

Evaluation of Surface Water Runoff from Fly Ash–Stabilized and Nonstabilized Soil Surfaces

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Abstract: This study evaluated the constituent make up of simulated rainwater runoff from Class C fly ash–stabilized and nonstabilized clay soil using laboratory test pads to assess the potential for impacts to surface water from the use of uncovered fly ash–stabilized soils as potential roadbed material. Recirculated runoff from test pads was sampled and tested during three simulated rainfall events over an 84-day trial period. All samples were analyzed for trace metals. Analytical results from the simulated runoff were screened to identify five indicator parameters in the runoff that were used as the basis for assessing potential environmental effects to surface waters. Runoff water results from fly ash–stabilized test pads for these indicator parameters were compared to water quality benchmarks. Based on the low concentrations measured in runoff relative to applicable criteria, and on the conservative nature of the experimental methods relative to typical field conditions, we concluded that surface runoff from fly ash–stabilized soil would not present significant adverse effects to surface water if used uncovered on low traffic exposed surfaces.

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Introduction

Large volumes of fly ash are produced from the coal combustion process in power plants and are collected from the combustion gases in electrostatic precipitators or baghouses. There are two classes of fly ash [Class C or Class F (ASTM 2004)] with properties that reflect minerals present in the type of coal that is burned.

The Class C fly ash produced in the electric generation process contains calcium aluminates and silicates, which cause the fly ash to form a cementitious matrix when combined with moisture, making it an excellent binding agent for soil stabilization applications. The use of fly ash in soil stabilization has been practiced in the United States for a vast array of construction projects for over 60 years.

The use of fly ash–stabilized soil as a paved road subgrade is a well established and widely accepted practice. The current study is intended to address the question of whether fly ash–stabilized

clay could be used without overlays for low traffic roads (such as plant access roads or utility line rights-of-way), parking lots, or yard storage areas without adverse environmental effects.

Project Objectives and Scope

The primary objective of this project was to determine the potential for leaching of fly ash constituents into surface water runoff over fly ash–stabilized clay soil and to assess the likelihood for adverse environmental impacts to surface water from such runoff. Laboratory simulations using natural soil and fly ash–stabilized soil were conducted using test pads exposed to synthetic rainfall over varying lengths of time. Measurements of analyte concentrations in the runoff water were then compared to benchmarks established for surface water quality protection.

Literature Review

The use of fly ash in the stabilization of soils for construction applications is a commonly used technology that has been proven to be both very economical and effective. The proper addition of Class C fly ash to subbase soils reduces pavement distress and frequency of maintenance, and lengthens the life of pavements [American Concrete Institute (ACI) 2005]. The U.S. EPA considers fly ash–stabilized base course to be advantageous over other base materials (U.S. EPA 2005). Fly ash–stabilized subgrades have also been used successfully with no apparent environmental impacts in parking lot construction and storage yard areas (Ramme and Tharaniyil 2004).

Previous studies have shown that Class C fly ash–stabilized subgrades have a *de minimus* impact on the environment due to water runoff and leachate produced from natural rainfall events

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Fig. 1. Test pad configuration of 91 cm × 91 cm



Fig. 2. Test pad during runoff simulation

[American Concrete Institute (ACI) 2005; Electric Power Research Institute (EPRI) 2001]. Research on subgrade leachate collected from lysimeters showed that trace metals such as cadmium, chromium, selenium, and silver were naturally attenuated as the water percolates through the fine-grained subgrade to the groundwater (Edil et al. 2002).

Fly ash-amended soils have also been used in the construction of many water retention and erosion control projects nationwide. Ponds lined with fly ash-stabilized soil cement have been used for irrigation of farm fields producing crops for human consumption, suggesting that the amount of leaching of dissolved constituents that may occur to overlying water is minimal [Portland Cement Association (PCA) 1992] and acceptable. The Electric Power Research Institute (EPRI) compared the chemical make up of leachate from fly ash with lime-stabilized subgrades [Electric Power Research Institute (EPRI) 2001]. The results indicated that in several cases, the leachate values for certain parameters in the fly ash-soil composite were higher than the leachate values for the lime-soil composite.

Researchers at Purdue University found that the application of dry coal combustion products and organic by-products to farm fields reduces soil erosion and produces fewer solids in storm-water runoff than nonstabilized soil (Tishmack et al. 2001). Grain size, total organic carbon, pH, and other natural physiochemical characteristics may affect mobility and attenuation of dissolved metals leached from the soil stabilization mixture (U.S. EPA 2005).

