

## TRACE ELEMENT LEACHING FROM RECYCLED PAVEMENT MATERIALS STABILIZED WITH FLY ASH

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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 fly ash was used to stabilize subgrade or base course. Data from control sections are also presented. Percolation rates from the base of a pavement profile vary seasonally in response to seasonal variations in meteorological conditions. Percolation rates typically range between 0.1-0.5 mm/d, with the average percolation rate falling between 0.1-0.2 mm/d depending on site conditions. Concentrations of six elements (B, Cd, Cr, Cu, Mo, and Zn) in leachate from roadway sections stabilized with fly ash have been elevated compared to concentrations from control sections at all field sites with control sections. Four elements from fly-ash-stabilized materials have been elevated in concentration relative to control section at some sites (As, B, Cd, Cr, and Mo) and have also exceeded MCLs. Both B and Mo persistently exceed MCLs. In contrast, concentrations of Cd and Cr have only exceeded MCLs in the first samples collected (PVF < 0.25), and then have remained well below MCLs.

### INTRODUCTION

Approximately 63.5 million Mg of fly ash was produced in the US in 2007, of which 45% was used in beneficial applications including roadway stabilization [ACAA 2008]. The primary limitation to greater use of fly ash in road construction is concern about environmental impacts to soil and groundwater from potentially toxic elements present in the ash [US DOE 2009]. Fly ash contains trace amounts of many metals and metalloids present in the coal, including As, B, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Sr, Tl, V, and Zn [NRC 2006].

Over the past decade, we have installed 10 large pan lysimeters beneath sections of roadway where the base or subgrade was stabilized with cementitious coal fly ash during construction. The purpose of the lysimeters was to monitor the temporal variation in percolation from the base of the roadway and the type, concentration, and pattern of trace elements in the percolate. These two quantities yield the mass flux discharged from the base of the pavement profile,

which is a key factor affecting risk assessments for groundwater beneath pavements. This paper provides a summary of the data from the pan lysimeters.

## FIELD SITES

Five field sites constructed using fly-ash-stabilized base course or subgrade are being monitored (Table 1). These sites are Wisconsin State Highway 60 (STH60) in Lodi, WI; US Highway 12 (US12) in Fort Atkinson, WI; the Scenic Edge subdivision (Scenic Edge) in Cross Plains, WI; 7<sup>th</sup> Avenue in Waseca, MN; and the Minnesota Department of Transportation's full-scale highway testing facility (MnROAD) in Albertville, MN, USA.

**Table 1: Properties of Stabilized Layers and Lysimeters**

Site	STH60	US12	Scenic Edge	MnROAD	Waseca
Layer Stabilized	Subgrade	Subgrade	Subgrade	Base Course	Base Course
Material Stabilized	Soil	Soil	Soil	Recycled Paving Material	Recycled Paving Material
USCS and AASHTO Classification	CL A-6	CL or SC A-6	CL A-7-6	GW-GM A-1-a	GW-GM A-1-a
Fly Ash Type	Columbia	Columbia	Columbia	Riverside 8	Riverside 7
% Fly Ash by Mass	10	12	12	14	10
Compacted Dry Density of Stabilized Layer (kN/m <sup>3</sup> )	15.4	18.9 - 20.0	15.9	19.6	15.9
Stabilized Layer Thickness (mm)	300	300	300	203	150
Lysimeter Dimensions (m)	3.75 x 4.75	3 x 3	3.75 x 4.75	3 x 3	4.0 x 4.0

During construction at least one pan lysimeter was installed at each site immediately below the stabilized materials to collect leachate discharging from the bottom of the layer. Lysimeters were also installed beneath control materials at STH60, US12, and MnROAD.

