-OES and CVAFS are determined for each instrument and set of calibration solutions according to US Code of Federal Regulations Title 40, Appendix B to Part 136. The method and analytes tested for are presented with MDLs in Table 3.4.

## SECTION 4

### 4. RESULTS AND DISCUSSION

#### 4.1. FIELD LEACHING BEHAVIOR

##### 4.1.1. Precipitation Patterns and Lysimeter Drainage

The flux of leachate from the bottom of the stabilized RPM and control layers was compared to the local precipitation rate for the site location. Short-term leachate fluxes and precipitation rates from stabilized RPM are shown in Fig. 4.1. Peak fluxes from the layers tend to occur in the spring months when heavy rains and snow melt occur, and again in late summer and early fall (Figs. 4.1). The minimum flux tends to occur in the winter when precipitation and pore water are often frozen, and in July or August when evaporation tends to exceed precipitation in the upper Midwest. Occasionally the flux from the stabilized layers approaches 15% of precipitation (Fig. 4.1). However, as shown subsequently, the long-term average is never more than 7.8% for stabilized RPM (Fig. 4.2). Short-term fluxes were calculated from the volume of leachate collected during each pumping event, the surface area of the lysimeter pan, and the time between pumping events ( $\text{Flux} = \text{Volume}/\text{Area}/\text{Time}$ ). The daily precipitation corresponds to an average of the precipitation per day during each month (Figs. 4.1 and 4.2) (NOAA 2009).

Long-term fluxes from the pavement layers and precipitation rates averaged over the entire time of the study are shown in Fig. 4.2. Long-term flux of leachate discharged from the fly-ash-stabilized layers was 7.8% of the local precipitation. Flux from the RPM control base course was 6.1% of precipitation and flux from the stone aggregate base course was 14% of precipitation (Fig. 4.2).

The regional average percentage of precipitation recharging the groundwater is estimated to range from 19% to 24% for the MnROAD site (USGS 2007). The asphalt wearing course on the roadway likely has lower permeability than adjacent road shoulder and native soils. Therefore recharge rates in the areas adjacent to a stabilized roadway may be significantly higher than the percentage of precipitation that leaches from the stabilized layers, which may affect the transport of leachate in the subsurface.

According to the US National Weather Service (May 2009), the annual precipitation in the region that includes MnROAD ranges from approximately 500 mm to 900 mm, with an average of 750 mm. Based on the leachate volumes collected, total annual flux from a stabilized base course in eastern-central Minnesota should range from 11 to 70 mm/year.

Long-term fluxes from the layers were calculated from the total volume of leachate collected, the surface area of the lysimeter pan, and the total time of leachate collection, and are shown in Fig. 4.2 with long-term average precipitation rates for each site during the testing periods (NOAA 2009). The long-term average precipitation was calculated as the total precipitation during the study divided by the total time of the study.

#### **4.1.2. Chemical Indicator Parameters**

The pH and Eh of the leachates collected in the lysimeters are presented in Fig. 4.3. The pH in field leachate ranged from 5.9 to 8.2, with most of the data between 7 and 8 (Fig. 4.3.a) for both stabilized and control materials. Ganglof *et al.* (1997) found near neutral pH in leachate collected from fly ash amended sandy soil using ceramic-cup pore-water lysimeters in an agricultural field. The leachate from all materials was oxidizing ( $Eh > 0$ ), with Eh data ranging from +121 to +143 mV. The Eh of leachate from

the stabilized RPM appears becoming more oxidizing as the total PVF increases (Fig. 4.3.b). All field leachates were clear to yellow and had no noticeable odor.

#### **4.1.3. Elements Released and Magnitude of Concentrations**

Of the twenty-three trace elements considered in the analysis (Ag, Al, As, B, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, and Zn), all except Al, Be, Pb, and Ti were present in detectable quantities in leachate from the fly-ash-stabilized RPM. The elements detected in the leachate are presented in Table 4.1 with the peak concentration and average peak concentration (average of the three highest concentrations). The following elements are presented in order of descending peak concentration observed in leachate from the fly-ash-stabilized materials (Table 4.1): Mo (peak concentration of 18,176  $\mu\text{g/L}$ ), Sr, B, Mn, and V (peak concentration between 10,000 and 1,000  $\mu\text{g/L}$ ), Fe, Se, Zn, Tl, Cr, and As (peak concentration between 1,000 and 100  $\mu\text{g/L}$ ), and Sb, Sn, Cu, Cd, Ni, Co, and Ag (peak concentration between 100 and 1  $\mu\text{g/L}$ ). Peak concentration of Hg was less than 0.1  $\mu\text{g/L}$ .

#### **4.1.4. Elution Patterns**

Concentrations of each element recorded in each lysimeter are reported as a function of PVF in Appendix B. Among elements that were detected at the site, 72% of elements had the peak concentration occur during the first two PVF (Table 4.2). As an example of early peak concentration, the leaching pattern of Cd and Cr is shown in Fig. 4.4.

## 4.2. POTENTIAL ENVIRONMENTAL IMPACTS

### 4.2.1. Field Concentrations Compared to Control Sections

An analysis was conducted to determine if element concentrations in leachate from stabilized materials were elevated relative to concentrations in leachate from adjacent control sections. The average peak concentration and the geometric mean of all observed concentrations for each site and element were compared. The determination of concentration elevation was conducted using Equation 1.

If

$$(C^*_c + 2\sigma) \geq (C^*_s - 2\sigma)$$

Then, the concentration from stabilized material *was not* significantly elevated relative to concentration from control material.

**Eq. 1**

If

$$(C^*_c + 2\sigma) \leq (C^*_s - 2\sigma)$$

Then, the concentration from stabilized material *was* significantly elevated relative to concentration from control material.

$C^*_s$  = Average peak or geometric mean concentration from stabilized materials

$C^*_c$  = Average peak or geometric mean concentration from control materials

$\sigma$  = Standard deviation

$\sigma$  was obtained as a product of the average peak or geometric mean concentration and the coefficient of variation (COV), and COV for each element was calculated from 7 replicates tested on the ICP-OES at 20  $\mu\text{g/L}$ .

10 of the 23 elements had average peak concentrations (average of the three highest concentrations) or geometric mean (of all samples) concentrations that were elevated in leachate from stabilized materials relative to the concentration from the control materials. These (in order of descending magnitude of concentration elevation): Mo, B, V, Sr, Cr, Se, As, Mn, Cu, and Cd (Table 4.3).

#### **4.2.2. Elements Exceeding Regulatory Maximum Contaminant Levels**

Concentrations of all elements observed in lysimeter leachates were compared to the maximum contaminant levels (MCLs) for groundwater or drinking water promulgated by the States of Minnesota (Minnesota - MN MDH IC 141-0791). The US government also has enforceable MCLs for groundwater (US CFR Title 40 Chapter 141.62), but the State MCLs are equal to or lower than those promulgated by the US government (Table 4.4). Please note that although Minnesota does not have a MCL for Mo, the Wisconsin MCL was used to compare Mo concentrations.

Concentrations of the following ten elements in lysimeter leachate from fly-ash stabilized materials exceeded MCLs at least once: As, B, Cd, Cr, Mo, Pb, Sb, Se, Tl, and V (Table 4.5). The other thirteen elements never exceeded an applicable MCL in leachate from stabilized materials. Concentrations observed in the lysimeters are only representative of leachate as it exits the bottom of the stabilized or control layer, and do not represent concentrations as leachate drains downward from the pavement through the unsaturated zone and then merges with local groundwater flow. Adriano *et al.* (2002) found elevated As, B, Be, Ba, Mo, and Se in pore water in fly ash amended soil, but found all these elements were below detection limits in groundwater collected from a depth of 3.6-m below the amended soil.

##### **4.2.2.1. Concentrations Exceeding MCL and Elevated Compared to Control**

Concentrations of B, Mo, V, Cr, As, and Cd in leachate from fly-ash-stabilized materials exceeded MCLs and were elevated relative to the adjacent control sections (Figs. 4.5 to 4.10) (Table 4.3).

#### **4.2.2.2. Concentrations Exceeding MCL but Not Elevated Compared to Control**

Concentrations of Pb, Sb, Se, and Tl in leachate from fly-ash-stabilized materials exceeded MCLs but were not elevated relative to the adjacent control sections (Figs. 4.11 to 4.14) (Table 4.3).

#### **4.2.3. Effects of pH and Eh on Element Mobility**

Chemical speciation of elements in the roadway pore water will affect element mobility and concentrations. Elements that exist as anions, oxy-anions, or non-ionic soluble molecules at the range of pH and Eh in the field leachate are less likely to be sorbed to solids, and therefore will have greater mobility than elements that form cations (which are likely to sorb on mineral surfaces) or elements that precipitate out as a solid (Jury and Horton 2004). For the elements that exceeded MCLs the most probable speciation was estimated by pH-Eh speciation diagrams produced by the Geologic Survey of Japan (2005). All probable species over the range of pH and Eh observed in the field leachates were included (Table 4.6). Speciation was not determined in the laboratory.

Six of the ten elements that exceeded MCLs are likely to form anions, oxy-anions, or non-ionic soluble molecules at the observed pH-Eh conditions (As, B, Mo, Sb, Se, and V). Four of the elements primarily form cations (Cd, Cr, Pb, and Tl) (Geologic Survey of Japan 2005) (Table 4.6).

Three elements had concentrations exceeding MCLs in early PVF and then fall below the MCL (Cd, Cr, and Se). Two of these elements (Cd and Cr) primarily form cations at field pH-Eh conditions. Se is likely to be present as an anion or oxy-anion.

Seven elements had concentrations that persistently exceed MCLs for at least two to three PVF (As, B, Mo, Pb, Sb, Tl, and V). Five of these elements (As, B, Mo, Sb, and V) form anions, oxy-anions, or non-ionic soluble molecules at field pH-Eh conditions (Table 4.6). The other two elements with concentrations that persistently exceed the MCL (Pb and Tl) primarily form cations at the observed field pH-Eh conditions.

### **4.3. LABORATORY TESTS**

Two laboratory leaching methods were employed on samples of fly-ash-stabilized and control materials prepared in the laboratory using materials obtained from the field sites, and using field conditions whenever possible. Chemical properties of the laboratory leachates were compared to those of the field lysimeter leachates to determine the effectiveness of the tests in predicting field leachate qualities. The tests performed were Column Leach Tests (CLTs) and Water Leach Tests (WLTs). CLTs and WLTs were conducted on stabilized RPM and two control materials; RPM and crushed stone.

#### **4.3.1. Chemical Indicator Parameters**

The pH of the CLT and field leachates are presented in Fig. 4.15. The pH of leachate from the fly-ash-stabilized CLTs is 3 to 4 pH units higher than from the same materials in the field (Fig. 4.15). All field leachate had pH near neutral (Fig. 4.4.a). The CLT leachate from the control materials also tended to be near neutral. In contrast, the pH of leachate from stabilized CLTs remained elevated relative to the field pH for over 45 pore volumes of flow, which is longer than the life-cycle flow for most of the field lysimeters. The lower pH in the field compared to WLTs and CLTs on stabilized material

may be due to unsaturated conditions in the field. Microbial respiration in the field can enhance soil pore gas CO<sub>2</sub> (Zwick *et al.*, 1984). Diffusion of CO<sub>2</sub> from the atmosphere or microbial respiration into pore water may form weak carbonic acid and may reduce the pH. In contrast, the CLTs are saturated and therefore have no opportunity for CO<sub>2</sub> to reduce the pH. The pH of WLT leachate from MnROAD materials was also 3 to 4 pH units higher than field leachate. Bin-Shafique *et al.* (2006) also found similar pH levels in leachate from CLT and WLT on stabilized soils and sand. The WLT data is given in Appendix C.

The Eh of the CLT and field leachates are presented in Fig. 4.16. Leachate from stabilized RPM consistently had positive oxidation-reduction potential (Eh), of approximately +150 mV, indicating oxidized conditions (Fig. 4.16). The stabilized RPM CLT leachate had lower Eh than the field, ranging generally from -5 mV to +40 mV. Leachate from control CLTs had similar Eh to the field leachates.

The differences in Eh between field and CLT concentrations are likely associated with the differences in pH between field and CLT concentrations. For field and CLT leachates (the only site with CLT, pH, and EH results), leachate Eh is linearly correlated moderately well (and statistically significant) with leachate pH ( $R^2 = 0.80$ , F-Test  $P = 5.7 \times 10^{-20}$ ) (Fig. 4.17). Altering the CLT method used in this study to obtain pH near neutral in CLT leachate may cause the Eh of CLT leachate to more closely match the observed field Eh.

### 4.3.2. Column Leach Tests

#### 4.3.2.1. Prediction of Field Leaching Concentrations

Average peak concentrations of 23 elements (calculated from the mean of the three highest concentrations) in leachate from the field lysimeters and CLTs on the same materials are compared in Fig. 4.18. The comparison of field and CLT concentrations was conducted to determine the usefulness of the CLTs in estimating field average peak concentrations. The average peak concentrations from the CLTs are within one order of magnitude of the average peak field concentration for 77% of elements (Fig. 4.18). Graphs of all field concentrations as a function of PVF are included in Appendix B and all CLT concentrations as a function of PVF are included in Appendix C.

Of the six elements in field leachate with concentrations elevated relative to the control section and exceeding MCLs (As, B, Cd, Cr, Mo, and V), four also exceeded the MCL and were elevated in the CLT leachate (B, Cr, Mo, and V) (Fig. 4.19) (Tables 4.7 and 4.8). Concentrations of these four elements were among the most elevated relative to the control concentrations. In addition, concentrations of B, Mo, and V may remain higher than MCL for many pore volumes of flow in both the field and CLTs.

The CLT provided measurable concentrations of all 23 elements analyzed, and was most successful at estimating the average peak field concentrations for the three elements most likely to leach at concentrations above MCL for long periods of time (B, Mo, and V).

Concentrations of As, Cd, and Pb exceeded the MCL and were elevated relative to control concentrations in the field but not in CLTs. Concentrations of these elements were only slightly elevated in the field but not in the CLT. Of these elements, only As had a peak field concentration greater than 20  $\mu\text{g/L}$ .

Average peak field concentrations of As and Cd may be significantly underestimated by the CLT procedure used in this study. The CLT concentrations of As and Cd tend to be below or near the detection limit and well below the MCL. In contrast, the peak field concentrations for these elements may exceed the MCL. For example, the average peak field concentration of As was 26 times the average peak from the CLT, and Cd was 15 times the peak from the CLT. Detection limits for Pb differed significantly for the field and CLT leachates. All field Pb concentrations were below the detection limit (above the MCL) and most CLT concentrations were below a lower detection limit (below the MCL). Because of these differences the ability of CLTs to predict field leaching of Pb can not be adequately assessed from this study.

Of the three elements that exceeded MCLs in the field but were not elevated relative to control materials (Sb, Se, and Ti) all three also exceeded the MCL in CLTs. However, Sb and Se concentrations were elevated relative to controls concentrations from the CLTs. These differences are possibly due to differences in pH and Eh between the field and CLT leachates.

#### **4.3.2.2. Comparison of Leaching Patterns**

Under saturated constant-flow conditions in the CLTs, concentrations of thirteen of the 24 elements displayed a first-flush elution pattern, with the peak concentration occurring during the first or second PVF (Ag, B, Be, Cd, Cr, Cu, Mo, Mn, Sb, Se, Sr, V, and Zn). All of these elements also had first-flush elution pattern for at least one field site. Concentrations of these thirteen elements peaked at an average of 1.5 PVF, with the latest peak at 6 PVF for Zn. The remaining 11 elements either had very low initial CLT concentrations (As, Co, Hg, Ni, Pb, Sn, Ti, and Tl) and long-term concentrations

just above or below the MDL, or had distinctly different leaching patterns (Al, Ba, and Fe). Elements that exceeded the MCL and did not have a first-flush pattern in the CLTs were As, Ni, Pb, and Tl.

Flow through the CLT columns was halted after approximately 40 pore volumes of flow. The columns were then left saturated with no flow for 54 days, and then restarted. Concentrations of 11 elements then increased when flow was restarted (As, B, Be, Cd, Cu, Mo, Sb, Se, Sr, V, and Zn). This spike in concentrations suggests that under the constant flow conditions in the CLT the flow rate prevented the aqueous concentrations from coming to an equilibrium state with the solids. Following the spike, concentrations decreased to those observed just before the flow was stopped (Fig. 4.21).

Three elements had the concentration rise back to original peak (Sb), or higher (1.5 to 2.9 times) after the columns were restarted (As and Cd), although As and Cd had very low initial CLT concentrations. For the other seven elements the initial peak concentration was significantly higher than the secondary peak concentration caused by the stoppage and restarting (1.5 to 14 times higher than the secondary peak).

### **4.3.3. Water Leach Tests**

#### **4.3.3.1. Prediction Of Field Leaching Concentrations**

Peak concentrations from the field are compared with concentrations from WLTs on the same materials in Figure 4.22.a. Four liquid to solid mass ratios were tested (3:1, 5:1, 10:1, and 20:1) to determine if decreasing the ratio from the standard 20:1 (ASTM D3987-85) improved the ability of the WLT to predict peak field concentrations. Figure 4.25.a shows that the 3:1 WLT most closely estimated the peak field concentrations. For

elements that were detectable in the 3:1 WLT the concentrations were within one order of magnitude of the peak field concentration for 91% of tests (Fig. 4.22.b). All further discussion of the WLTs will refer to the 3:1 WLT.

Of twenty elements that were detected in field leachate, eight elements (Ag, Cd, Co, Fe, Mn, Se, Sn, and Ti) were not detected in 3:1 WLTs on the materials. Of these elements, three (Cd, Se, and Ti) had concentrations that exceeded the MCL in field leachate from stabilized materials, but only Cd was found to be elevated relative to the control sections.

The WLT was most useful in predicting field concentrations of elements when peak field concentration was greater than 200 µg/L. Seven of the eight elements that were not detected in WLT leachate had peak field concentrations of 170 µg/L or less. All elements with peak field concentrations of 500 µg/L or greater were detected in the WLT

#### **4.3.4. Comparison of CLT and WLT Prediction Of Field Leaching**

The detection limits for the WLT samples was generally higher than those for the CLT samples, and are shown in Table 3.4. Figure 4.23.a shows the predictive ability of the CLT and WLT with two differing sets of detection limits. When the CLT has lower detection limits than the WLT, the CLT detects all elements, and is better at predicting the field concentrations of elements that have lower (< 500 µg/L) peak field concentrations. If the higher WLT detection limits are applied to the CLT data, the WLT and CLT become very similar in their ability to predict peak field concentrations of elements that exceeded MCLs in the field (Fig. 4.23.b). The WLT may have been more

successful at predicting elements with lower peak field values if the WLT samples were analyzed with lower detection limits similar to those for the CLT leachates (Table 3.4)

Using the same higher (WLT) detection limits for both tests, the WLT fails to detect 45% of elements detected in the field, 36% of elements that exceeded MCLs in the field (Cd, Sb, Se, and Tl), and 13% of elements that exceeded MCL and were elevated relative to the control in the field (Cd). The CLT fails to detect 25% of elements detected in the field, 27% of elements that exceeded MCLs in the field (Cd, Ni, and Pb), and 38% of elements that exceeded MCL and were elevated relative to the control in the field (Cd, Ni, and Pb).

## SECTION 5

### 5. CONCLUSIONS

#### 5.1. Conclusions from Field Results

- Flux discharged from the stabilized roadway layers is expected to be 2% to 8% of precipitation for stabilized RPM base course. Flux discharged from the stabilized roadway layers is also less than the average regional recharge rates likely to occur in areas immediately adjacent to the road (average recharge is approximately 20% of precipitation).
- Peak volumetric fluxes from the layers tend to occur in the spring months when heavy rains and snow melt occur, and again in the late summer and early fall. Minimum fluxes tend to occur in the winter when precipitation and pore water are often frozen, and in July or August. Occasionally the flux from the stabilized materials approaches 15% of precipitation for a period of several months, but the long-term average is never more than 7.8% of precipitation.
- All field cells had pH near 7 and predominantly oxidizing Eh of approximately +150 to +300 mV.
- Among elements that were tested for during the entire operation of the site and that were detected at the site, 61% of elements had the peak concentration occur during the first two PVF.
- B, Mo, and V concentrations in leachate from the fly-ash-stabilized materials were elevated relative to concentrations from the control sections, have peak concentrations above the MCL, and exceed the MCL for many PVF.

- Both As and Pb have concentrations that remain near the MCL and were observed to periodically exceed the MCL over many PVF. The concentrations of As and Pb are only slightly statistically elevated relative to the control concentrations.
- At sites where Cd and Cr exceeded the MCL, they only exceeded the MCL during the first sampling event (PVF at Peak  $\leq 0.26$ ) and were below in all subsequent PVF.