## METHODS AND MATERIALS

### Fly Ashes

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 US is used in concrete and classifies as Class C or F. Off-specification ash with higher carbon content often cannot be used in Portland cement concrete due to effects on strength and longevity and therefore is not used at the same frequency as Class C and F ashes. However, off-specification ashes can be used in

non-concrete applications such as roadway stabilization [US EPA 2008]. Two of the ashes used in this study were Class C ashes; the other ash was an off-specification ash.

The field sites in this study employed three cementitious fly ashes for stabilization of base course or subgrade: Columbia, Riverside 7, and Riverside 8. Columbia fly ash is from Alliant Energy's Columbia Power Station in Portage, WI, USA, whereas the Riverside 7 and Riverside 8 fly ashes are from Xcel Energy's Riverside Power Plant in Minneapolis, MN, USA. Columbia ash was used at the STH60, Scenic Edge, and US12 sites. The Riverside ashes were used at the MnROAD and Waseca sites. Columbia ash classifies as Class C. Riverside 7 is classified as Class C, whereas Riverside 8 is an off-specification ash due to its high carbon content (>5%).

### **Leachate Monitoring**

The pan lysimeters were constructed with 1.5-mm-thick linear low-density polyethylene (LLDPE) geomembrane overlain with a drainage layer comprised of a geonet between two layers of geotextile. Leachate collected in each lysimeter is routed to a 120-L high-density polyethylene (HDPE) leachate collection tank via polyvinyl chloride (PVC) pipe. The tanks are buried approximately 2 m deep along the shoulder of the roadway.

Leachate in the tanks is pumped and sampled periodically. Volume of leachate discharged from the layer is recorded and total pore volumes of flow (PVF) are calculated. Samples are collected from the pumped leachate for chemical analysis in HDPE sample bottles with zero headspace. Within 24 hr of sampling, pH and oxidation-reduction potential (Eh) are measured in the laboratory. The sample is then filtered with a 0.2  $\mu\text{m}$  micropore filter and preserved to pH<2 using trace-metal-grade  $\text{HNO}_3$ .

### **Leachate Chemical Analysis**

Chemical analysis of the leachate samples has been conducted with several methods over the course of the project due to the availability of equipment and changing requirements for certain analytes. The methods include atomic adsorption (EPA Standard Methods 213.2, 218.2, 270.2, and 272.2), inductively coupled plasma-mass spectrometry (USEPA Method 200.8), inductively coupled plasma-optical emission spectrometry (USEPA Method 200.8), and cold vapor atomic fluorescence spectrometry (USEPA Methods 1631, 1669) for Hg. The elements analyzed are Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, and Zn. Concentrations of all elements were not measured at all sites or at all times during the study.

## **RESULTS**

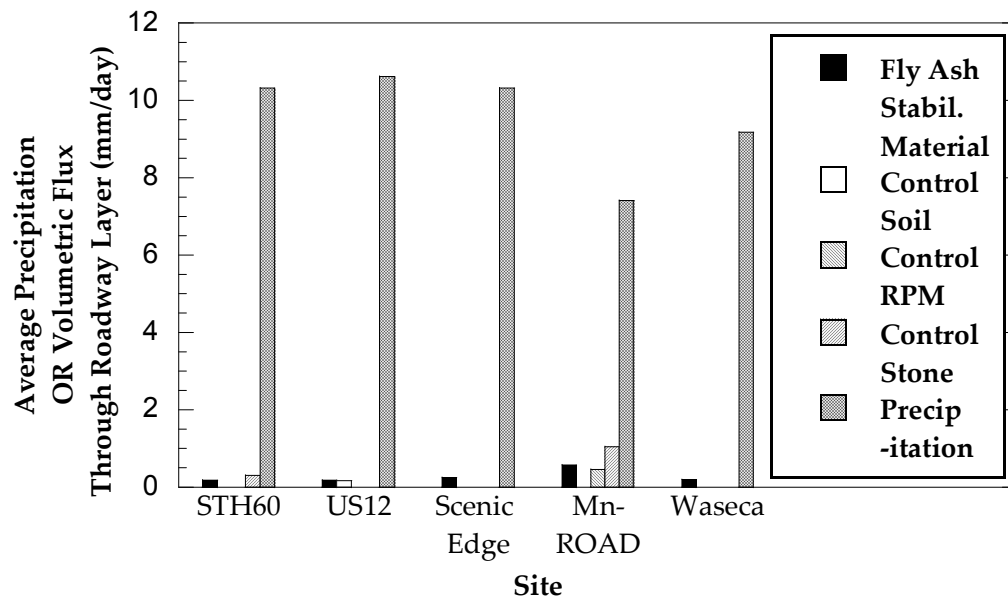
### **Precipitation Patterns and Lysimeter Drainage**