## 5.2. Conclusions from Laboratory Results

- When using lab tests to predict field leaching concentrations, an analytical method with minimum detection limits equal to or less than the lowest MCL should be used. Peak concentrations of many elements in leachate from the CLTs and WLTs are likely to be less than peak concentrations from the field leachate. Elements that are not detected in the lab tests may be present in field leachate, and may exceed the MCL in the field. The method detection limits should be determined before testing of samples begins.
- The pH of leachate from CLT and WLT on stabilized materials (generally 10 to 11) is higher than from the same materials in the field (6 to 8). Eh of leachate from CLT and WLT on stabilized materials is lower (-5 to +40 mV) than from the same materials in the field (mostly between +150 to +300 mV), where leachate was generally oxidizing. The differences in pH and Eh between stabilized materials in the field and in a CLT may be caused by the difference in conditions (saturated flow in CLTs and unsaturated flow in the field. This may affect element speciation, solubility, and mobility, and therefore affect the prediction of field concentrations using the CLT and WLT methods employed in this study.
- CLT average peak concentration was within one order of magnitude of the average peak field concentration 77% of the time. CLT provides similar results (concentrations above the MCL, elevated relative to the control, and 1.1 to 3.5 times higher than the field average

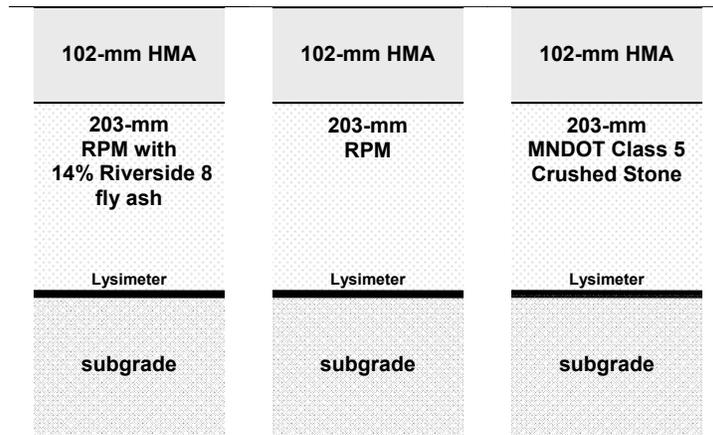
peak) for the elements consistently elevated relative to the control concentrations and MCLs (B, Mo, and V), as well as for Cr (CLT average peak 8.6 times higher than the field average peak).

- Three elements exceed the MCL in the field, but not in the CLTs (As, Cd, and Pb). These were either only slightly elevated in the field but not in the CLT (As, Cd, and Pb), or elevated in both the field and CLT (Ni).
- Three elements exceeded MCLs in the field but were not elevated relative to control materials (Sb, Se, and Tl), and also exceeded the MCL in CLTs. However, Sb and Se were elevated relative to controls in the CLT.
- B, Cd, Cr, Mo, Sb, Se, and V exceeded MCLs in field leachate and had first-flush leaching patterns in CLTs. As, Pb, and Tl exceeded the MCL in the field and did not have a first-flush CLT patterns.
- Stopping and restarting the CLTs caused concentrations of 11 of the elements to experienced a spike (As, B, Be, Cd, Cu, Mo, Sb, Se, Sr, V, and Zn). This spike in concentrations suggests that under the constant flow conditions in the CLT the flow rate prevented the aqueous concentrations from coming to an equilibrium state with the solids. Following the spike, concentrations decreased to those observed just before the flow was stopped.
- Of the four liquid to solid ratios tested, the 3:1 WLT provides the best prediction of field peak concentrations. Of twenty elements that were detected in field leachate at the MnROAD site, eight of these were not detected in 3:1 WLTs on the materials. Seven of the eight elements that were not detected in WLT leachate had peak field concentrations of 170 µg/L or less. All elements with peak field concentrations of 500 µg/L or greater were detected in the WLT. If

the WLT leachates were analyzed with lower detection limits, the 3:1 WLT may have detected more or all of the elements detected in the field.

- When CLT and WLT results are compared using the same detection limits the ability of both tests to predict peak field concentrations is similar. Both have peak or average peak within one order of magnitude of the field for B, Mo, and V, which have peak concentrations above the MCL for many PVF.

**FIGURES**



HMA = Hot Mix Asphalt

RPM = Recycled  
Pavement Material

Fig. 2.1. Profiles of Fly-Ash Stabilized and Control Roadway Sections Being Evaluated at the Field Site

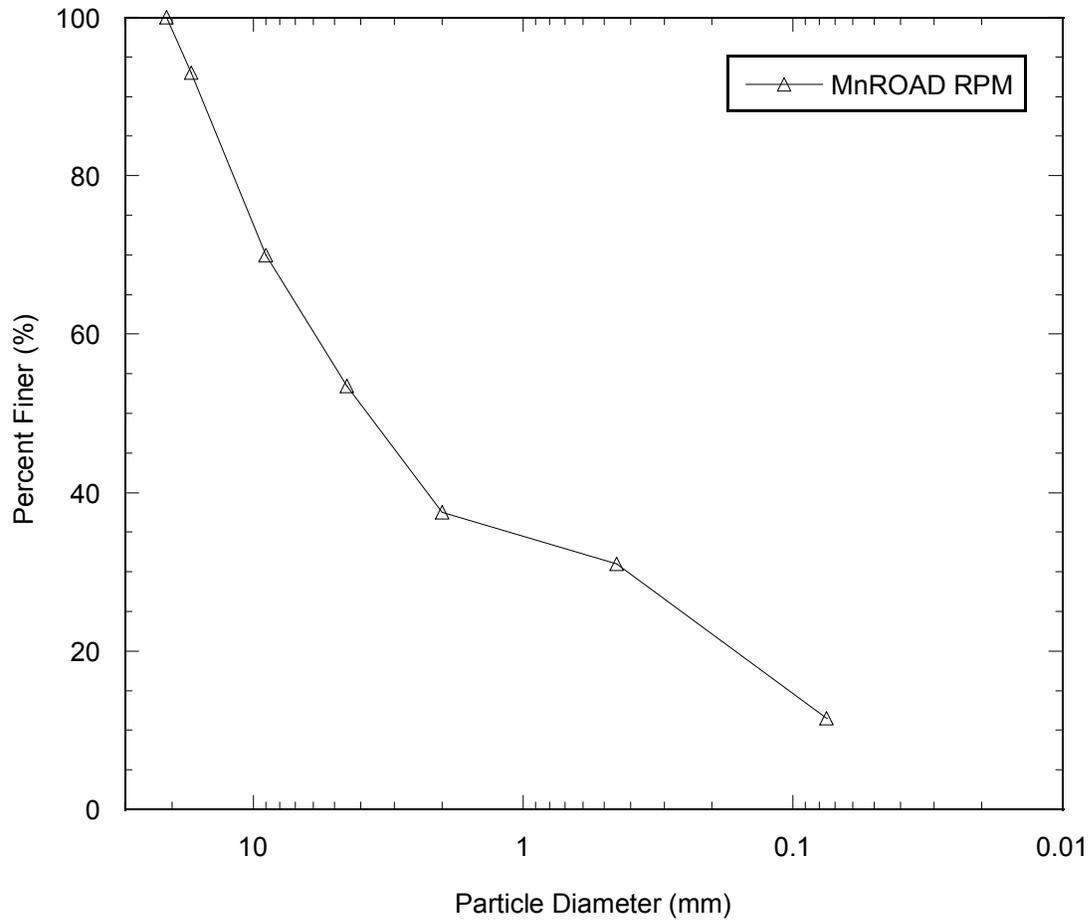


Fig. 3.1. Particle Size Distribution of RPM

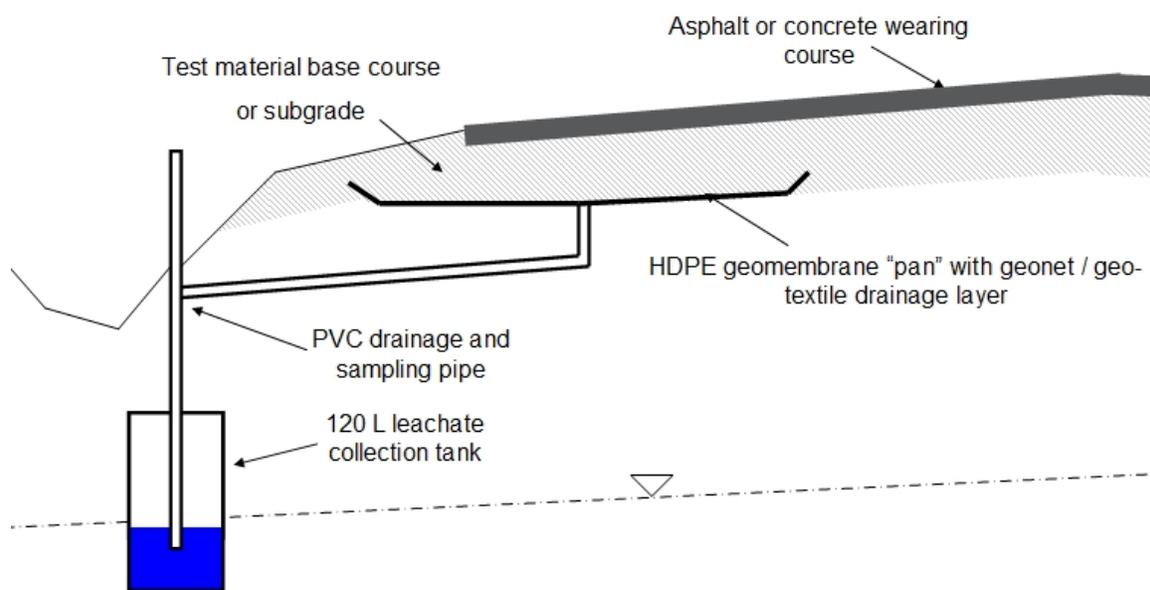


Fig. 3.2. Profile of pan lysimeter construction

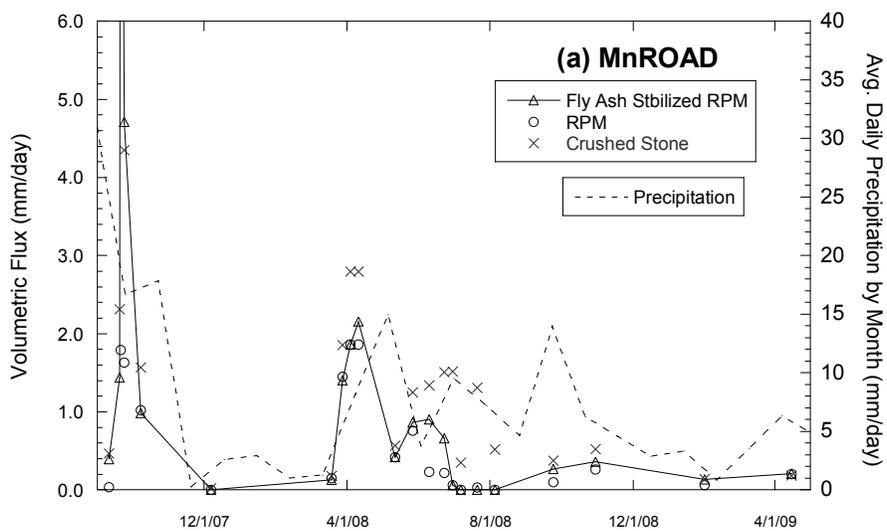


Fig. 4.1. Volumetric flux from the stabilized RPM base courses and control layers with local average daily precipitation rates

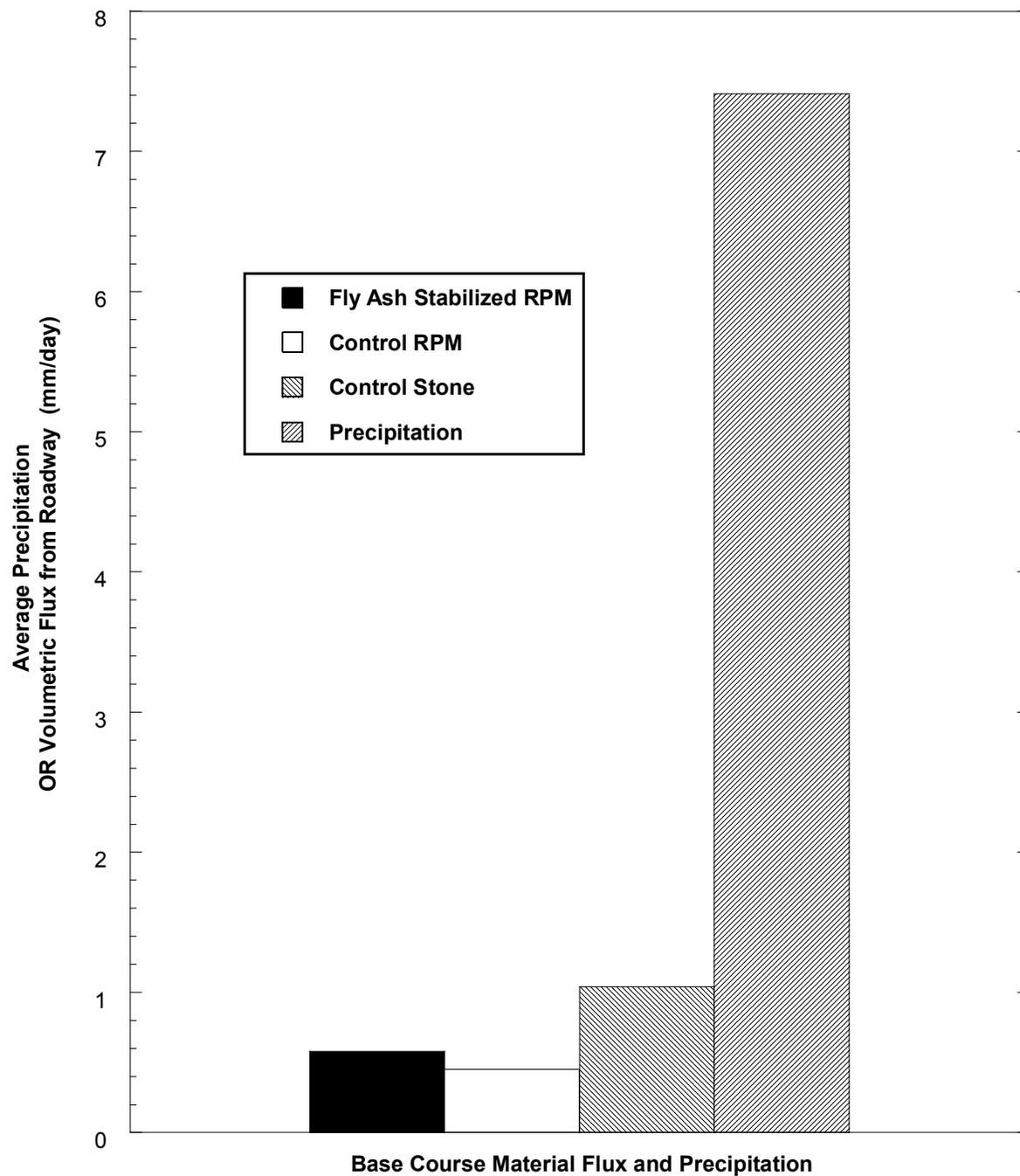


Fig. 4.2. Comparison of Long-term Volumetric Flux from the Road Layers Relative to Average Daily Precipitation

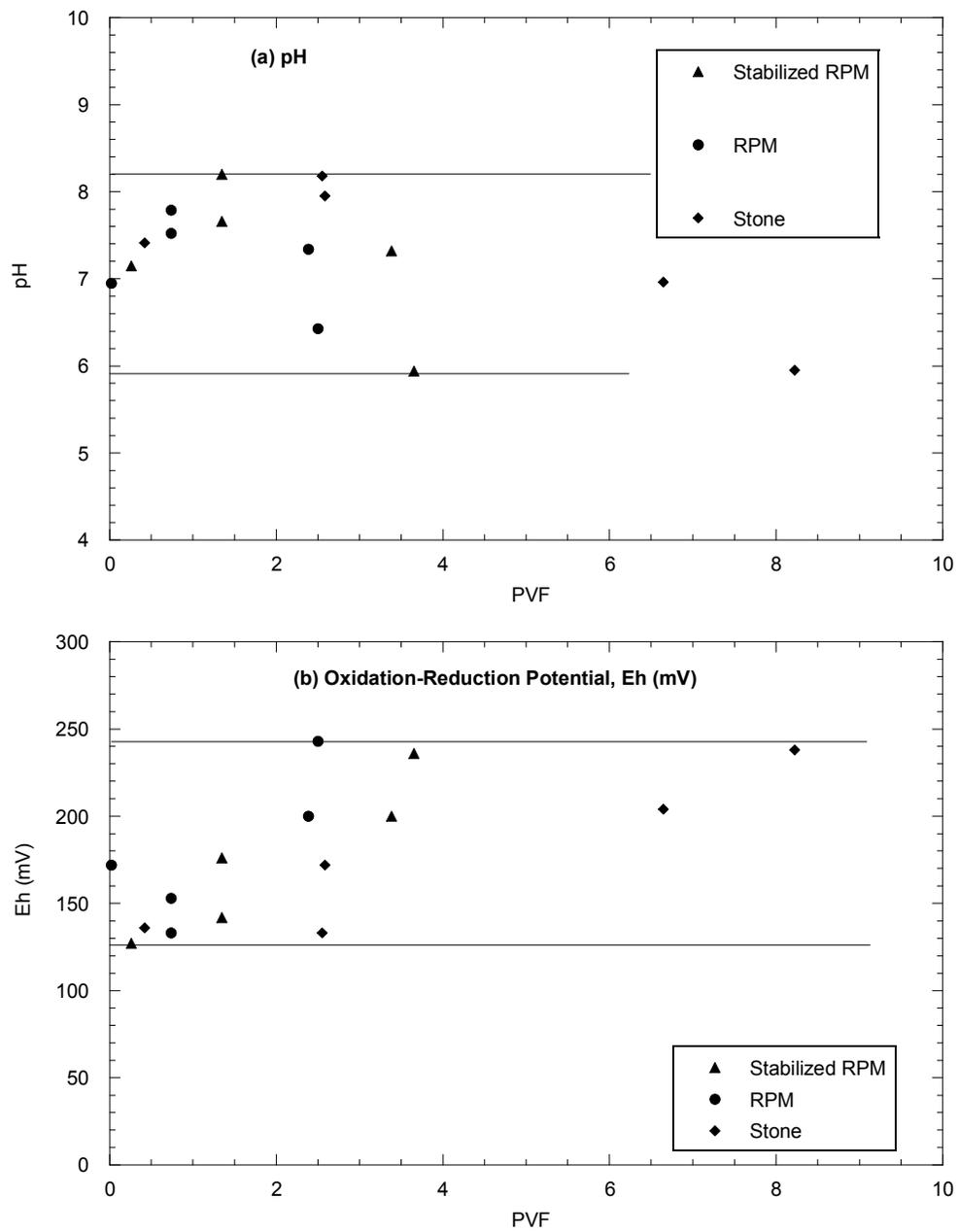


Fig. 4.3. (a) pH and (b) Eh of Leachate from Field Lysimeters for Fly-ash-stabilized and Control Materials.

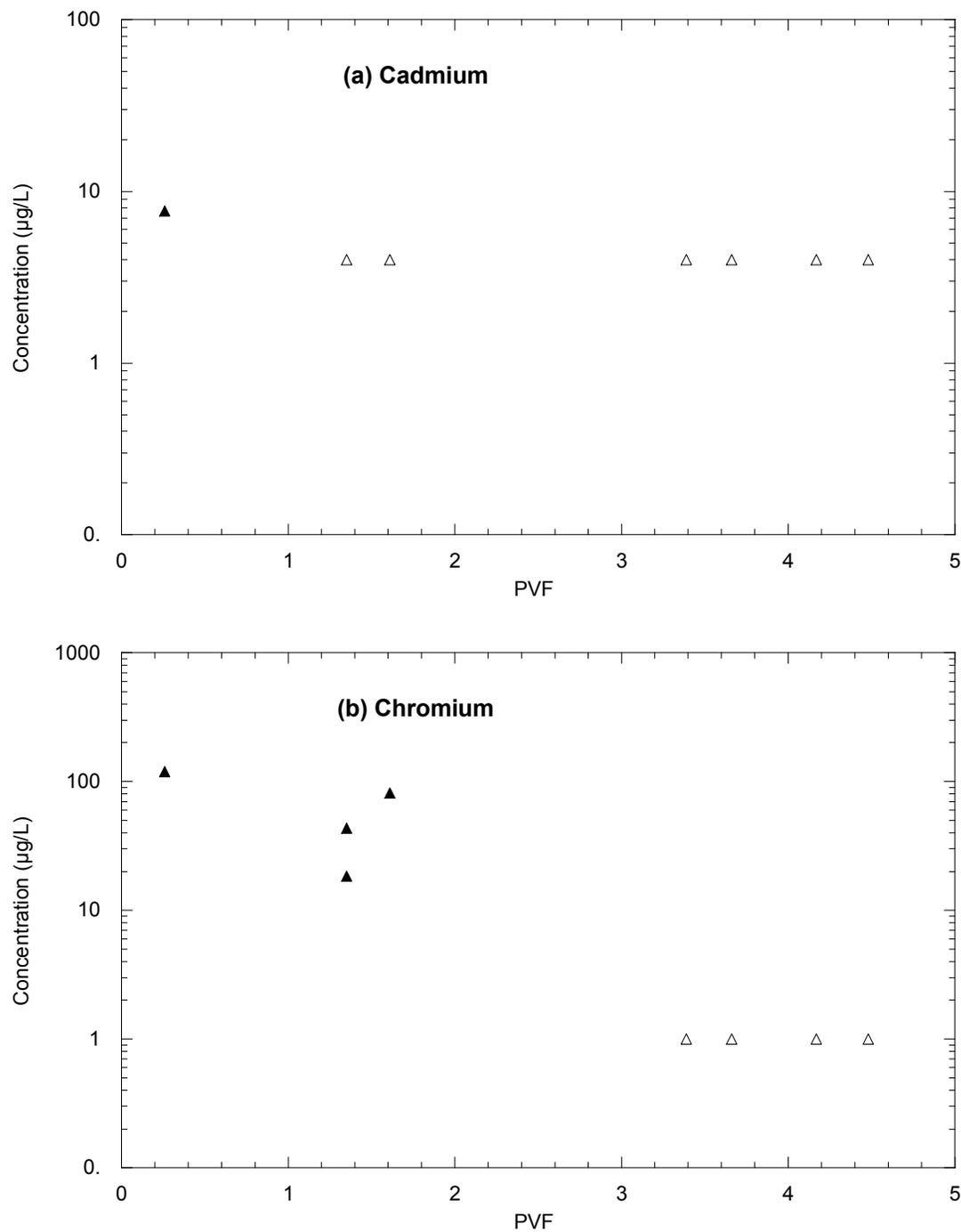


Fig. 4.4. Peak Concentrations occurring during first 0.2 PVF for (a) cadmium and (b) chromium.

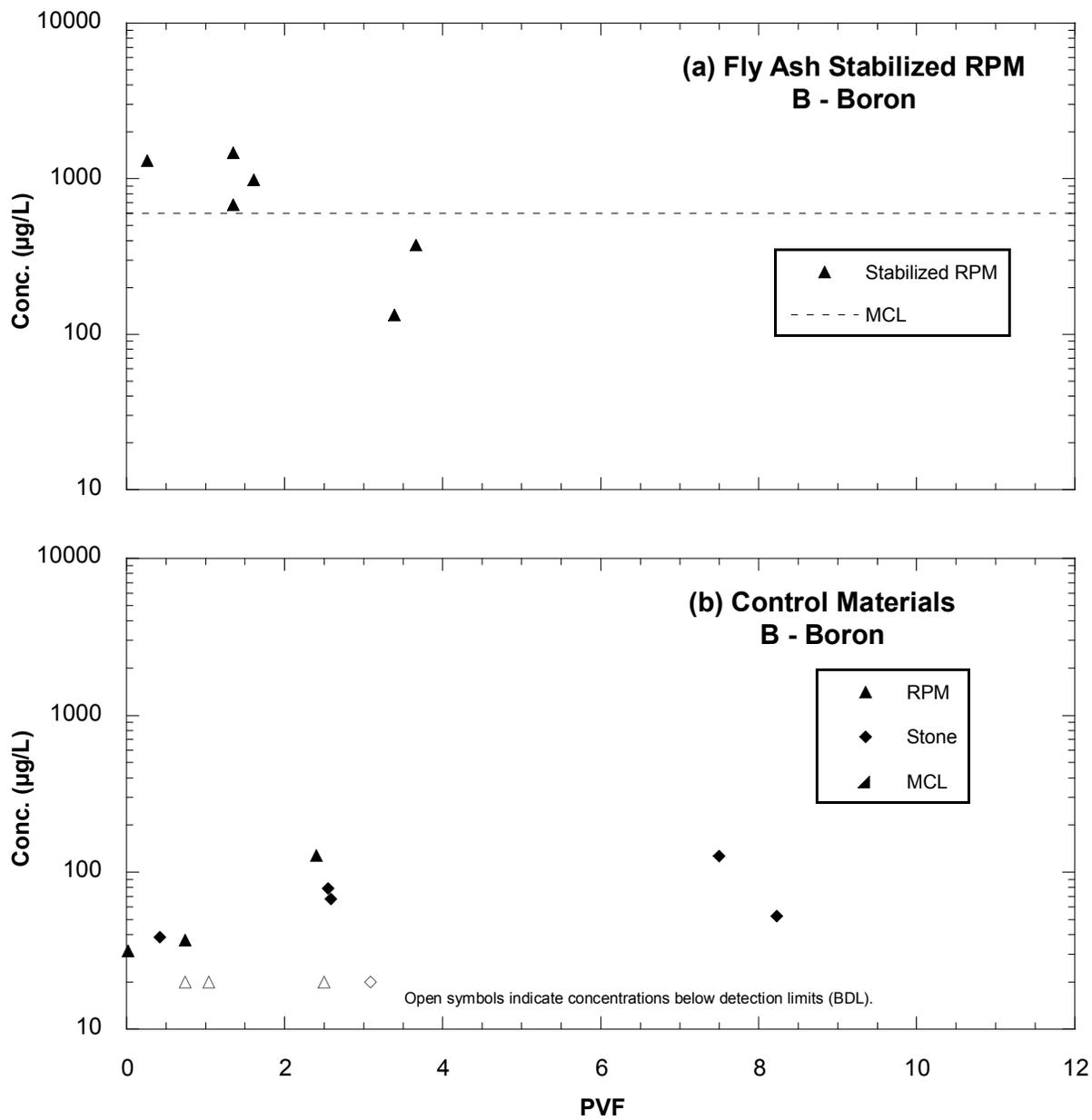


Fig. 4.5. Boron (B) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

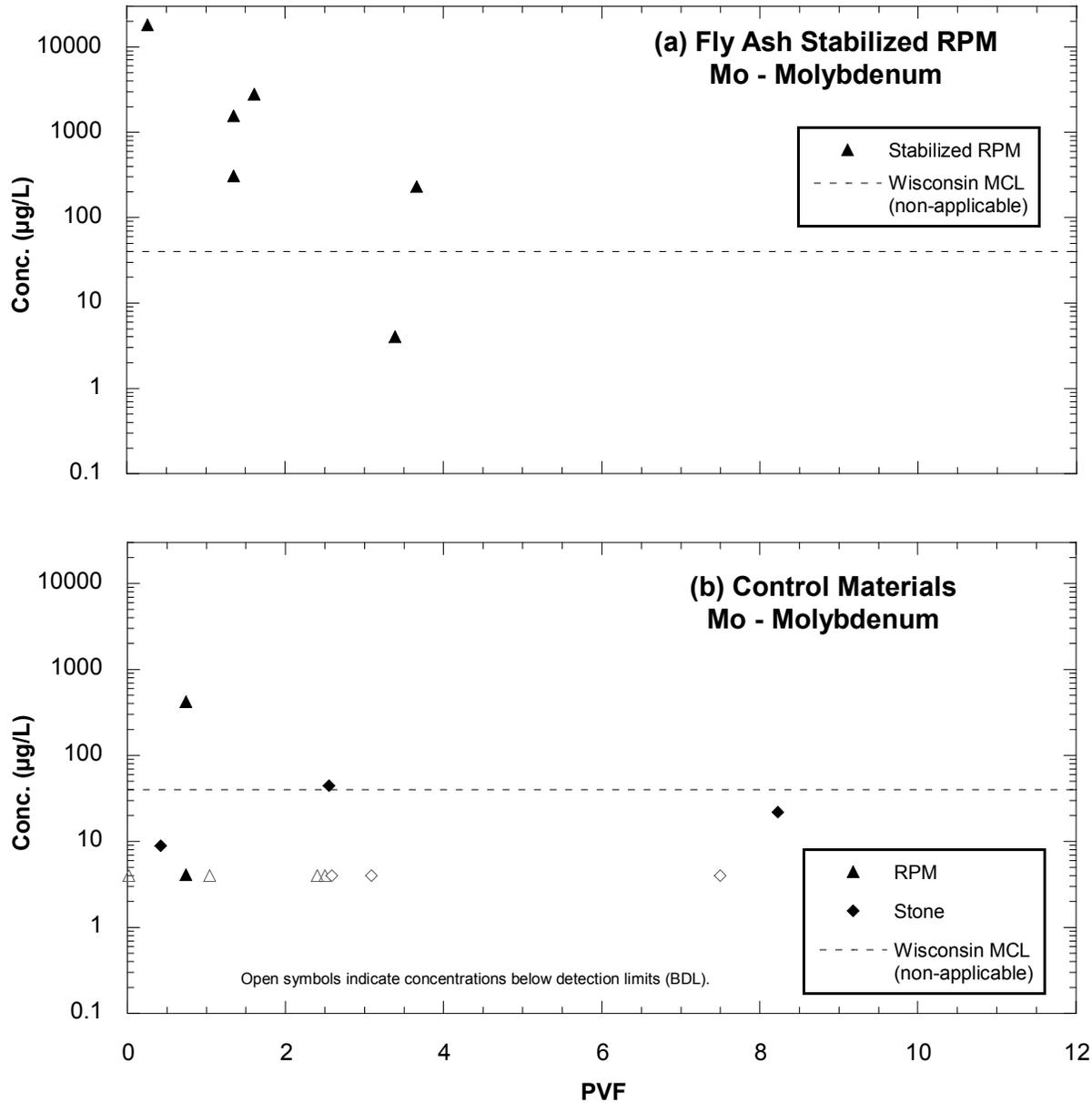


Fig. 4.6. Molybdenum (Mo) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials. Concentrations are compared to the MCL from Wisconsin.