Long-term flux of leachate discharged from the fly-ash-stabilized layers has been less than 8% of the local precipitation, and often only 1-3% of precipitation (Fig. 1). Percolation rates typically range between 0.1-0.5 mm/d, with the average percolation rate falling between 0.1-0.2 mm/d depending on site conditions. Regional average groundwater recharge rate for the sites is estimated to range from 19% to 24% of precipitation for the Minnesota sites and from 20% to 21% of precipitation for the Wisconsin sites. This indicates that the recharge rate in areas adjacent to a stabilized roadway may be significantly higher than the rate of leaching

from the roadway. This difference in recharge rates will affect subsurface transport by diluting elements discharged from the roadway.

Greater discharge of leachate relative to precipitation occurs in the fly-ash-stabilized base course layers (2.1 to 7.8% of precipitation) compared to the stabilized subgrades (1.8 to 2.4% of precipitation) (Fig. 1). The control base courses also had greater leachate flux than the control subgrades in terms of percentage of precipitation.

Peak fluxes from the layers tend to occur in the spring months when heavy rains and snow melt occur, and again in a period in the late summer and early fall. There is a delay of peak fluxes of one to two months after peak precipitation events. Minimum fluxes tend to occur in the winter when precipitation and pore water are often frozen, and in a period in July or August. Occasionally the flux from the base course layers approaches 15% of precipitation for a period of several months, but the long-term average has never been more than 7.8%.



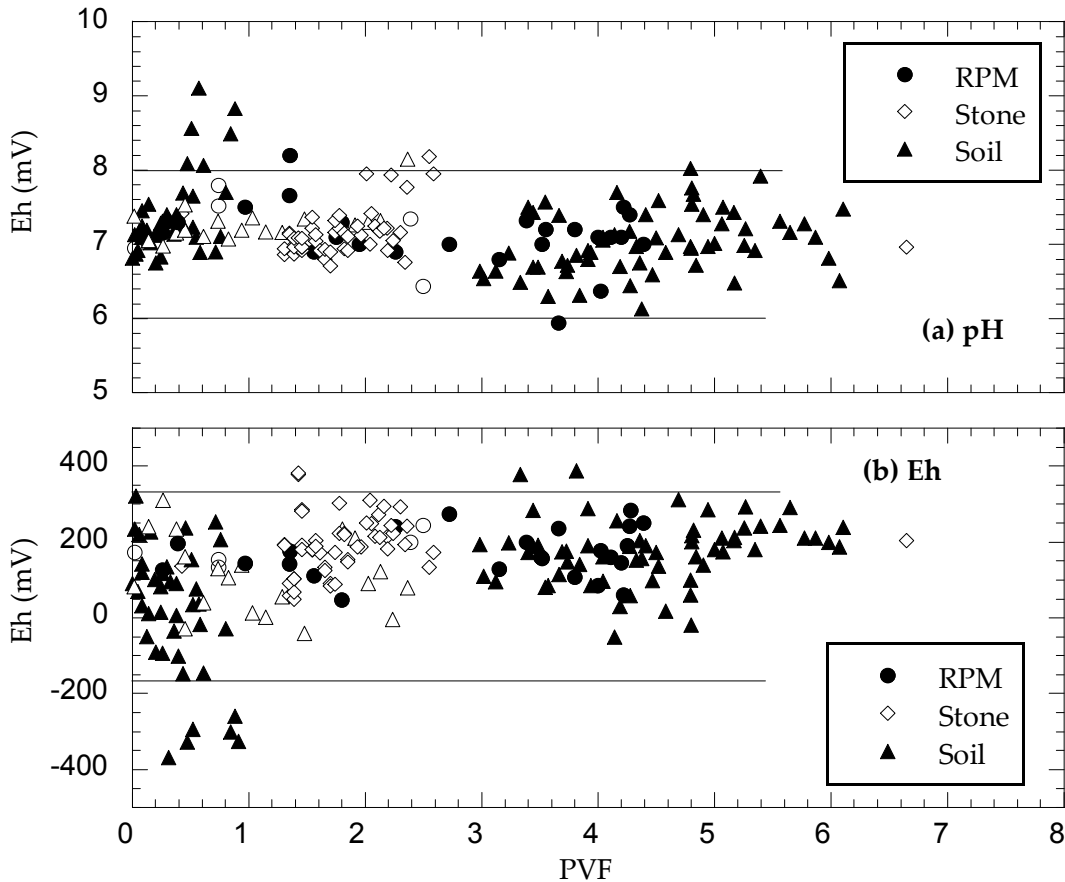
**Fig. 1. Comparison of Long-term Volumetric Flux from the Roadway Layers Relative to Local Average Daily Precipitation**