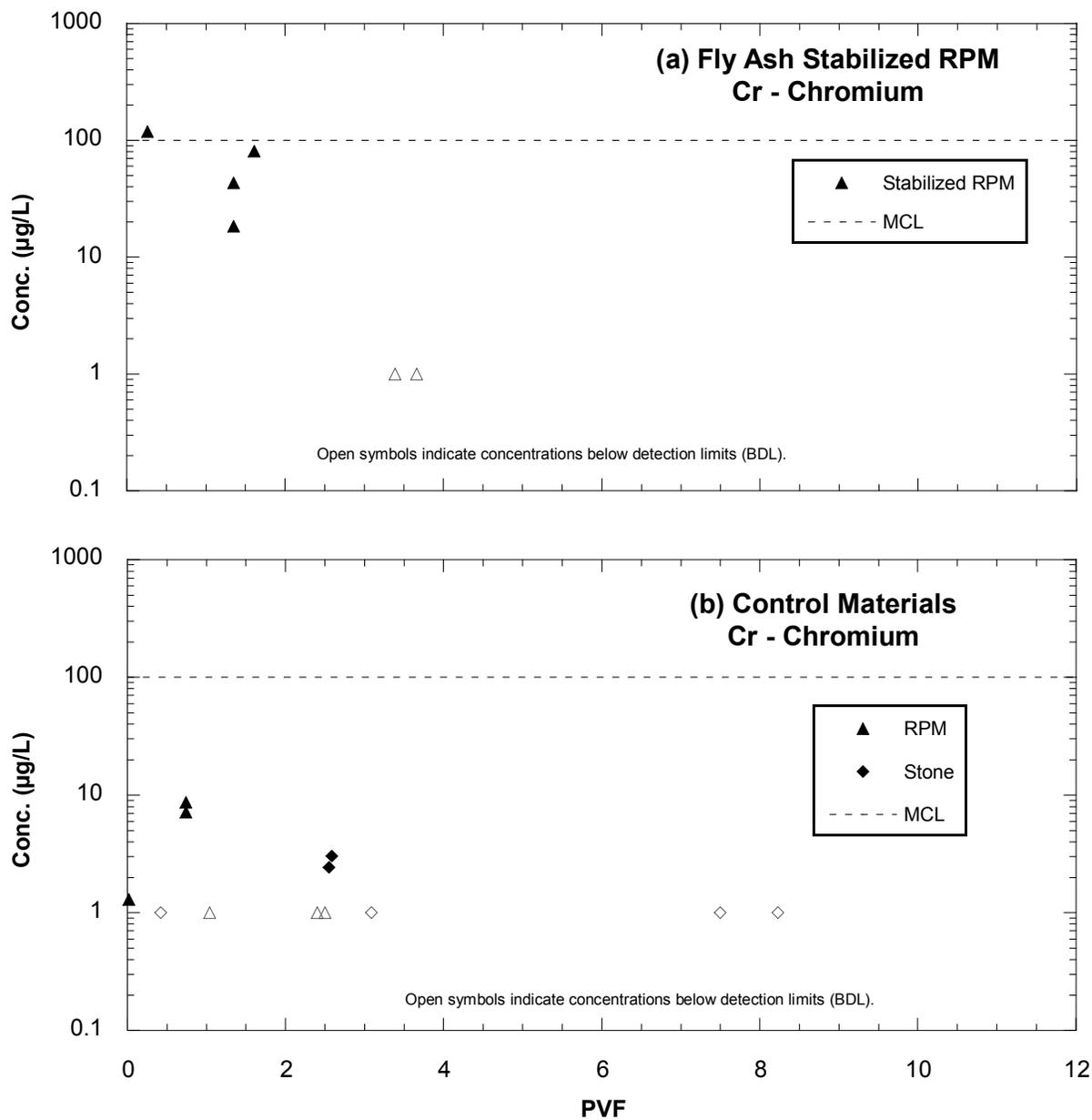


Fig. 4.7. Chromium (Cr) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

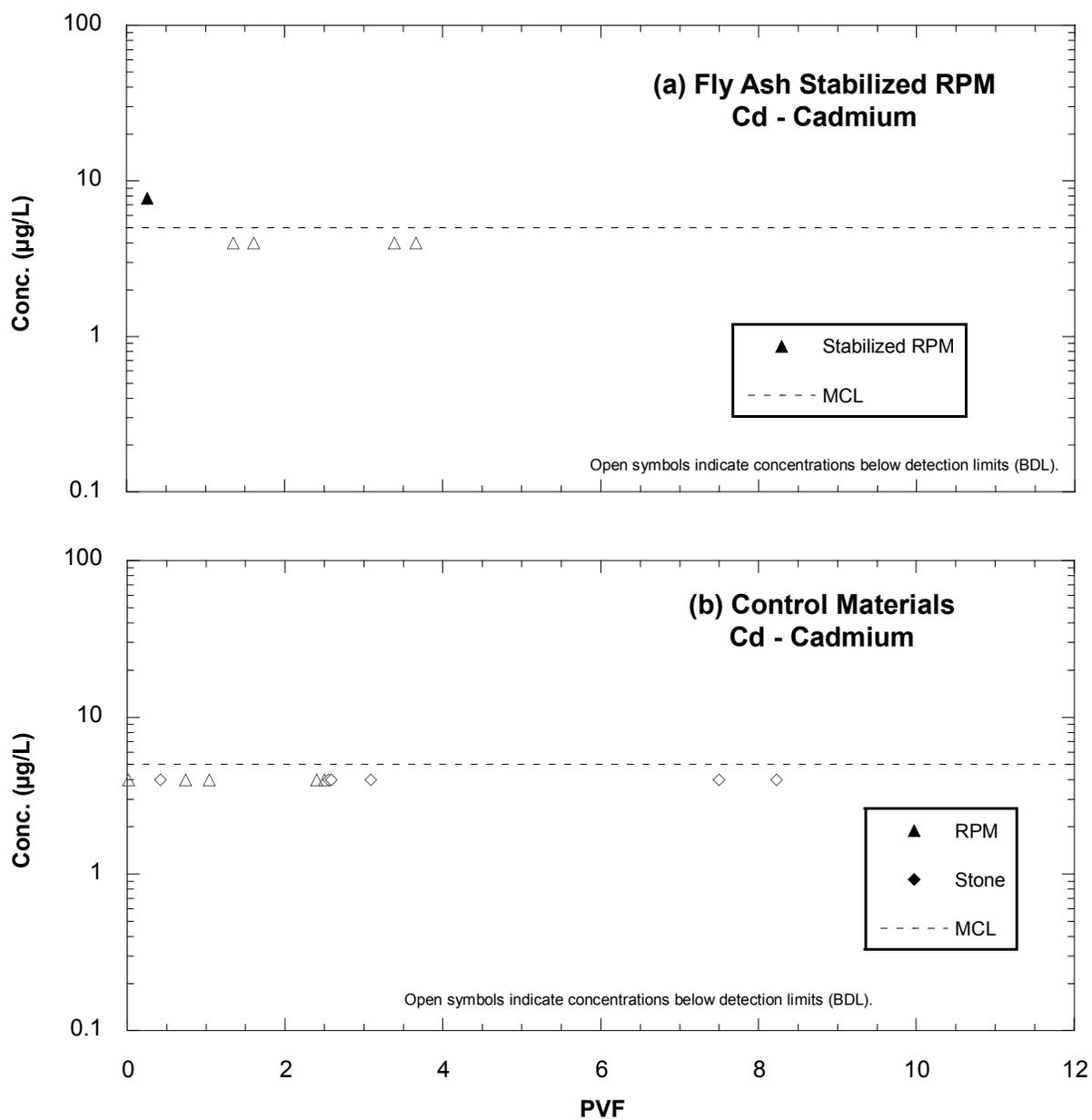


Fig. 4.8. Cadmium (Cd) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

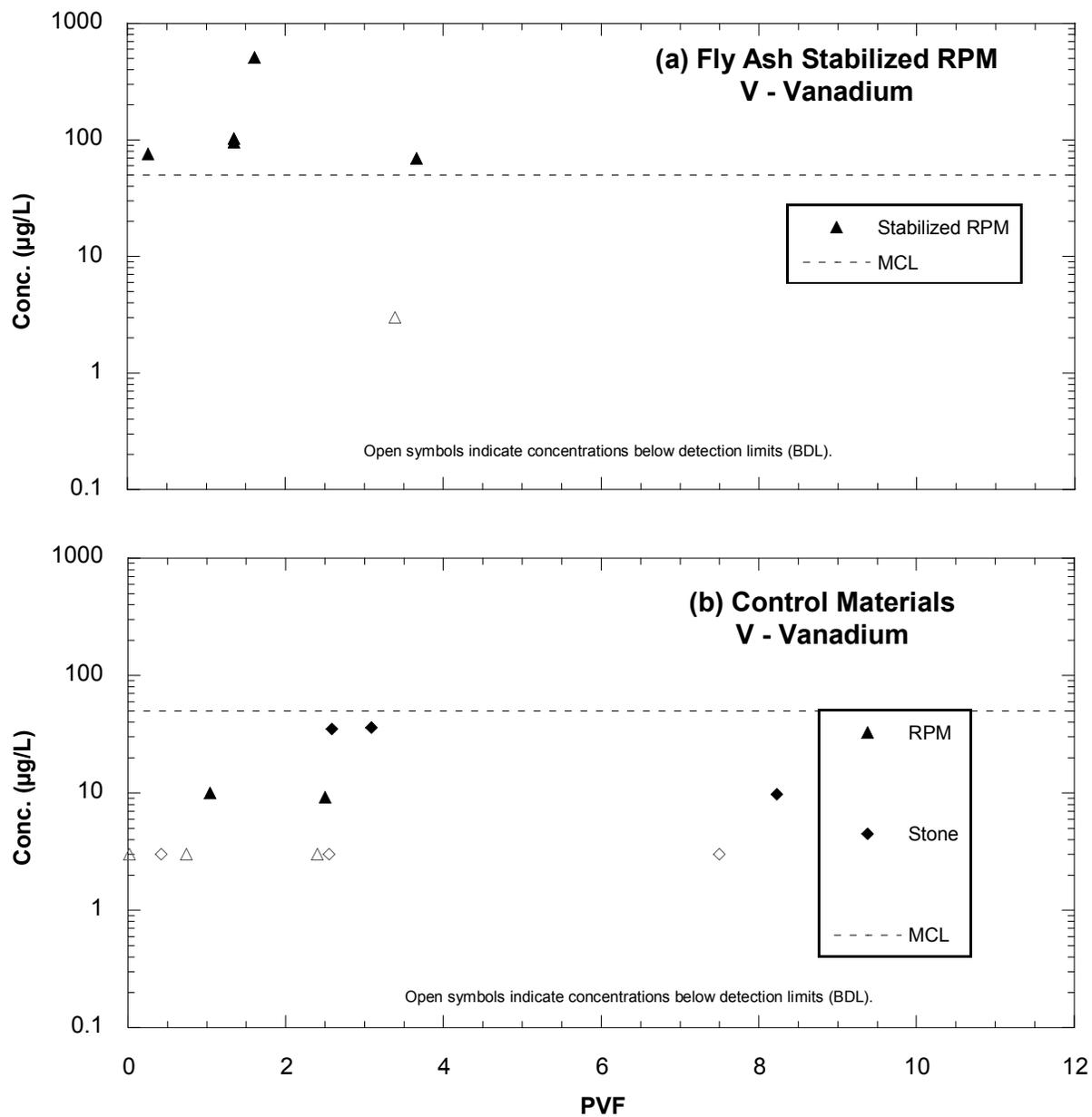


Fig. 4.9. Vanadium (V) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

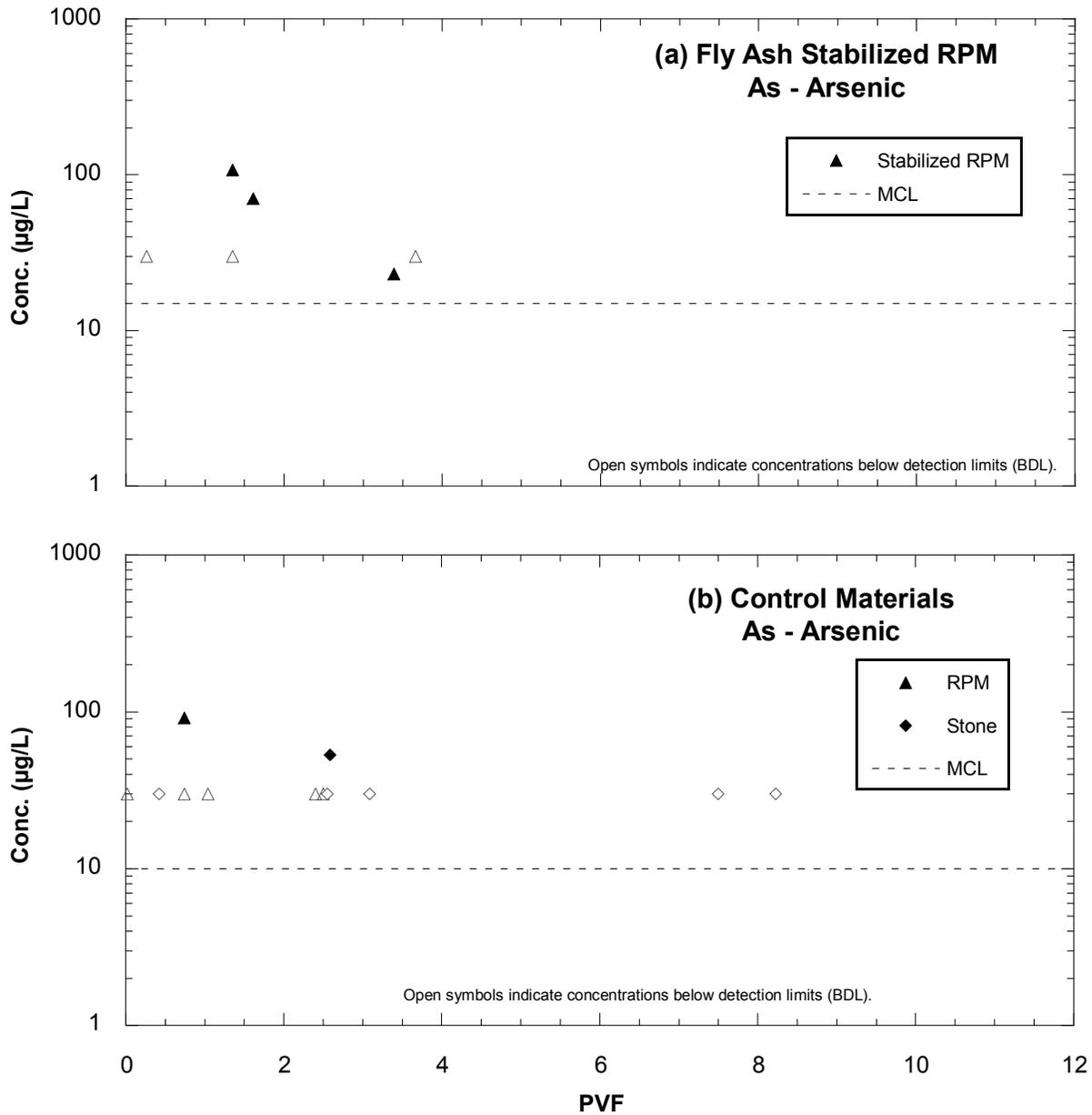


Fig. 4.10. Arsenic (As) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

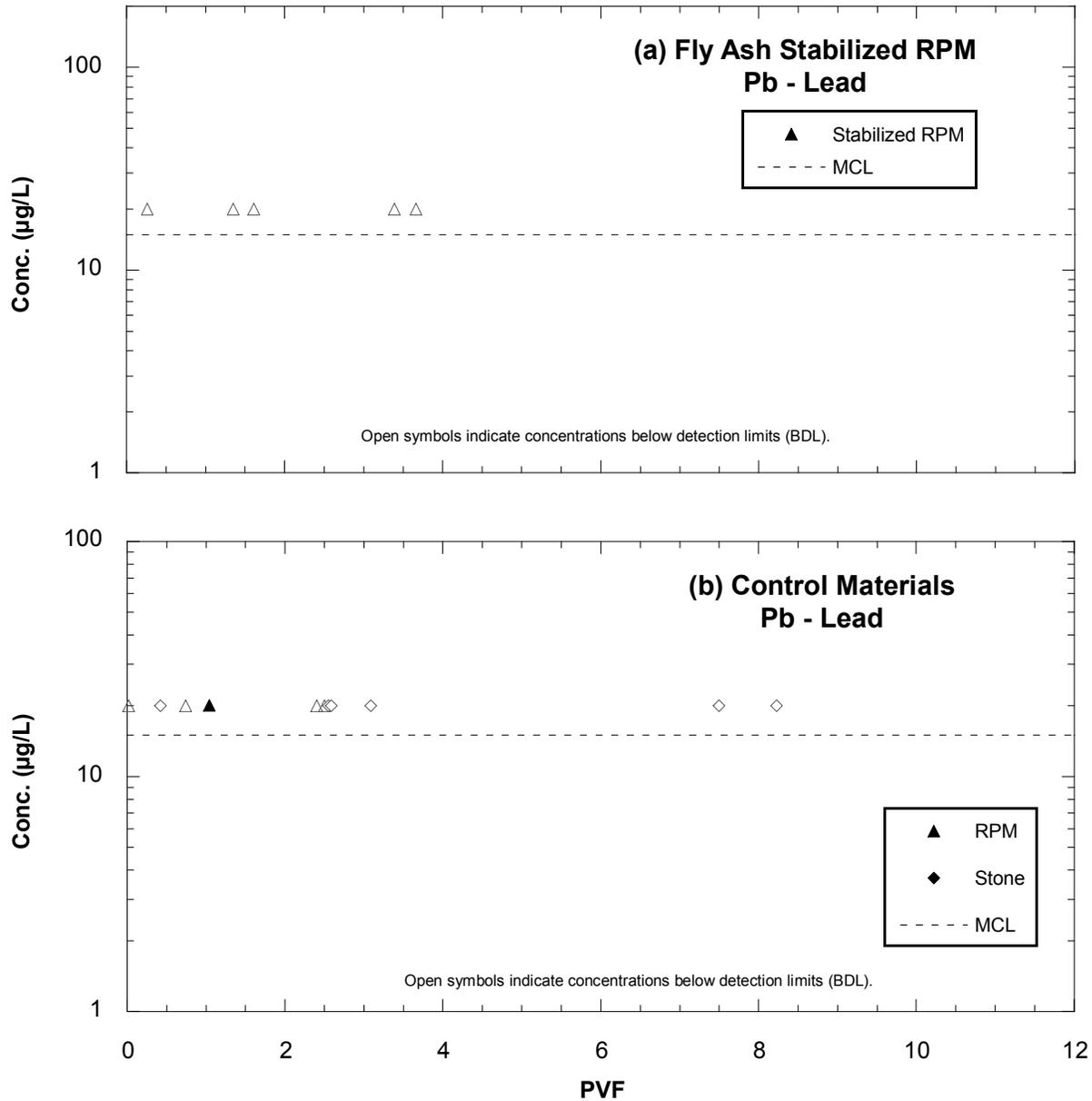


Fig. 4.11. Lead (Pb) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

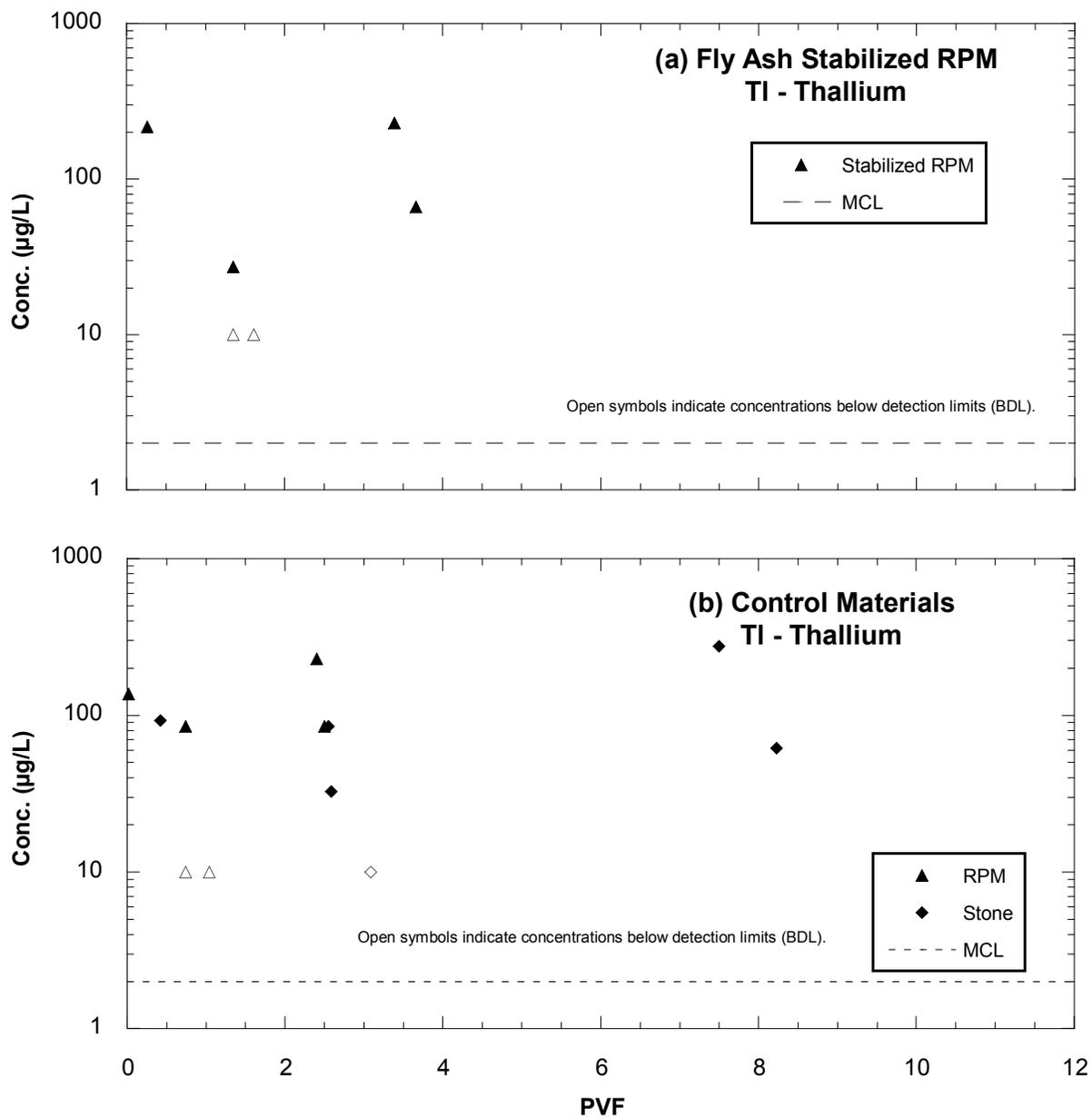


Fig. 4.12. Thallium (TI) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

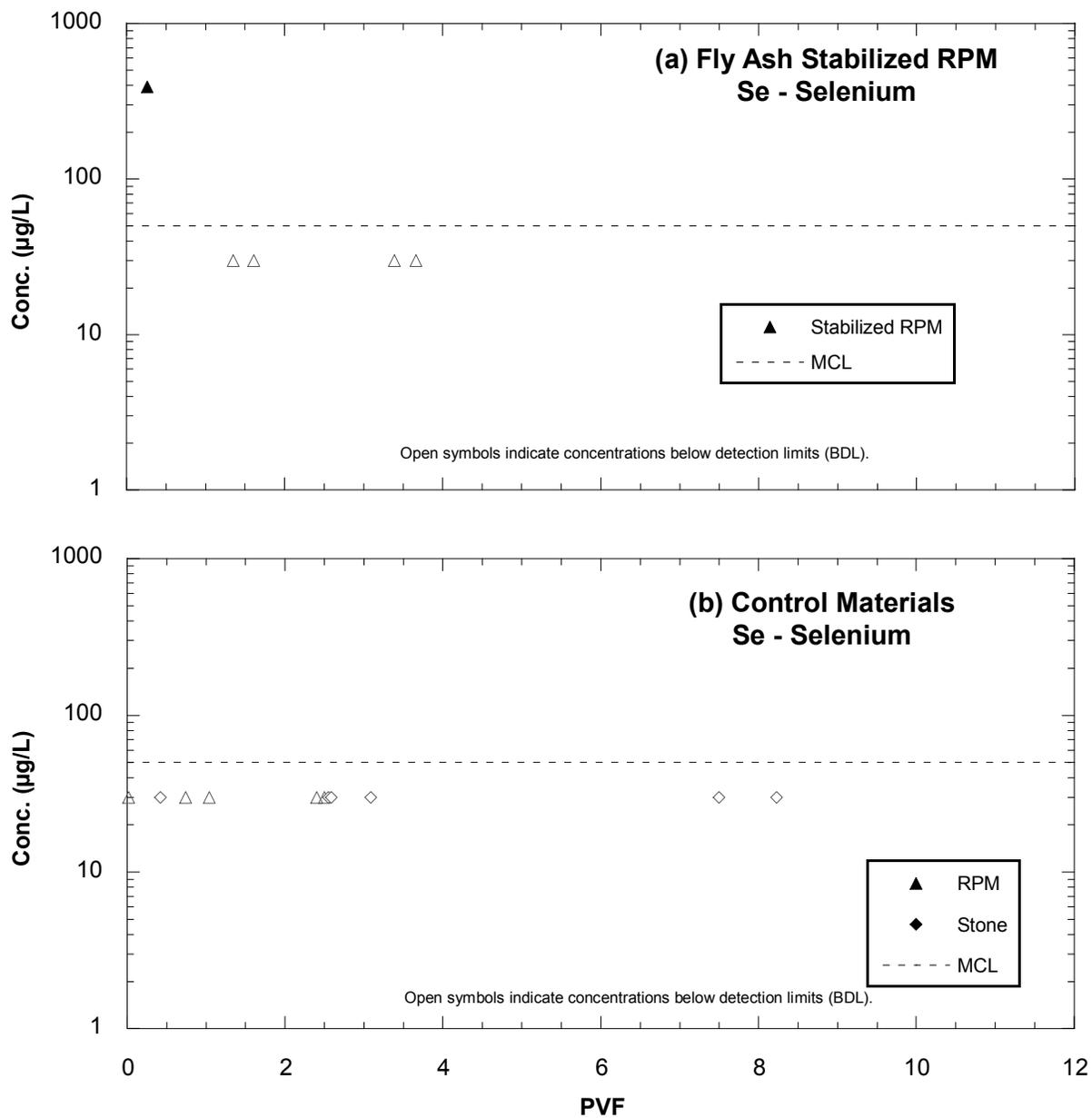


Fig. 4.13. Selenium (Se) concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

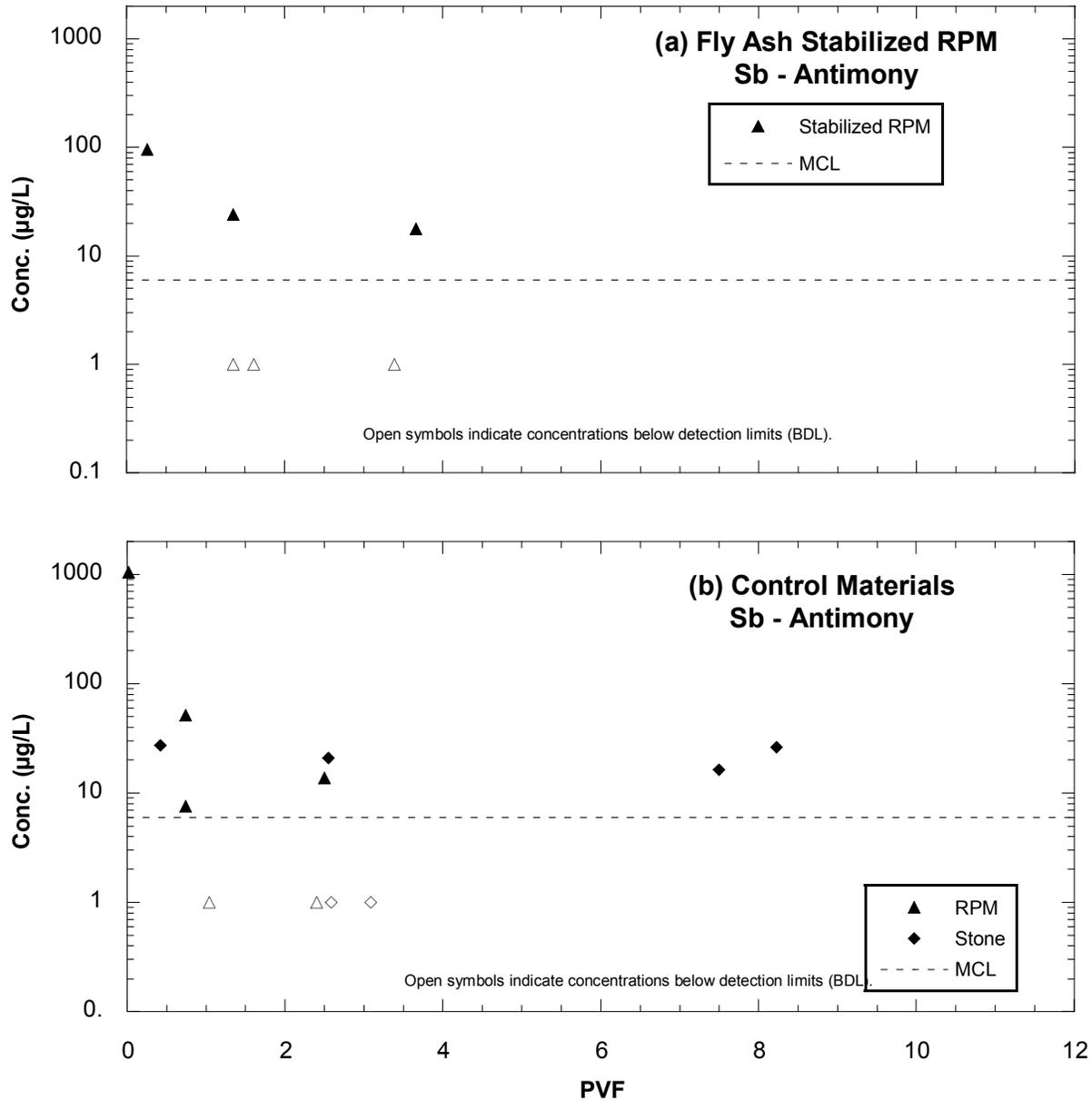


Fig. 4.14. Antimony (Sb concentrations in leachate from field base course composed of (a) fly-ash-stabilized RPM, and (b) control materials.