#### Chemical Indicator Parameters

The pH and Eh of leachates collected in the lysimeters are presented in Fig. 2. The pH in field leachate ranges from 6 to 9, with most of the data near neutral (Fig. 2a) for both stabilized and control materials. Only the east stabilized lysimeter at the US12 site regularly has pH greater than 8, possibly because this is the only site with concrete pavement. The leachate Eh generally ranges from +300 to -150 mV, with most data predominantly oxidizing ( $Eh > 0$ ) and occasional samples in a reducing state ( $Eh < 0$ ) (Fig. 2b). Only the east lysimeter at the US12 site has Eh less than -150 mV on a regular basis (Fig. 2b). The US12 east lysimeter regularly has leachate that is grey in color and has a strong odor of anaerobic decay. Other field leachates generally are clear to yellow, and have no odor.

### Elements Released and Magnitude of Concentrations

Of the twenty-four trace elements considered in the analysis (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, and Zn), all except Be were present in detectable quantities in leachate from fly-ash-stabilized layers. Only Mo had a peak concentration greater than 10000  $\mu\text{g/L}$ . Sr, Al, Fe, B, and Mn have maximum peak concentrations between 10,000 and 1000  $\mu\text{g/L}$ ; Sn, Ba, V, Se, Zn, As, Cu, Tl, and Ni have maximum peak concentration between 1000 and 100  $\mu\text{g/L}$ ; and Pb, Cr, Sb, Ti, Co, Cd, and Ag have maximum peak concentration between 100 and 10  $\mu\text{g/L}$ . Peak concentrations of both Hg and Be have been less than 1  $\mu\text{g/L}$ .