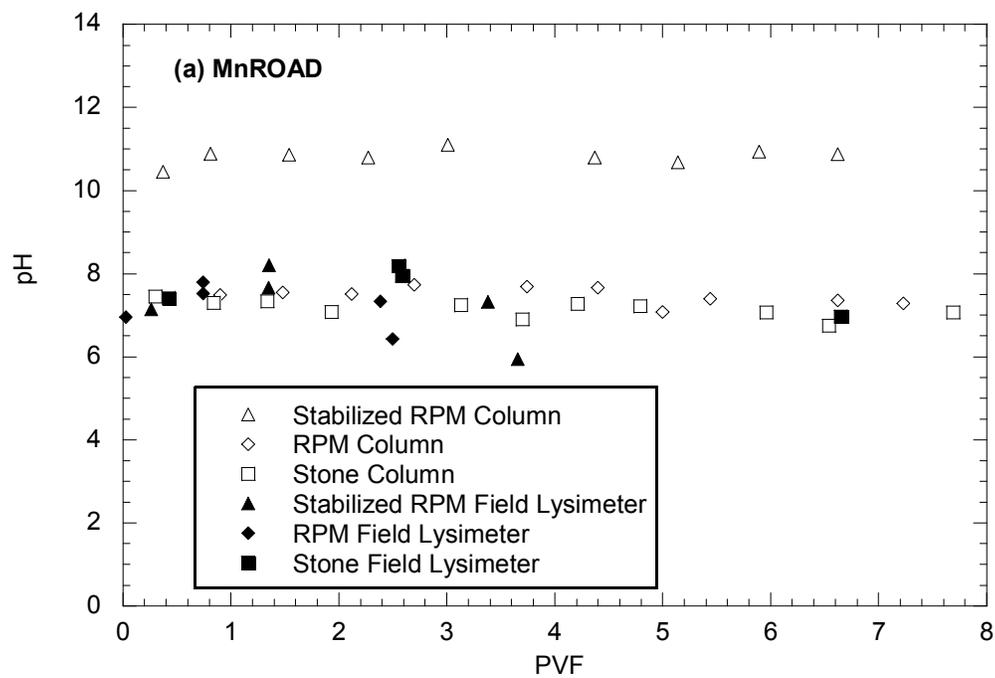


Fig. 4.15. Comparison of leachate pH from Field Lysimeters and CLTs

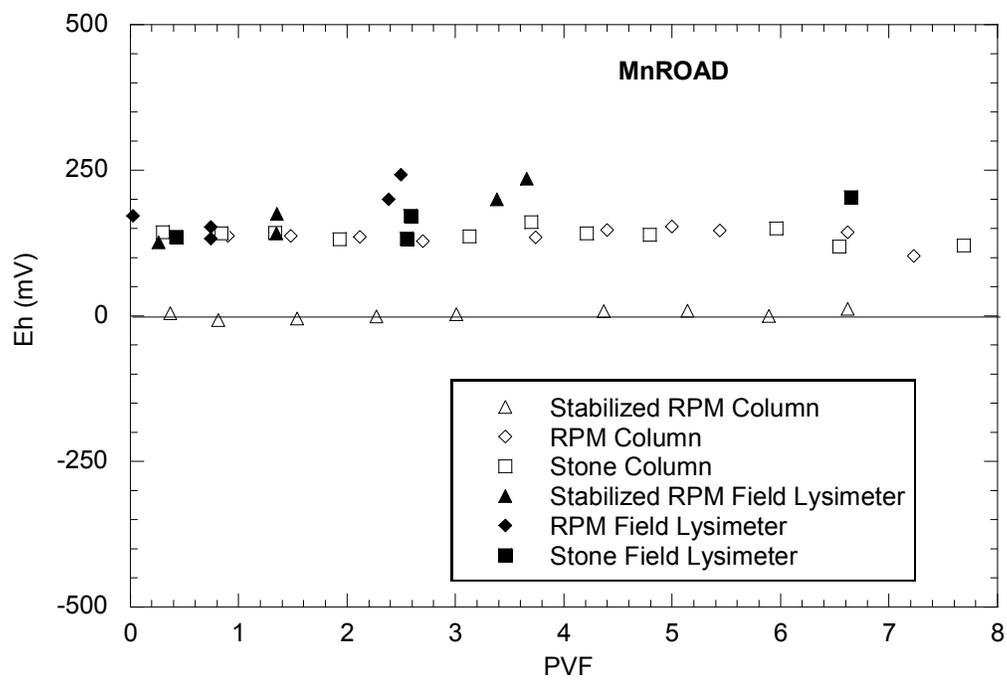


Fig. 4.16. Comparison of leachate Eh from Field Lysimeters and CLTs

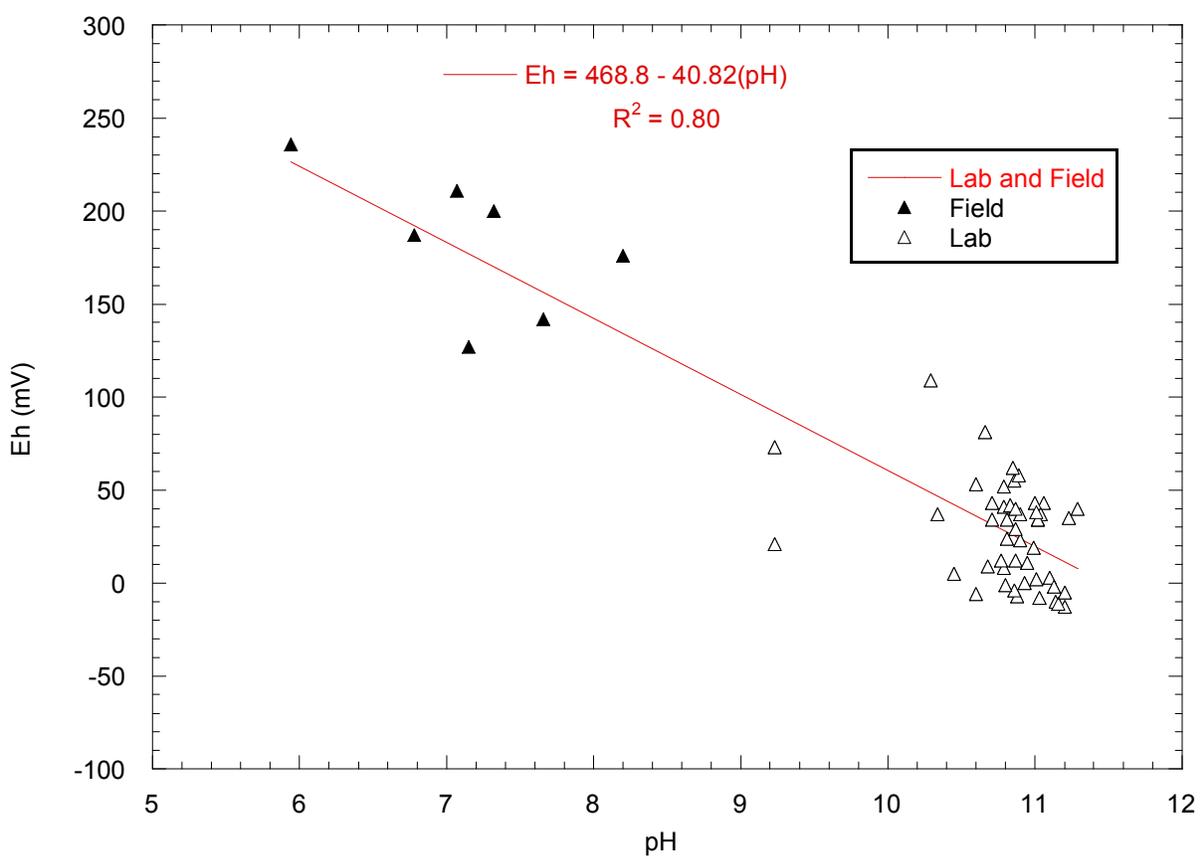


Fig. 4.17. Analysis of Eh and pH relationship in field and CLT leachate

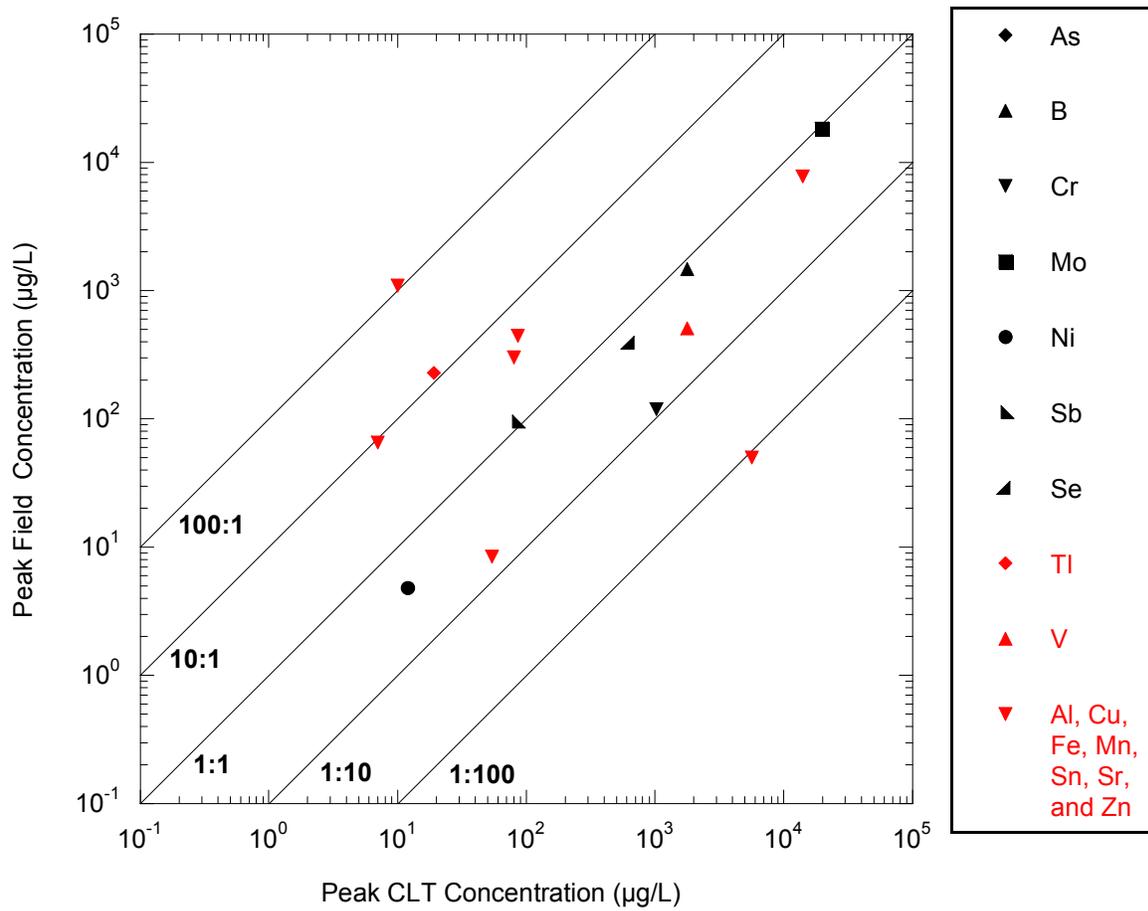


Fig. 4.18. Comparison of peak concentrations in field lysimeters and column leach tests

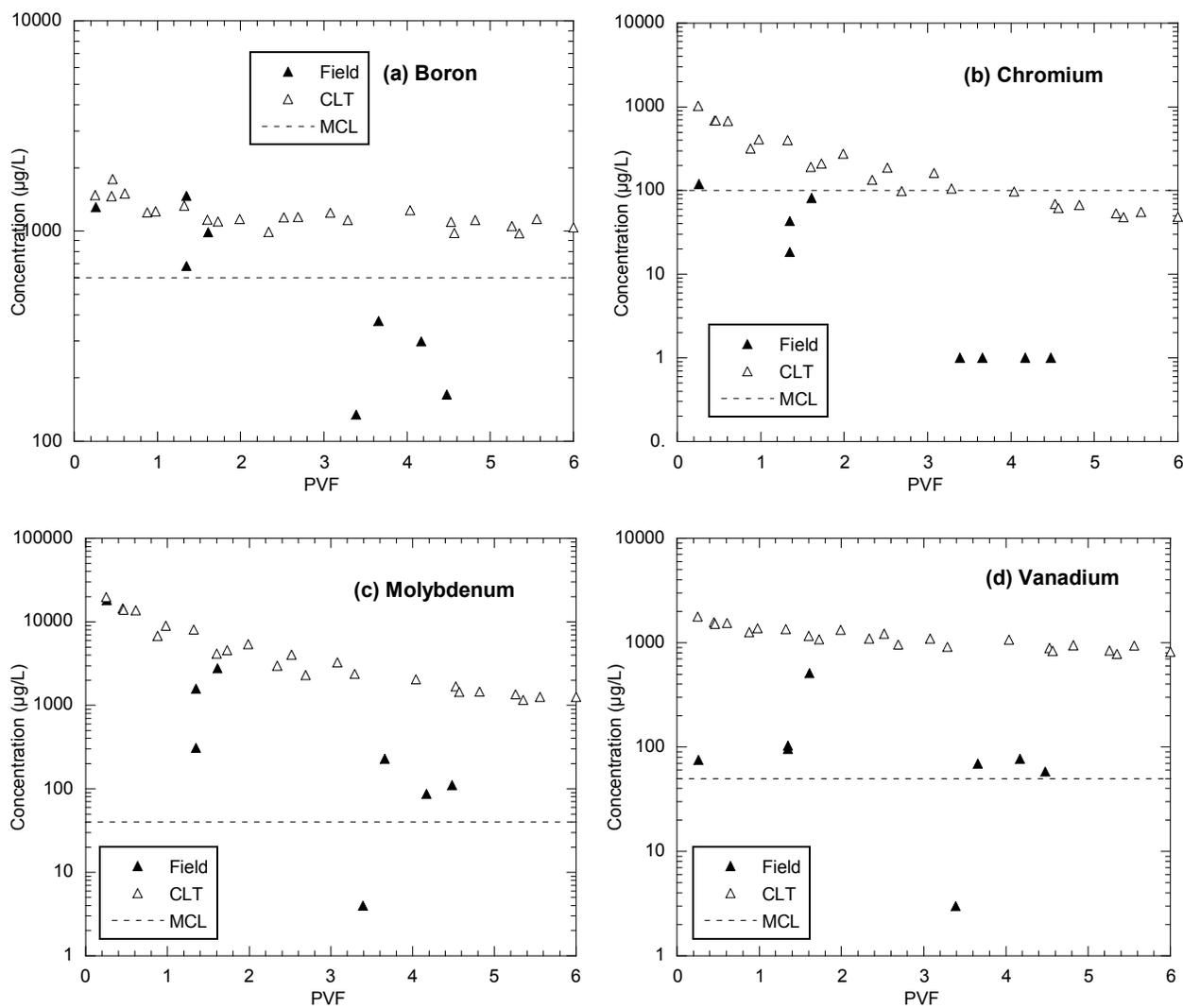


Fig. 4.19. Elements in both field and CLT Leachate that were elevated relative to the control and exceeded the MCL. Downward facing triangles indicate concentrations that are BDL.

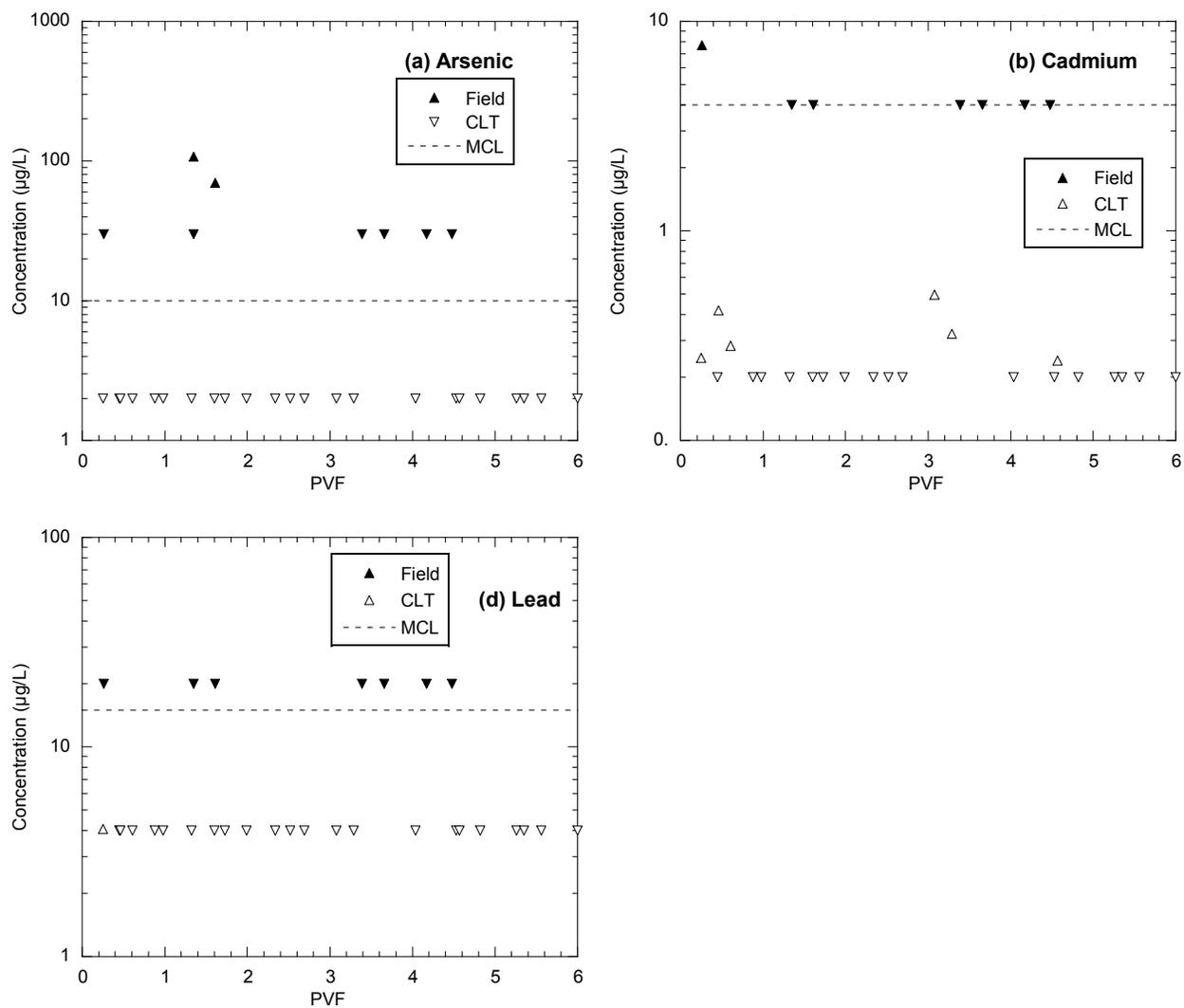


Fig. 4.20. Elements that were elevated relative to the control and exceeded the MCL in the field but not in CLT leachate. Downward facing triangles indicate concentrations that are BDL.

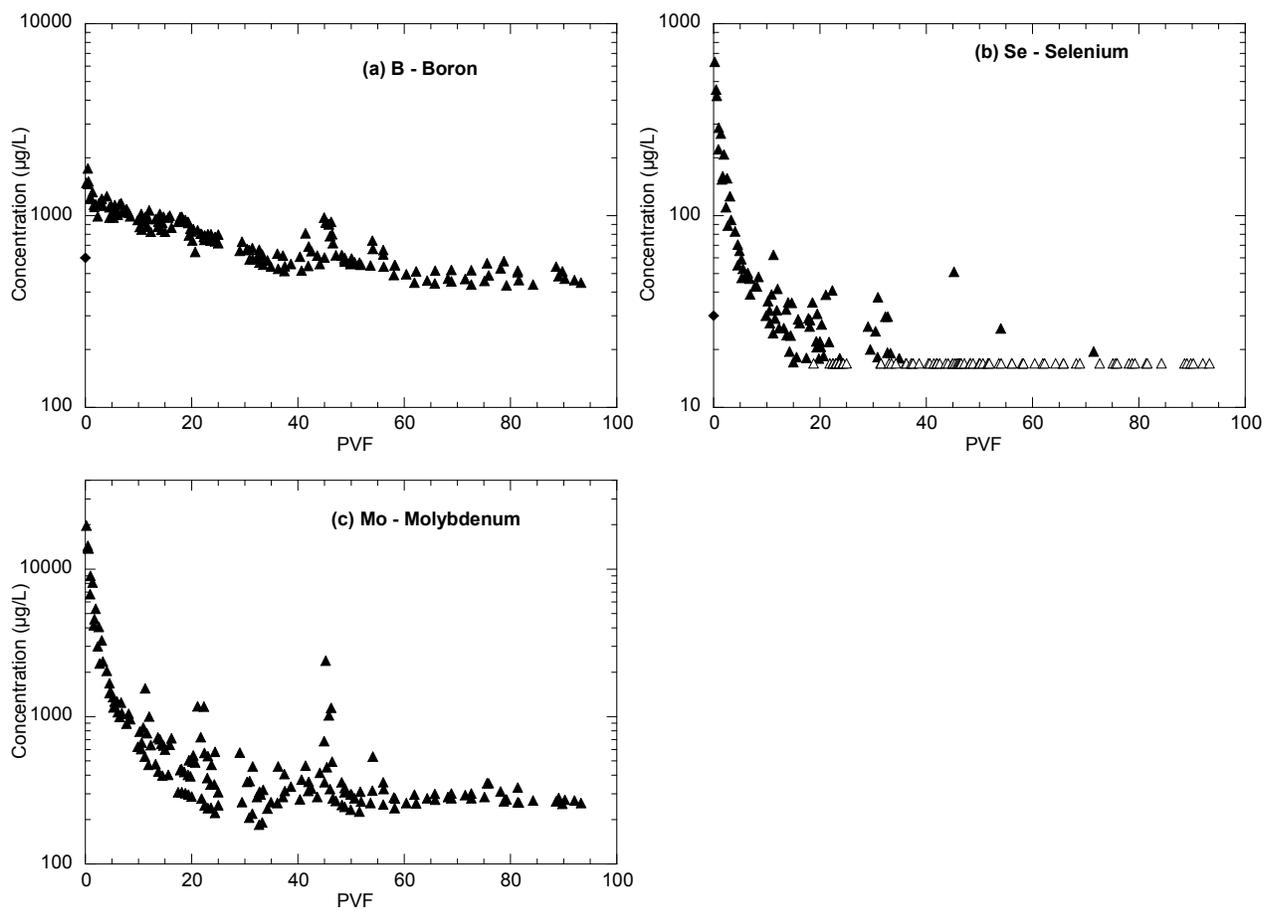


Fig. 4.21. Typical first-flush leaching patterns from CLTs for (b) B, (b) Se, and (c) Mo, and increase in concentrations after MnROAD columns were left saturated with no flow

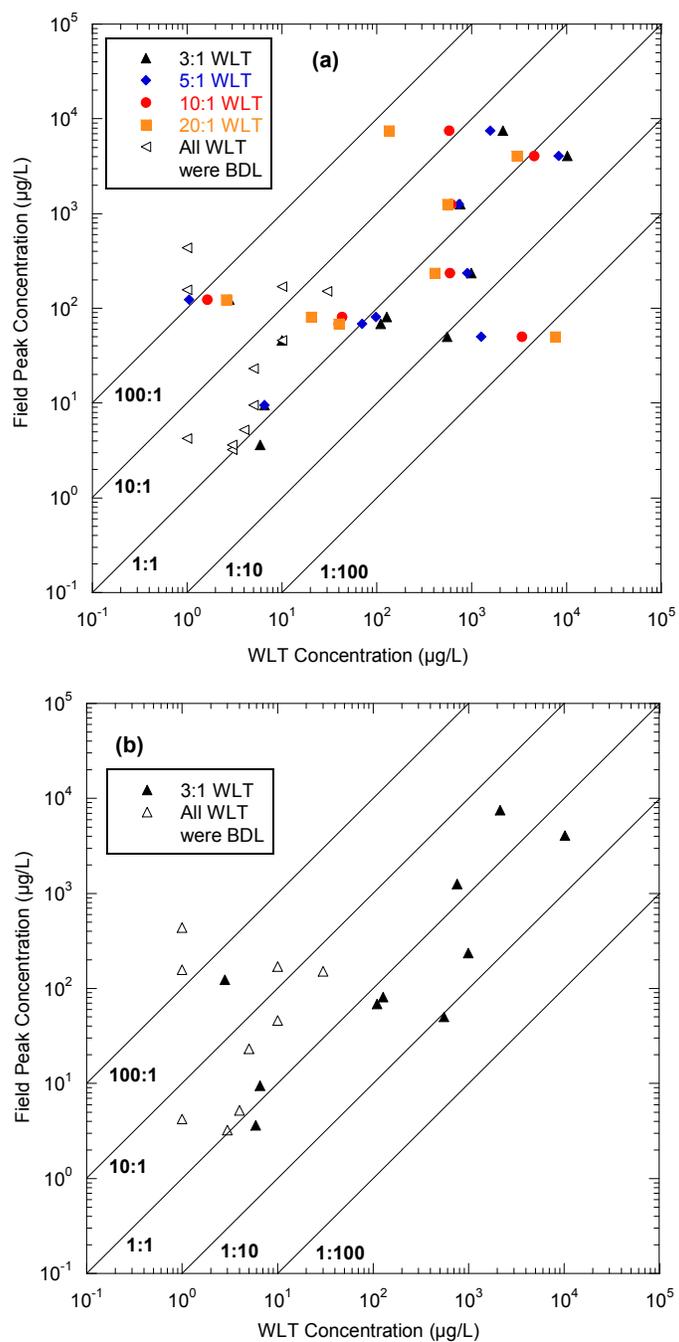


Fig. 4.22. Comparison of average peak field concentrations and WLT concentration for (a) all WLT liquid:solid ratios, and (b) only the 3:1 WLT. Only elements detected in the field are shown. Open Symbols indicate WLT below detection limit

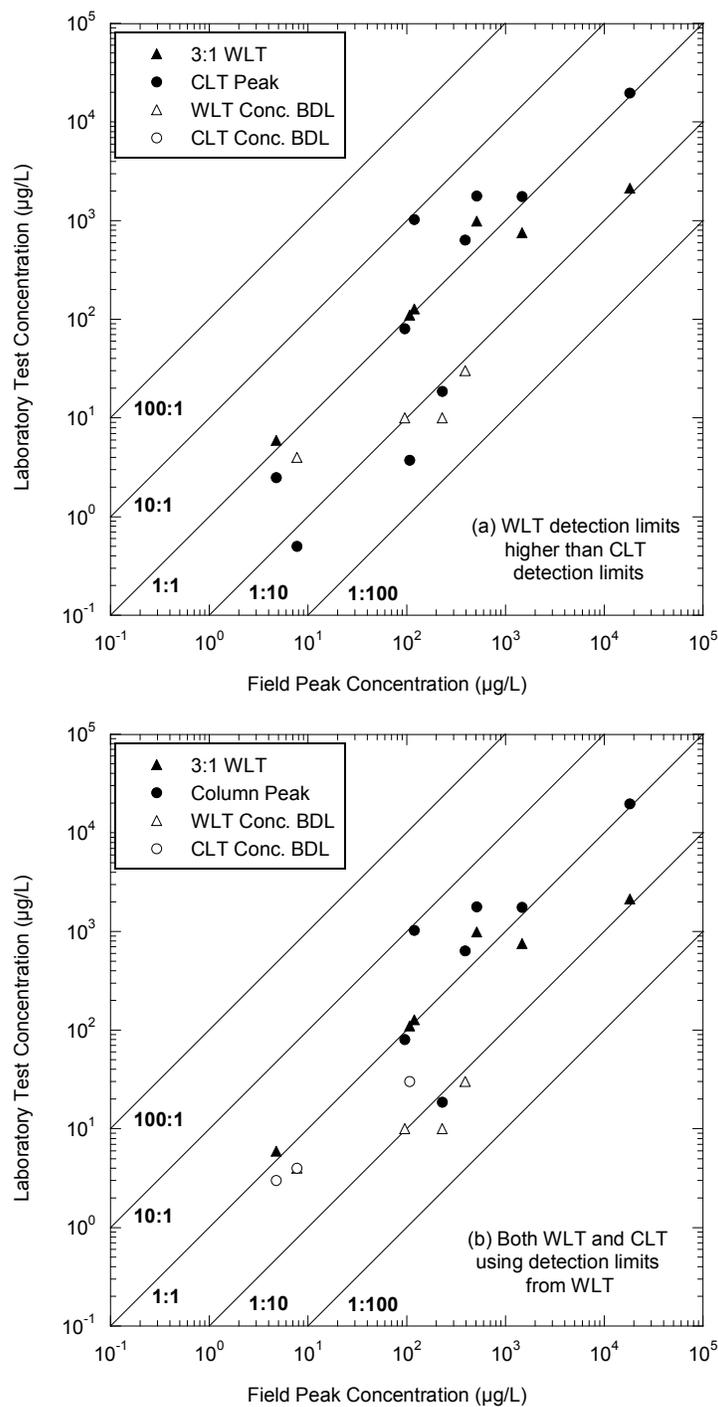


Fig. 4.23. Comparison of ability of CLT and WLT to predict peak field concentration of elements that exceeded MCLs in field leachate when (a) detection limits were lower for the CLT, and (b) when both tests use the WLT detection limits

**TABLES**

Table 2.1. Properties of Stabilized Layers and Lysimeters

<b>Site</b>	<b>MnROAD</b>
<b>Layer Stabilized</b>	Base Course
<b>Material Stabilized</b>	Recycled Paving Material
<b>USCS and AASHTO Class.</b>	GW-GM, A-1-a
<b>Fly Ash Type</b>	Riverside 8
<b>Percent Fly Ash by Mass (%)</b>	14
<b>Compacted Dry Unit Weight of Stabilized Layer (kN/m<sup>3</sup>)</b>	19.6
<b>Porosity</b>	0.25
<b>Water Content at Compaction Relative to Optimum Standard Proctor (<math>w_{opt}</math>)</b>	1% wet of $w_{opt}$
<b>Stabilized Layer Thickness (mm)</b>	203
<b>Lysimeter Dimensions (m)</b>	3.00 x 3.00

Table 3.1. Use Classification of Riverside 8 Fly Ash

Parameter	Percent of Composition	Specifications	
		ASTM C 618	AASHTO M 295
		Class C	Class C
SiO <sub>2</sub> (silicon dioxide) (%)	19		
Al <sub>2</sub> O <sub>3</sub> (aluminum oxide) (%)	14		
Fe <sub>2</sub> O <sub>3</sub> (iron oxide) (%)	6		
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> (%)	39	50 Min	50 Min
CaO (calcium oxide) (%)	22		
MgO (magnesium oxide) (%)	5.5		
SO <sub>3</sub> (sulfur trioxide) (%)	5.4	5 Max	5 Max
CaO/SiO <sub>2</sub>	1.18		
CaO/(SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> )	0.68		
Loss on Ignition (%)	16.4	6 Max	5 Max
Moisture Content (%)	0.32	3 Max	3 Max
Specific Gravity	2.65		
Fineness, amount retained on #325 sieve (%)	15.5	34 Max	34 Max
Classification	Off-Spec.		

Table 3.2. Total Elemental Analysis of Riverside 8 Ash

Element	Riverside 8 Ash	
	(mg/kg)	% of Total Mass
Ag	0.40	0.000040
Al	66000	6.6
As	24	0.0024
B	780	0.078
Ba	2600	0.26
Be	5.3	0.00053
Ca	120000	12
Cd	5.4	0.00054
Co	28	0.0028
Cr	71	0.0071
Cu	230	0.023
Fe	36000	3.6
Hg	0.80	0.000080
K	2600	0.26
Mg	29000	2.9
Mn	120	0.012
Mo	140	0.014
Na	15000	1.5
Ni	620	0.062
P	4800	0.48
Pb	63	0.0063
S	41100	4.11
Sb	3.3	0.00033
Se	16	0.0016
Si	6700	0.67
Sn	ND	-
Sr	ND	-
Ti	130	0.013
Tl	1.1	0.00011
V	1400	0.14
Zn	130	0.0130

Table 3.3. Properties of Column Leach Testing

<b>Site</b>	<b>Material</b>		
<b>Material</b>	<b>RPM</b>	<b>Class 5 crushed stone</b>	<b>Stabilized RPM</b>
<b>Rigid or Flexible Wall Permeameter</b>	Rigid		
<b>Specimen Diameter (mm)</b>	202		
<b>Specimen Length (mm)</b>	102		
<b>Specimen Volume (mL)</b>	3269		
<b>Effective Confining Pressure (kPa)</b>	0		
<b>Porosity</b>	0.25	0.21	0.25
<b>Dry Unit Weight (kN/m<sup>3</sup>)</b>	19.4	20.5	19.6
<b>Approx. Darcy Flux (mm/day)</b>	16		

Table 3.4. Minimum detection limits of chemical analytical methods used throughout the monitoring program. All MDLs are in  $\mu\text{g/L}$ . Hyphens indicate elements that were not tested with the method indicated

<b>Site</b>	<b>MnROAD</b>	
<b>Element</b>	ICP-OES	CVAFS
<b>Ag</b>		-
<b>Al</b>	2.5	-
<b>As</b>	2.0	-
<b>B</b>	4.0	-
<b>Ba</b>	0.04	-
<b>Be</b>	1.0	-
<b>Cd</b>	0.2	-
<b>Co</b>	0.6	-
<b>Cr</b>	0.5	-
<b>Cu</b>	0.7	-
<b>Hg</b>		0.001
<b>Fe</b>	3.2	-
<b>Mn</b>	0.05	-
<b>Mo</b>	0.5	-
<b>Ni</b>	0.7	-
<b>Pb</b>	4.0	-
<b>Sb</b>	3.0	-
<b>Se</b>	17	-
<b>Sn</b>	5.0	-
<b>Sr</b>	0.3	-
<b>Ti</b>	0.4	-
<b>Tl</b>	4.7	-
<b>V</b>	0.1	-
<b>Zn</b>	0.1	-

Table 4.1. Magnitude of Peak Concentrations and the Average of the Three Highest Concentrations in Field Leachate

Element	Peak Conc. (µg/L)	Average Peak Conc. (µg/L)
Mo #	18176	7511.14
Sr #	7770	4057.37
B #	1470.55	1252.82
Mn ^	1094.57	438.17
V #	510	236.48
Fe ^	442.81	157.75
Se *	392.84	150.95
Zn ^	301.58	123.82
Tl ^	228.8	170.4
Cr *	119.18	81.25
As ^	107.46	69.15
Sb ^	95.2	45.73
Sn #	65.5	23.17
Cu ^	8.44	9.47
Cd *	7.69	5.23
Ni ^	4.84	3.61
Co ^	3.44	3.22
Ag *	2.8	4.23
Hg \$	0.01	0.01
Al ^	All BDL	All BDL
Pb ^	All BDL	All BDL
Ti #	All BDL	All BDL
Be ^	All BDL	All BDL

BDL - below detection limit

NT - element not tested for at site

@ - concentration is out of method calibration range, and is estimated from linear extrapolation

Table 4.2. Elements with peak concentrations occurring during or after the first 2 PVF

<b>Element</b>	<b>Timing of Peak Concentration</b>
Ag	▼
Al	ND
As	▼
B	▼
Be	ND
Cd	▼
Co	▼
Cr	▼
Cu	▼
Fe	X
Mn	X
Mo	▼
Ni	▼
Pb	ND
Sb	▼
Se	▼
Sn	X
Sr	▼
Ti	ND
Tl	X
V	▼
Zn	X

▼ - Peak Concentration occurred during the first 2 PVF

X - Peak Concentration occurred after the first 2 PVF

ND - All concentrations were below detection limit

Table 4.3. Comparison of field concentrations from fly ash stabilized sections and control sections to determine if element is statistically elevated in the stabilized material leachate. Elevated concentrations in stabilized material leachate are highlighted.

Element	Ratio of Stabilized Concentration / Control Concentration	
	Average Peak Concentration	Geometric Mean of Concentrations
Mo	52.2	48.5
B	19.2	16.1
V	28.6	15.2
Sr	10.1	4.7
Cr	14.2	4.2
Se	5	1.4
As	1.4	1.3
Mn	0.6	1.3
Cu	1.8	1.2
Cd	1.3	1.1
Al	1	1
Be	1	1
Co	0.9	1
Ni	1	1
Pb	1	1
Ti	1	1
Ag	0.4	0.9
Fe	1	0.9
Sb	0.1	0.7
Tl	1.1	0.7
Zn	0.7	0.6
Hg	0.5	0.2
Sn	0.03	0.1

Table 4.4. USEPA and Minnesota, maximum contaminant limits (MCLs) for groundwater and drinking water

<b>Element</b>	<b>MN MCL (µg/L)</b>	<b>USEPA MCL (µg/L)</b>
Ag	-	30
As	10	-
B	600	-
Ba	2000	2000
Be	4	0.08
Cd	4	5
Co	-	-
Cr	100	100
Cu	-	-
Hg	2	-
Mo*	-	-
Ni	100	-
Pb	15	-
Sb	6	6
Se	30	50
Sn	4000	-
Tl	0.6	2
V	50	-
Zn	-	2000

\*WI

Table 4.5. Ratio of average peak concentration or geometric mean of all concentrations to MCLs in field leachate.

<b>Ratio for Average Peak Concentrations</b>										
<b>Element</b>	<b>As</b>	<b>B</b>	<b>Cd</b>	<b>Cr</b>	<b>Mo</b>	<b>Pb</b>	<b>Sb</b>	<b>Se</b>	<b>TI</b>	<b>V</b>
Stabilized RPM	11	2.5	1.5	1.2	450*	1.3	24	13	380	10
RPM	9.1	-	-	-	11*	1.3	260	-	380	-
Stone	5.3	-	-	-	-	1.3	6.8	-	460	-
<b>Ratio for Geometric Mean of Concentrations</b>										
<b>Element</b>	<b>As</b>	<b>B</b>	<b>Cd</b>	<b>Cr</b>	<b>Mo</b>	<b>Pb</b>	<b>Sb</b>	<b>Se</b>	<b>TI</b>	<b>V</b>
Stabilized RPM	3.8	-	1.1	-	8.7	1.3	2.7	-	52.0	1.3
RPM	2.9	-	-	-	-	1.3	3.6	-	73.9	-
Stone	3.2	-	-	-	-	1.3	2.5	-	87.2	-

Table 4.6. Speciation of Select Trace Elements under Eh-pH Conditions

Element	pH	Species			
		Eh (mV)			
		-150	0	150	+300
<b>As</b>	6	HAsO <sub>2</sub> <sup>(aq)</sup>		H <sub>2</sub> AsO <sub>4</sub> <sup>[-]</sup>	
	7			HAsO <sub>4</sub> <sup>[2-]</sup>	
	8				
	9				
<b>B</b>	6	H <sub>3</sub> BO <sub>3</sub> <sup>(aq)</sup>			
	7				
	8				
	9				
<b>Cd</b>	6	Cd <sup>[2+]</sup>			
	7				
	8				
	9				
<b>Cr</b>	6	CrOH <sup>[2+]</sup>			
	7	Cr <sub>2</sub> O <sub>3</sub> <sup>(s)</sup>			
	8				
	9				
<b>Mo</b>	6	MoO <sub>4</sub> <sup>[2-]</sup>			
	7				
	8				
	9				
<b>Ni</b>	6	Ni <sup>[2+]</sup>			
	7				
	8				
	9				
<b>Pb</b>	6	Pb <sup>[2+]</sup>			
	7	PbOH <sup>[+]</sup>			
	8				
	9				
<b>Sb</b>	6	HSbO <sub>2</sub> <sup>(aq)</sup>		SbO <sub>4</sub> <sup>(s)</sup>	
	7				
	8				
	9				
<b>Se</b>	6	HSe <sup>[-]</sup>		HSeO <sub>3</sub> <sup>[-]</sup>	
	7			SeO <sub>3</sub> <sup>[2-]</sup>	
	8				
	9				
<b>Tl</b>	6	Tl <sup>[+]</sup>			
	7				
	8				
	9				
<b>V</b>	6	VO <sup>[2+]</sup>		HVO <sub>4</sub> <sup>[2-]</sup>	
	7	VO <sub>3</sub> <sup>[-]</sup>			
	8				
	9				

Table 4.7. Concentrations of Elements Elevated in the CLT Stabilized Leachate relative to the Control Leachate

Average Peak Concentration		Geo. Mean of Concentrations	
Element	Avg. Magnitude of elevated concentration ( $\mu\text{g/L}$ ) (more negative indicates a greater difference between stabilized and control concentrations)	Element	Avg. Magnitude of elevated concentration ( $\mu\text{g/L}$ ) (more negative indicates a greater difference between stabilized and control concentrations)
Mo	-15021.91	Sr	-4512.66
Sr	-12187.36	Al	-2721.92
Al	-4828.99	V	-764.32
V	-1473.99	B	-667.87
B	-1168.34	Mo	-629.6
Cr	-790.71	Ba	-168.48
Ba	-325.89	Cr	-16.48
Cu	-37.78	Cu	-0.41
Sb	-31.39	Ti	0.01
Se	-4.66	Cd	0.02
Ni	-3.36	Co	0.03
Be	-3.24	Be	0.05
Ti	-0.1	Ni	0.07
Co	0.03	As	0.51
Cd	0.67	Zn	0.81
As	2.13	Sn	1.9
Pb	2.88	Pb	2.07
Sn	2.89	Fe	3.12
Zn	23.46	Sb	3.57
Tl	25.02	Tl	10.77
Fe	64.04	Mn	14.42
Mn	980.51	Se	29.71
Ag	Not Tested in CLT	Ag	Not Tested in CLT
Hg	Not Tested in CLT	Hg	Not Tested in CLT

Table 4.8. Comparison of Field and CLT Leachate MCL Exceedances and Concentration Relative to Control Materials

All Elements	Elevated in the field	Exceeded MCL in Field	<b>Exceeded MCL and Elevated</b>	Exceeded MCL but the same or less than Controls (Field)	Elevated in Columns	Exceeded MCL in Columns	<b>Exceeded MCL and Elevated in Columns</b>	Exceeded MCL but the same or less than Controls (Columns)
Ag	Ag				Ag			
Al	Al				Al			
As	As	As	<b>As</b>					
B	B	B	<b>B</b>		B	B	<b>B</b>	
Ba	Ba				Ba			
Be								
Cd	Cd	Cd	<b>Cd</b>					
Co	Co							
Cr	Cr	Cr	<b>Cr</b>		Cr	Cr	<b>Cr</b>	
Cu	Cu				Cu			
Fe	Fe							
Hg								
Mn	Mn							
Mo	Mo	Mo	<b>Mo</b>		Mo	Mo	<b>Mo</b>	
Ni	Ni	Ni	<b>Ni</b>		Ni			
Pb	Pb	Pb	<b>Pb</b>					
Sb		Sb		Sb	Sb	Sb	<b>Sb</b>	
Se		Se		Se	Se	Se	<b>Se</b>	
Sn	Sn							
Sr	Sr				Sr			
Ti	Ti				Ti			
Tl		Tl		Tl		Tl		Tl
V	V	V	<b>V</b>		V	V	<b>V</b>	
Zn	Zn							

Note; Bold indicates elements that were both elevated and in exceedance of the MCL

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**APPENDIX A - PHOTOGRAPHS**



Fig. A-1. Preparing indentation in sub-base for lysimeter geomembrane.



Fig. A-2. Preparing drainage pipe from lysimeter to collection tank.



Fig. A-3. Installing geomembrane for lysimeter.



Fig. A-4. Welding geomembrane to lysimeter drainage pipe assembly.



Fig. A-5. Preparing hole for leachate collection tank and trench for drainage pipe.



Fig. A-6. Assembling leachate collection tank.



Fig. A-7. Installing leachate collection tank.



Fig. A-8. Installing leachate collection tank.



Fig. A-9. Collecting lysimeter leachate using submersible pump.



Fig. A-10. Column leach test on MnROAD materials.



Fig. A-11. Water leach test rotator.



Fig. A-12. MnROAD water leach test samples immediately after rotation.

**APPENDIX B – LYSIMETER LEACHATE CHEMICAL CONCENTRATIONS**

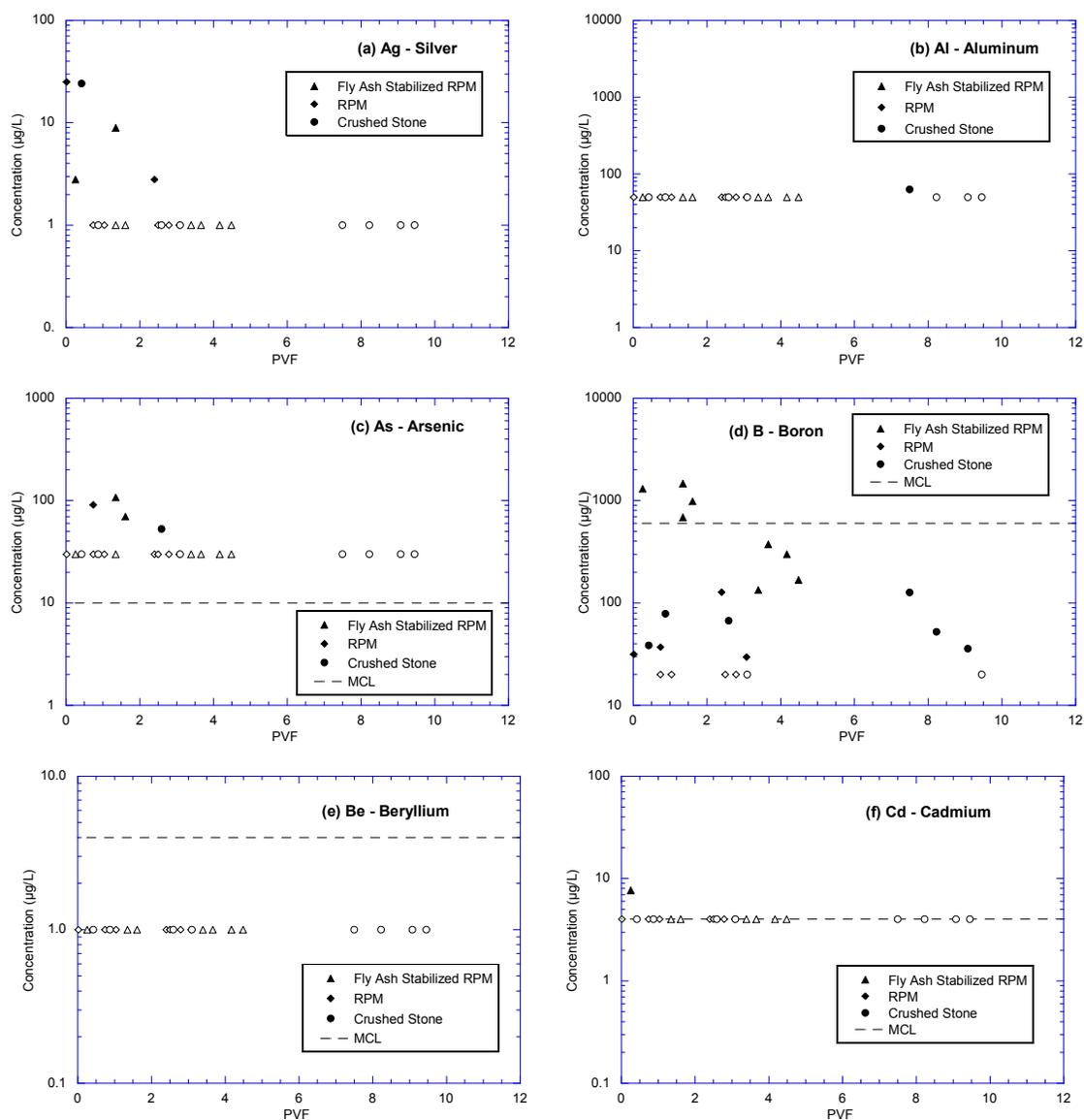


Fig. B-1. (a) Silver, (b) Aluminum, (c) Arsenic, (d) Boron, (e) Beryllium, and (f) Cadmium concentrations in leachate from field lysimeters. Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol.