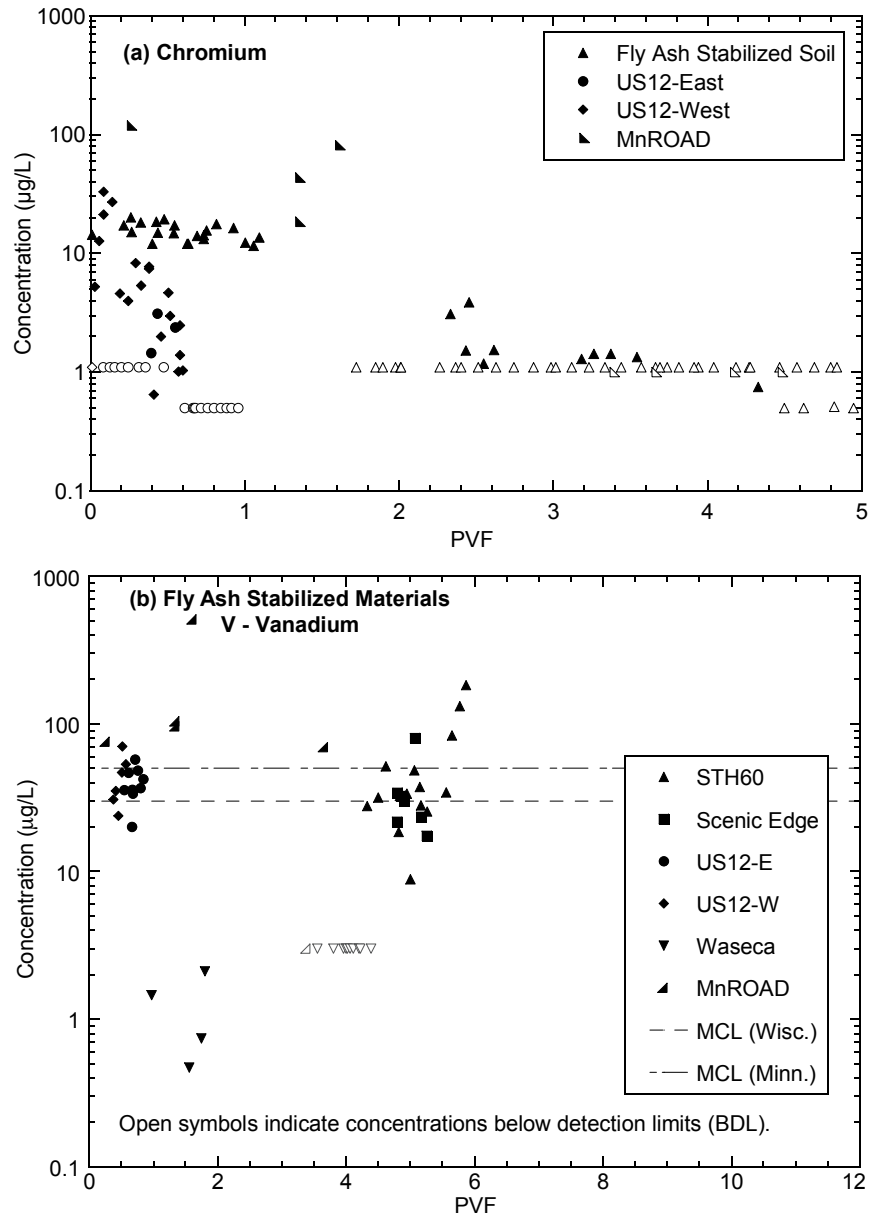


**Fig. 2. pH (a) and Eh (b) of Leachate from Lysimeters Beneath Stabilized and Control Materials**

### Elution Patterns

Leachate concentrations were observed to rise and then fall over time or pore volumes of flow (PVF). Several elements in the leachate were observed to reach peak concentration during the first or second PVF and to remain lower than the peak in all subsequent samplings events (a first-flush leaching pattern). Others would remain relatively constant over time. Examples of these patterns are shown in Fig. 3.

The number of elements at a site with concentrations exceeding maximum contaminant levels (MCLs) typically decreased with increasing PVF, with concentrations typically dropping below MCLs within 2-4 PVF. However, environmental conditions vary in the roadway materials over time scales of hours to seasonally, including temperature, moisture content, precipitation and infiltration rate, pH, biological activity, and freeze-thaw cycles. As a consequence, leaching and mobility of elements may change temporally with changing environmental conditions.