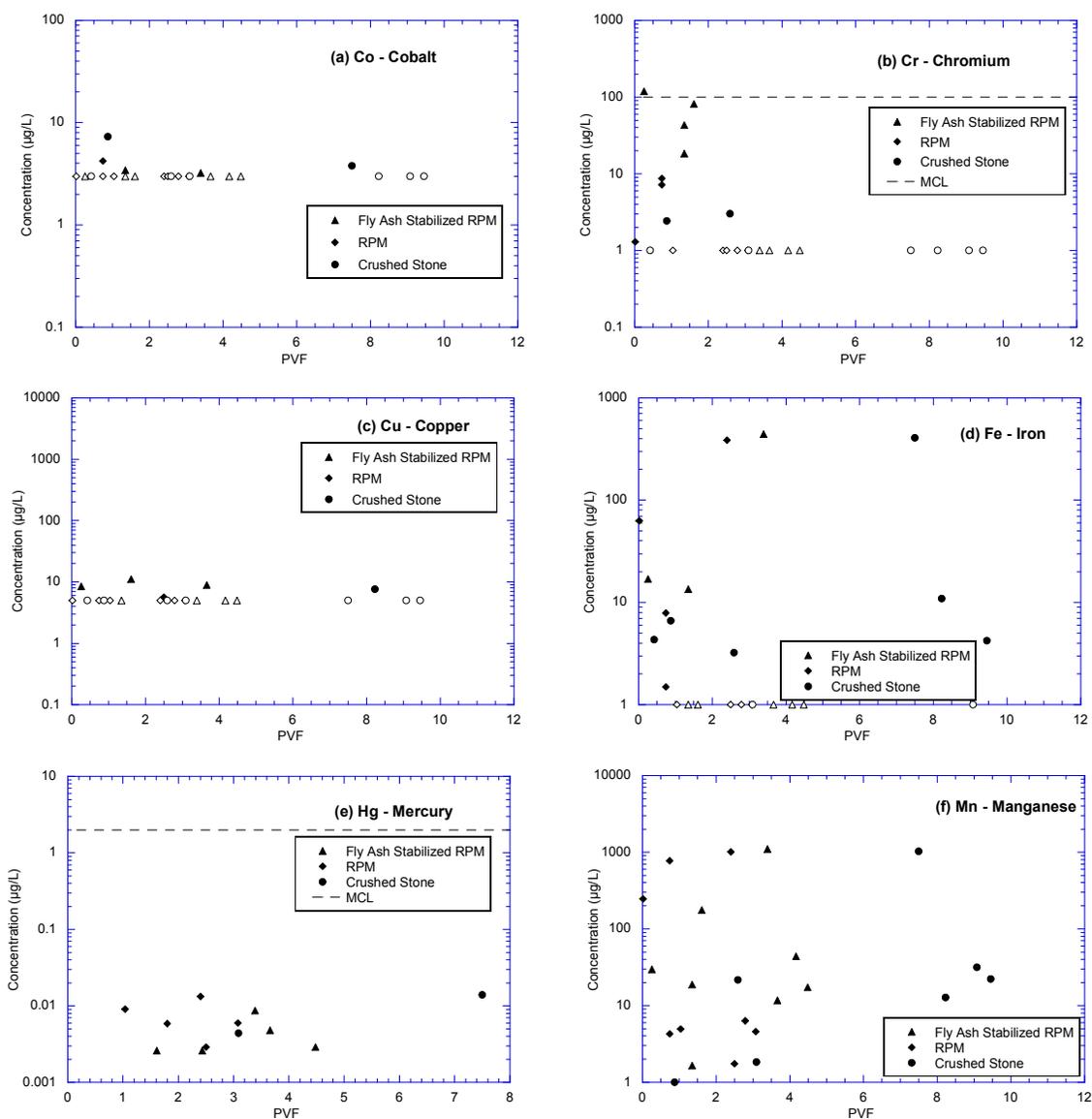


Fig. B-2. (a) Cobalt, (b) Chromium, (c) Copper, (d) Iron, (e) Mercury, and (f) Manganese concentrations in leachate from field lysimeters. Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol.

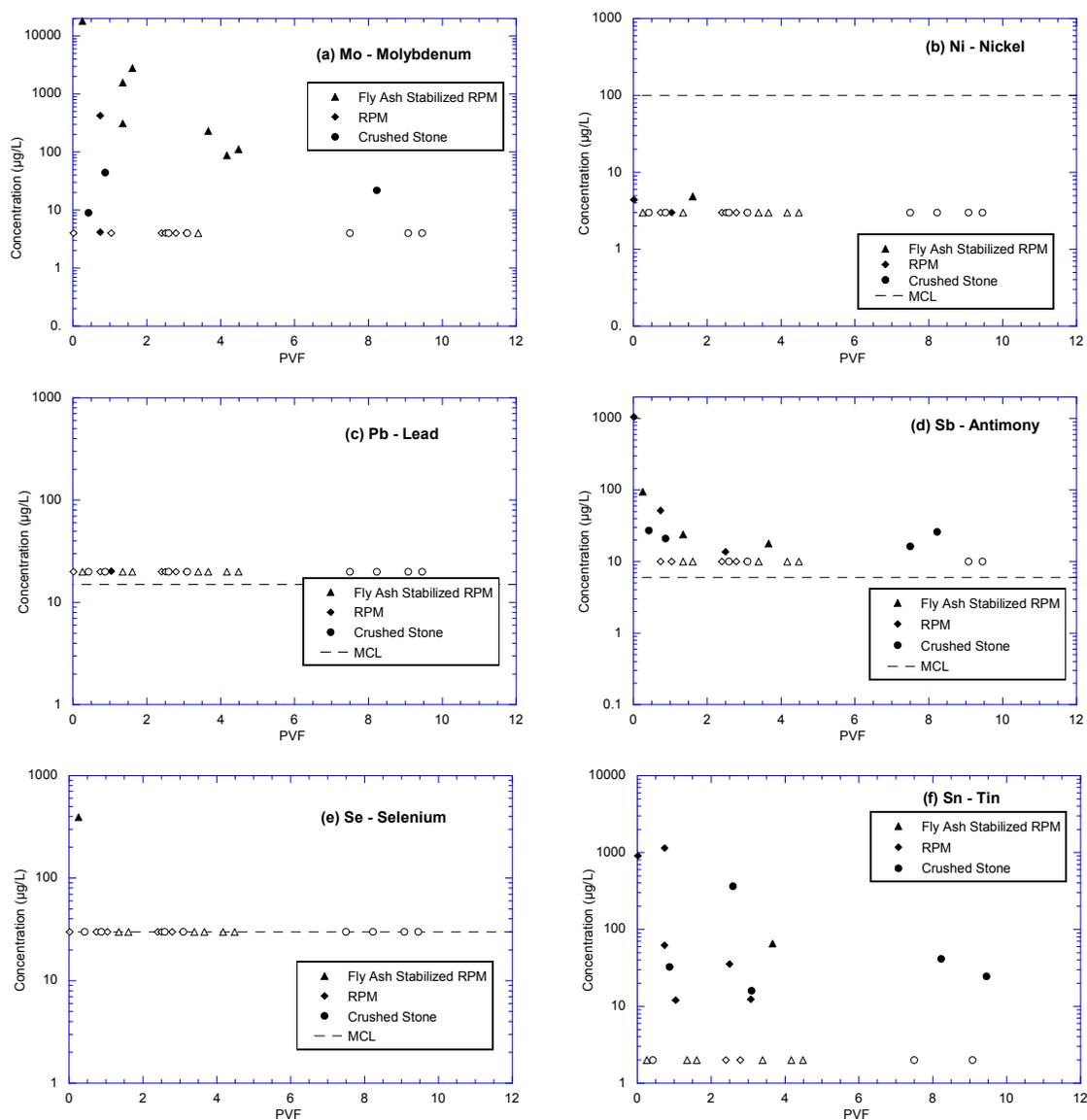


Fig. B-3. (a) Molybdenum, (b) Nickel, (c) Lead, (d) Antimony, (e) Selenium, and (f) Tin concentrations in leachate from field lysimeters. Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol.

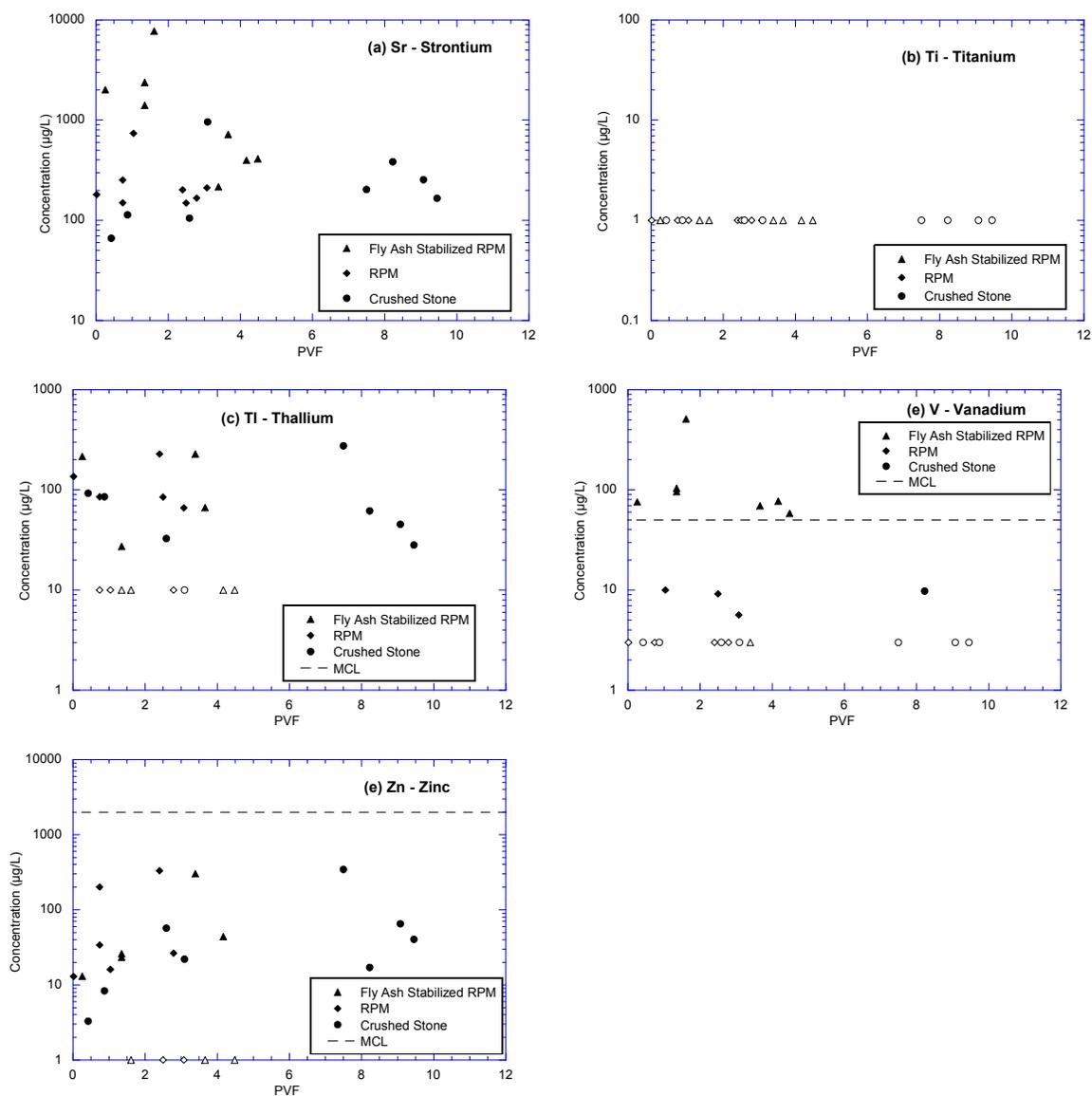


Fig. B-3. (a) Strontium, (b) Titanium, (c) Thallium, (d) Vanadium, and (e) Zinc concentrations in leachate from field lysimeters. Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol.

**APPENDIX C – LABORATORY CHEMICAL CONCENTRATIONS**

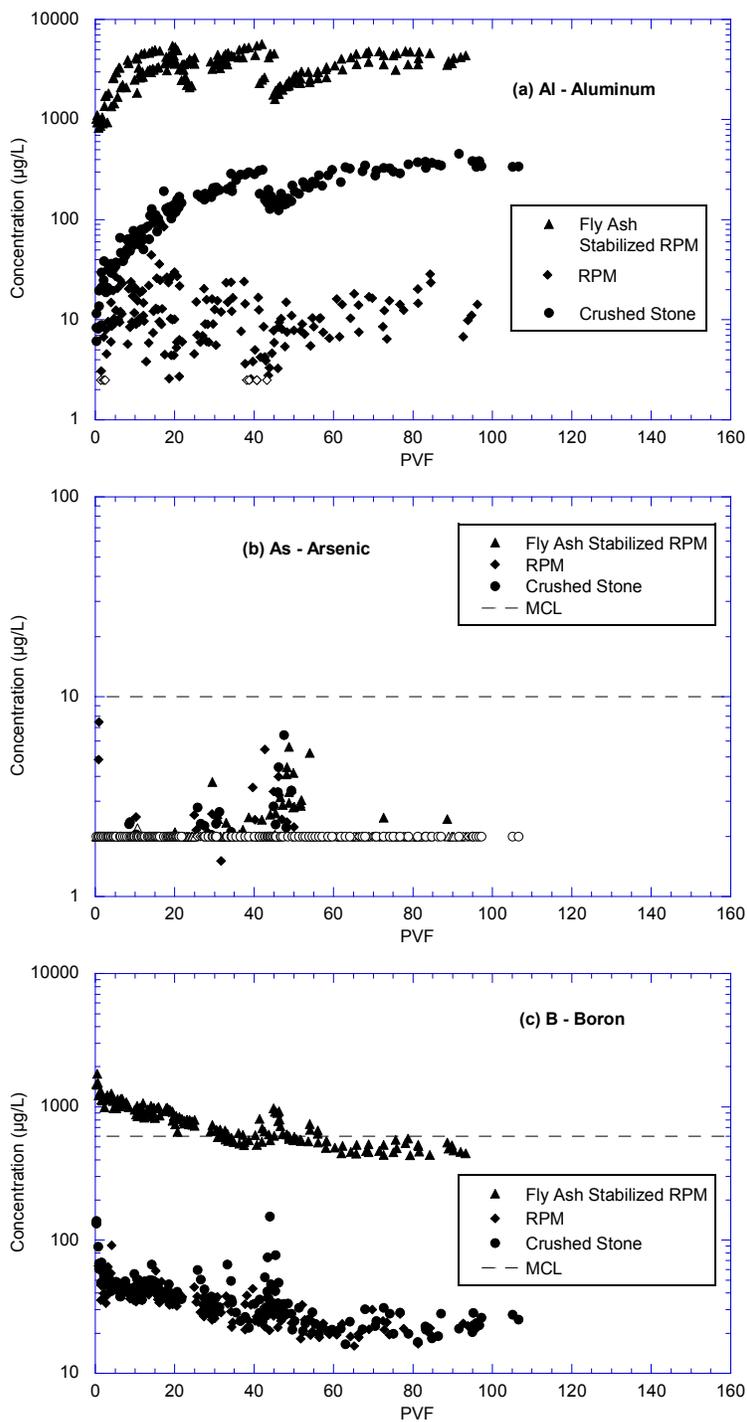


Fig. C-1. (a) Aluminum, (b) Arsenic, and (c) Boron concentrations in leachate from column leach tests (CLTs). Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol. Tests stopped and restarted at approximately 45 PVF.

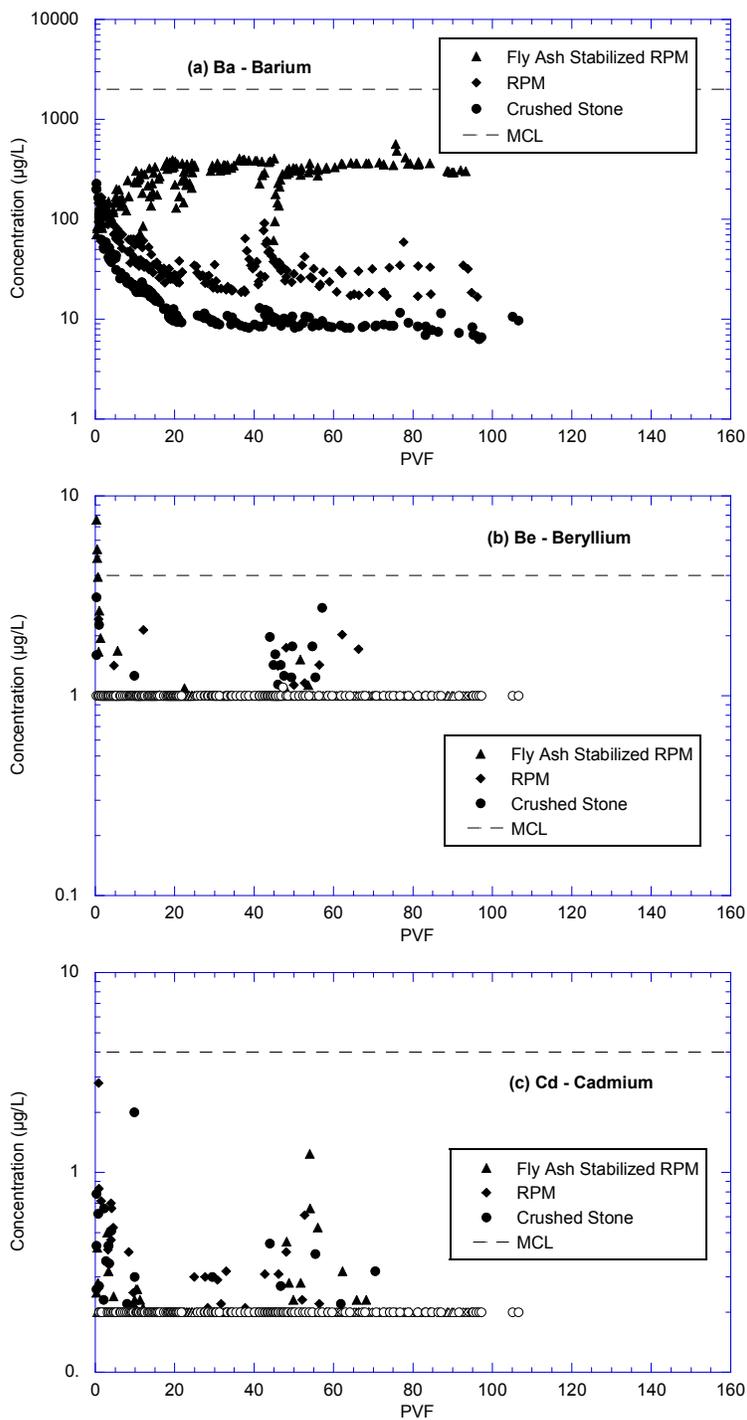


Fig. C-2. (a) Barium, (b) Beryllium, and (c) Cadmium concentrations in leachate from column leach tests (CLTs). Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol. Tests stopped and restarted at approximately 45 PVF.

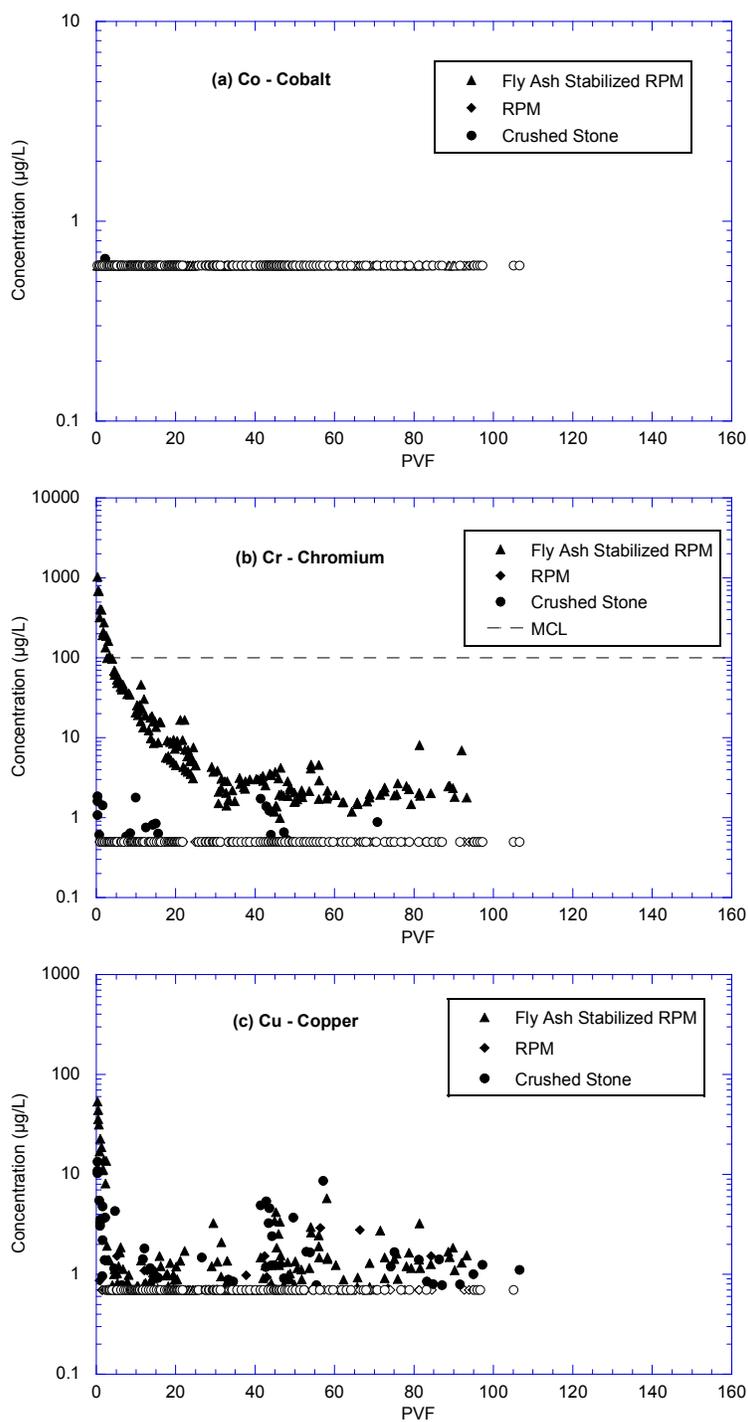


Fig. C-3. (a) Cobalt, (b) Chromium, and (c) Copper concentrations in leachate from column leach tests (CLTs). Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol. Tests stopped and restarted at approximately 45 PVF.