**Fig. 3. Examples of elements showing a decrease in concentration with PVF (a) and relatively consistent concentration with PVF (b)**

## EVALUATION OF LEACHATE CONCENTRATIONS

### Field Concentrations Compared to Control Sections

Concentrations of elements in leachate from a material stabilized with fly ash were considered elevated relative to concentrations from control materials if the confidence interval associated with the peak concentration from the material stabilized with fly ash was greater than and did not overlap the confidence interval associated with the peak concentration of the control material. Confidence intervals were computed using coefficients of variation (COV) from 7 replicate analyses of each element tested via ICP-OES.

Nineteen of the 24 elements tested were found to have elevated concentrations relative to control concentrations. Six elements (Mo, B, Cu, Cr, Cd, and Zn) had elevated concentrations at all 3 field sites with control sections. Eleven elements (Sr, Al, Ba, Ti, Co, Fe, Sn, As, V, Ni, and Mn) were elevated at two of the three sites, and both Pb and Ag were elevated at one of the sites. Concentrations of Hg, Be, Se, Tl, and Sb were not elevated in leachate from the stabilized materials.

### Elements Exceeding MCLs

Eleven elements in lysimeter leachate were found to exceed MCLs: As, B, Cd, Cr, Mo, Ni, Pb, Sb, Se, Tl, and V. Of these eleven elements, eight were elevated in concentration relative to the control sections (As, B, Cd, Cr, Mo, Ni, Pb, and V). The concentrations of Sb, Se, and Tl in leachate from stabilized materials were found to be equal or less than the concentrations from control materials.

Four of the elements from fly-ash-stabilized materials that exceeded MCLs were elevated at all sites relative to the control section. In order of descending level of elevation, these elements are B, Mo, Cr, and Cd. Molybdenum has no MCL in Minnesota, but the peak Mo concentration at MnROAD was 470 times higher than the Wisconsin MCL. Cd and Cr concentrations only exceeded MCLs in the first samples collected (PVF < 0.25), and then remained well below the MCL in all subsequent samples. In contrast, the B and Mo persist at elevated concentrations.

Four of the elements that exceeded MCLs were elevated in leachate from stabilized materials at only one or two of the three sites with controls. In order of descending level of concentration elevation, these elements are V, Ni, As, and Pb. V continues to leach at concentrations above the MCL at all sites where the concentration has exceeded the MCL. Ni only exceeded the MCL or was elevated relative to the control at the US12 site, which has more acidic and reducing conditions than the other sites.

Both As and Pb have relatively low and constant concentrations that periodically exceed the MCL over many PVF. However, the concentrations of As and Pb from stabilized materials are only slightly elevated relative to control concentrations.

## CONCLUSIONS

The field data indicate that the percolation rate from the base of a pavement profile varies seasonally in response to seasonal variations in meteorological conditions. Percolation rates

typically range between 0.1-0.5 mm/d, with the average percolation rate falling between 0.1-0.2 mm/d depending on site conditions.

Concentrations of many trace elements, particularly those with relatively low water quality standards, diminish over time as water flows through the pavement profile. For many elements, concentrations below US water drinking quality standards are attained at the bottom of the pavement profile within 2-4 pore volumes of flow.

Concentrations of six elements (Mo, B, Cu, Cr, Cd, and Zn) in leachate from roadway sections stabilized with fly ash were elevated compared to concentrations from controls at all sites with control sections. Concentrations of four elements from fly-ash-stabilized materials were elevated relative to the control sections at all sites (As, B, Mo, Cr, and Cd) and also exceeded MCLs. Of these elements, both B and Mo have exceeded the MCL for many PVF. In contrast, concentrations of Cd and Cr only exceeded MCLs in the first samples collected (PVF < 0.25), and then remained well below the MCL in all subsequent samples.

## ACKNOWLEDGEMENT

Financial support for this study has been provided by US EPA, US DOE, MnDOT, the Wisconsin Department of Transportation, and the US Federal Highway Administration's Recycled Materials Resource Center. Endorsement by the sponsors is not implied and should not be assumed.

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