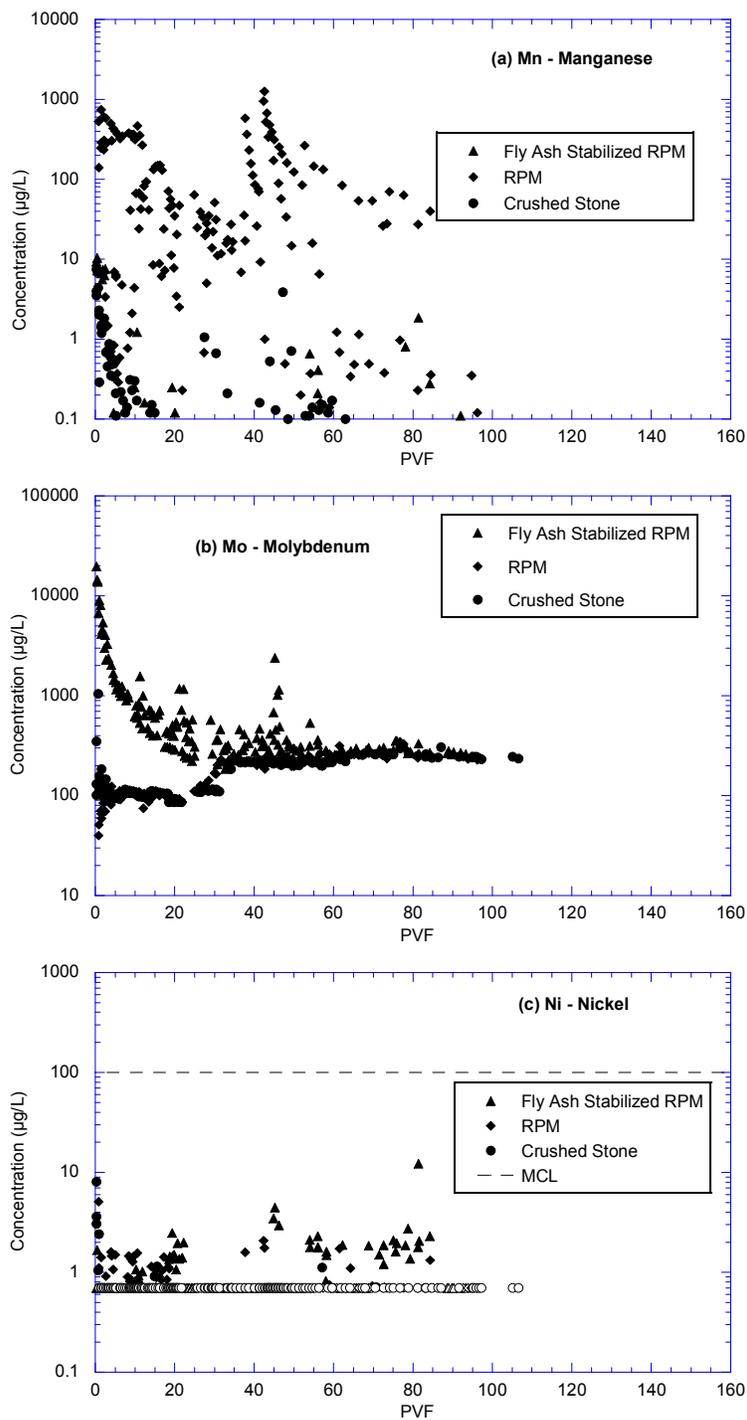


Fig. C-4. (a) Manganese, (b) Molybdenum, and (c) Nickel concentrations in leachate from column leach tests (CLTs). Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol. Tests stopped and restarted at approximately 45 PVF.

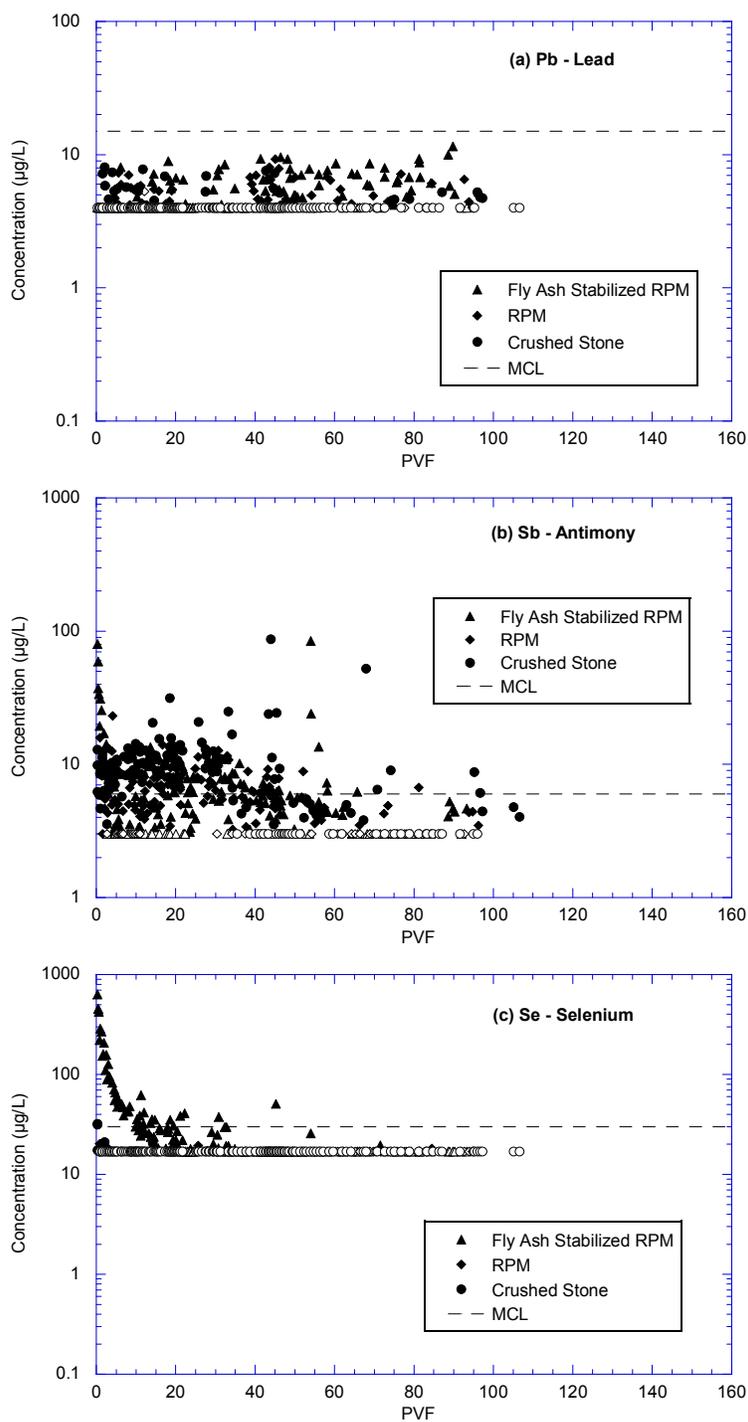


Fig. C-5. (a) Lead, (b) Antimony, and (c) Selenium concentrations in leachate from column leach tests (CLTs). Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol. Tests stopped and restarted at approximately 45 PVF.

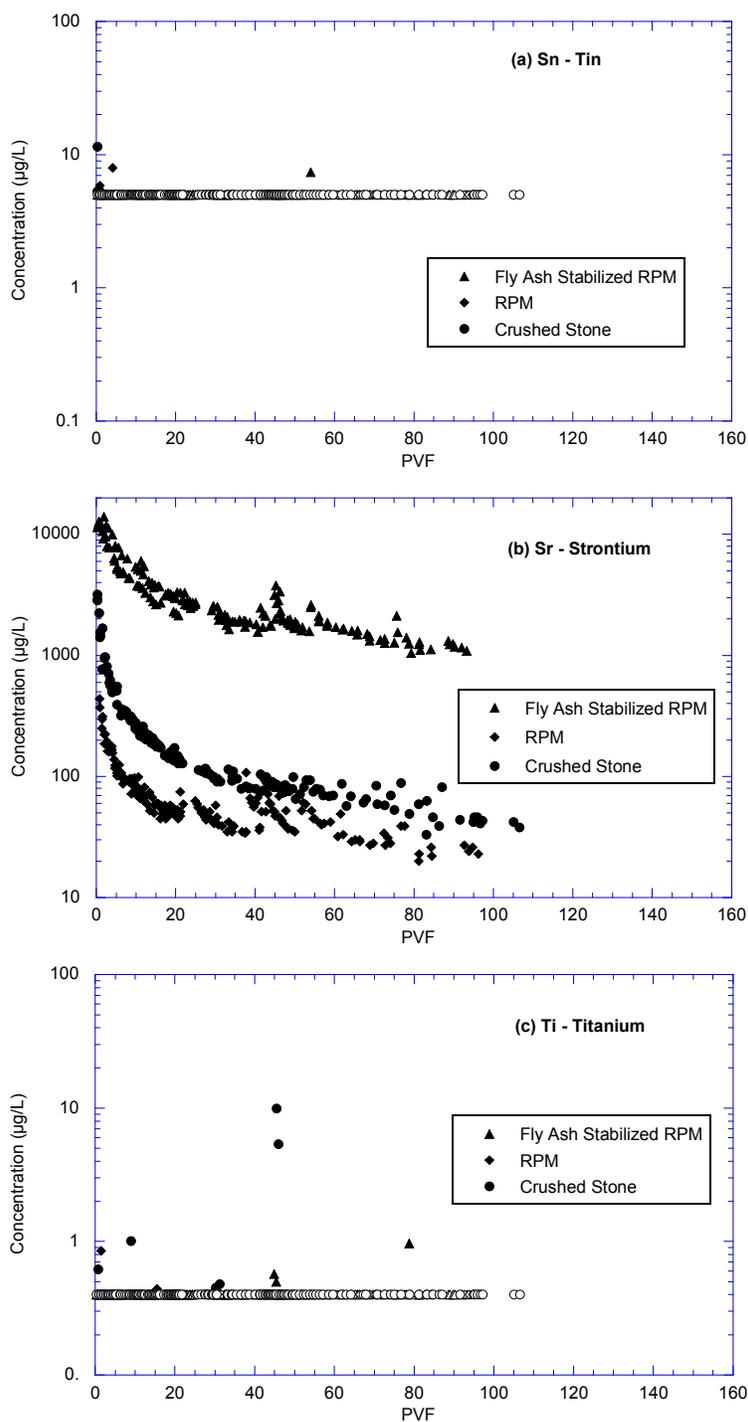


Fig. C-6. (a) Tin, (b) Strontium, and (c) Titanium concentrations in leachate from column leach tests (CLTs). Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol. Tests stopped and restarted at approximately 45 PVF.

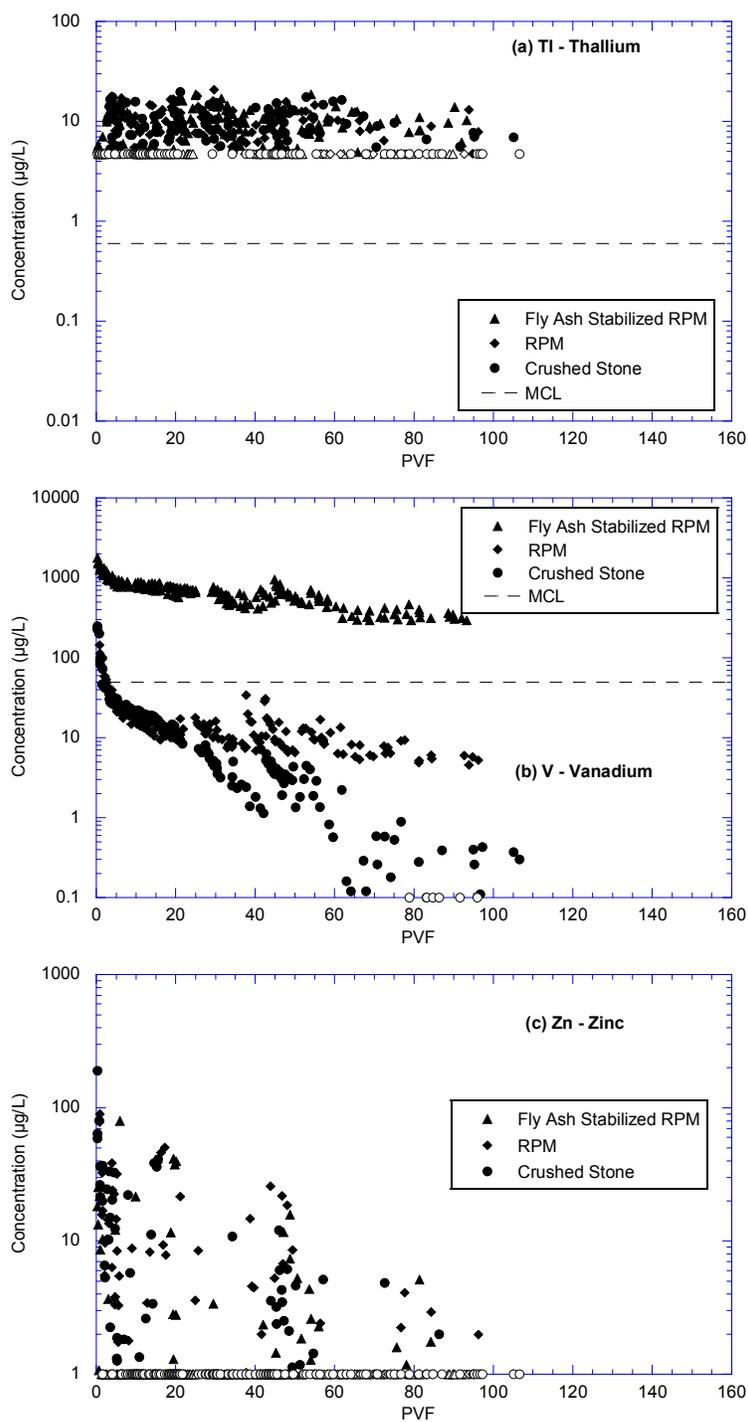


Fig. C-7. (a) Thallium, (b) Vanadium, and (c) Zinc concentrations in leachate from column leach tests (CLTs). Concentrations below minimum detection limits are plotted at the limit, and represented with an open symbol. Tests stopped and restarted at approximately 45 PVF.

Table C-1. MnROAD Water Leach Test Results

Sample	Ag	Al	As	B	Be	Cd	Co	Cr	Cu	Fe	Mn	Mo
Material and L:S Ratio	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
Crushed Stone - 3:1	3	56.6	<30	<20	<1	<4	<3	<1	<5	230.2	2.7	<4
Crushed Stone - 5:1	<1	128.4	<30	<20	<1	<4	<3	1.1	<5	207.4	1.7	<4
Crushed Stone - 10:1	3	167.2	<30	<20	<1	<4	<3	<1	<5	52.8	0.5	<4
Crushed Stone - 20:1	<1	61.9	<30	<20	<1	<4	<3	<1	<5	<1	<1	<4
RPM - 3:1	<1	<50	<30	<20	<1	<4	<3	<1	<5	<1	2.2	<4
RPM - 5:1	<1	<50	50	<20	<1	<4	<3	1.9	<5	<1	0.6	<4
RPM - 10:1	<1	<50	<30	<20	<1	<4	<3	<1	<5	<1	5.5	<4
RPM - 20:1	<1	<50	<30	<20	<1	<4	<3	<1	<5	14.3	10.1	<4
Fly-ash-stabilized RPM - 3:1	<1	554.9	110	755.7	<1	<4	<3	127.0	6.6	<1	<1	2127.5
Fly-ash-stabilized RPM - 5:1	<1	1263.6	70	739.8	<1	<4	<3	98.4	6.6	<1	<1	1574.8
Fly-ash-stabilized RPM - 10:1	<1	3395.1	40	608.1	<1	<4	<3	42.9	<5	<1	<1	581.3
Fly-ash-stabilized RPM - 20:1	<1	7667.8	40	557.8	<1	<4	<3	20.5	<5	<1	<1	134.3

Sample	Ni	Pb	Sb	Se	Sn	Sr	Ti	Tl	V	Zn	pH
ID	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	
Crushed Stone - 3:1	<3	<20	<10	<30	<5	24	<1	<10	<3	5.7	7.9
Crushed Stone - 5:1	<3	24.4	<10	<30	<5	24	<1	<10	<3	5.3	7.6
Crushed Stone - 10:1	<3	<20	<10	<30	26	24	<1	<10	<3	3.2	6.9
Crushed Stone - 20:1	<3	<20	<10	<30	<5	21	<1	<10	<3	5.1	7.2
RPM - 3:1	<3	<20	<10	<30	<5	41	<1	<10	<3	3.0	7.3
RPM - 5:1	<3	<20	<10	<30	14	31	<1	<10	<3	5.9	7.2
RPM - 10:1	<3	<20	<10	<30	<5	22	<1	<10	<3	11.8	7.0
RPM - 20:1	<3	<20	<10	<30	<5	15	<1	<10	<3	44.7	7.0
Fly-ash-stabilized RPM - 3:1	5.9	<20	<10	<30	<5	10258	<1	<10	990	2.8	11.3
Fly-ash-stabilized RPM - 5:1	<3	37.8	<10	<30	<5	8293	<1	<10	900	1.1	11.2
Fly-ash-stabilized RPM - 10:1	<3	<20	<10	<30	<5	4566	<1	<10	590	1.6	10.8
Fly-ash-stabilized RPM - 20:1	<3	<20	<10	<30	<5	2978	<1	<10	410	2.6	10.4

**APPENDIX D – STATE REGULATIONS REGARDING FLY ASH USE**

Table D-1. Fly ash regulatory status in US states

State	Haz. Waste Status	Status	Use in PCC Specifically Authorized	Road/Soil Use Specifically Authorized	If No, Use Possible on case by case basis?
Alabama	Exempt	Special Waste	No	No	Yes
Alaska	Exempt	Indust. Solid or Inert	No	No	Yes, with TCLP and metals, meet requirements
Arizona	Exempt	None	No	No	No
Arkansas	Exempt	Recovered Materials	No	No	Yes, if not "disposal"
California	NOT Exempt	Haz. Waste unless proven not by TCLP	No	No	No
Colorado	Exempt	None	No	No	No
Connecticut	Exempt	Special or Regulated	No	No	Yes
Delaware	Exempt	Nonhaz. Indust.	No	No	Yes, TCLP required
Florida	Exempt	Solid or Indust. Byproduct	Yes	No	Yes
Georgia	Exempt	Indust. Solid	No	No	No
Hawaii	Exempt	None	No	No	Yes, with metals
Idaho	Exempt	Indust. Solid	No	No	No
Illinois	Exempt	CCW or CCB	Yes	Yes	-
Indiana	Exempt	Indust. Solid	Yes	Yes	-
Iowa	Exempt	None	Yes	Yes	-
Kansas	Exempt	Indust. Solid	No	No	No
Kentucky	Exempt	Special	Yes	Yes	-
Louisiana	Exempt	Indust. Solid	No	No	Yes
Maine	Exempt	Haz. Waste unless proven not	Yes	No	No
Maryland	Exempt	Pozzolan	No	Yes	-
Massachusetts	Exempt	Solid unless beneficial reuse	Yes	Yes	-
Michigan	Exempt	Low Hazard Indust.	Yes	Yes	-
Minnesota	Exempt	None	No	No	Yes

State	Haz. Waste Status	Status	Use in PCC Specifically Authorized	Road/Soil Use Specifically Authorized	If No, Use Possible on case by case basis?
Mississippi	Exempt	Indust. Solid	No	No	Yes
Missouri	Exempt	None	Yes	No	Yes
Montana	Exempt	Indust. Solid	Yes	No	Yes
Nebraska	Exempt	Special	Yes	Yes	-
Nevada	Exempt	None	No	No	No
New Hampshire	Exempt	waste derived product	Yes	Yes	-
New Jersey	Exempt	Solid unless beneficial reuse	Yes	Yes	-
New Mexico	Exempt	Indust. Solid	No	No	Yes
New York	Exempt	None	Yes	Yes	-
North Carolina	Exempt	None	Yes	Yes	-
North Dakota	Exempt	None	No	No	Yes
Ohio	Exempt	None	Yes	Yes	-
Oklahoma	Exempt	None	Yes	Yes	-
Oregon	Exempt	None	No	No	No
Pennsylvania	Exempt	None	Yes	Yes	-
Rhode Island	NOT Exempt	Haz. Waste unless proven not by TCLP	No	No	No
South Carolina	Exempt	Indust. Solid	No	No	Yes
South Dakota	Exempt	Solid or Indust. Byproduct	No	No	Yes
Tennessee	NOT Exempt	Haz. Waste unless proven not by TCLP	Yes	No	No
Texas	Exempt	Indust. Solid	Yes	Yes	-
Utah	Exempt	None	Yes	Yes	-
Vermont	Exempt	None	No	No	No
Virginia	Exempt	None	Yes	Yes	-
Washington	NOT Exempt	Haz. Waste unless proven not by TCLP	No	No	No
West Virginia	Exempt	None	Yes	Yes	-
Wisconsin	Exempt	Indust. Byproduct	Yes	Yes	-
Wyoming	Exempt	Indust. Solid	No	No	No