Even though leaching of fly ash constituents is possible from nonencapsulated applications, it does not occur in high concentrations in real time, and has not been shown to migrate far from the site because the leachate constituents are readily attenuated in soil (U.S. EPA 2005). Moreover, Electric Power Research Institute (EPRI) (1998) reported that monitoring results from five construction sites in different regions of the United States, having varying climatic and soil conditions, showed that measurable levels of chemicals leached from fly ash-stabilized road bases or embankments were limited to soils within 6 ft of the surface.

Electric Power Research Institute (EPRI) (2001) performed test pad studies with lime-stabilized Class C fly ash-stabilized soils and unamended soil. Materials were tested using simulated rainfall over one square meter test pads graded at a 5% slope. Each pad was subjected to two 2-h rainfall simulation events, one about 2 h after pad construction and another event 2 weeks later. Soluble (dissolved) and total concentrations of 22 elements and sulfate were measured in runoff water from the test pad simulations. None of the mean concentrations measured for fly ash-amended soil in these tests exceeded Minnesota Pollution Control Agency Discharge Water Quality Standards [Electric Power Re-

search Institute (EPRI) 2001], indicating a very low probability for environmental effects.

Experimental Methods

Test Materials

Laboratory test simulations of rainfall runoff over nonstabilized and fly ash-stabilized soil were performed by GESTRA Engineering (Milwaukee, Wisc.) in May 2004 [GESTRA 2005 (“Laboratory testing of surface water runoff on fly ash stabilized soil.” GESTRA Project No.: 04023-40, GESTRA Engineering, Inc., Milwaukee, Wisc. Unpublished Report, April 11, 2005 for We Energies, Milwaukee)]. Prior to test simulations, testing of physiochemical characteristics of the soil, fly ash, and fly ash-stabilized soil were performed. The Class C fly ash used in our tests was produced at We Energies Oak Creek Power Plant (OCPP), located in Milwaukee County, Wisc.

Native soils used in the testing and simulations consisted of lean silty clay collected from the We Energies Ash Landfill site in Caledonia, Wisc. Generally, surface soils in the area are formally classified as Marley silt loams [Soil Conservation Service (SCS) 1970]. These soils consist of dense, fine grained, and highly plastic silty clays that are often abundant in surficial and vadose zone deposits in southeastern Wisconsin.

Simulated rain water was formulated for use in the runoff simulations by We Energies state-certified environmental laboratory based on specifications prescribed for synthetic precipitation to be used in assessing leachability of soils at sites east of the Mississippi River (U.S. EPA 1994). The simulated rainfall water recipe consisted of purified reagent water combined with an extractant fluid of 60/40 weight percent mixture of sulfuric and nitric acids to achieve an unbuffered pH of 4.2 for the solution (U.S. EPA 1994).

Testing Apparatus

The bench-scale testing apparatus consisted of two 91 cm × 91 cm test pads (one for nonstabilized soils and another for fly ash-stabilized soils) along with a surface water application and runoff collection system for each test pad. The pads were contained in 10-in.-thick boxes and configured with a 2% slope to facilitate runoff flow. Unamended and fly ash-stabilized soils were placed in the containers in three lifts of 7.6- to 10.2-cm. thickness, and each lift was individually compacted to at least 95% of standard Proctor densities after placement in the containers. The system for applying and recovering the simulated rain water to and from the

Table 1. Summary of Analytical Results for Unused (Control) Runoff Water (mg/L)

Analyte	Nonstabilized clay						Stabilized clay					
	28-day simulation		56-day simulation		84-day simulation		28-day simulation		56-day simulation		84-day simulation	
	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved
Aluminum ^a	<0.032	<0.032	0.056	<0.032	<0.032	<0.032	<0.032	<0.032	<0.032	0.047	<0.032	0.038
Antimony ^c	<0.023	<0.023	<0.00093	<0.00093	<0.00093	<0.00093	<0.023	<0.023	<0.00093	<0.00093	<0.00093	<0.00093
Arsenic ^c	<0.00054	<0.00054	<0.00054	<0.00049	<0.0012	<0.00049	<0.00054	<0.00054	<0.00054	<0.00049	<0.00049	<0.00049
Barium ^b	0.0011	0.0015	<0.001	<0.001	<0.001	<0.001	0.03	<0.001	<0.001	<0.001	<0.001	<0.001
Beryllium ^c	<0.00018	<0.00018	<0.000065	<0.000065	<0.00018	<0.00018	<0.00018	<0.00018	<0.000065	<0.000065	<0.00018	<0.00018
Boron ^c	<0.0077	<0.0077	<0.0077	<0.0077	<0.0077	<0.0077	<0.0077	<0.0077	<0.0077	<0.0077	<0.0077	<0.0077
Cadmium ^b	0.000039	0.000064	0.00019	0.00024	0.000044	0.0001	0.000025	0.000056	<0.00002	0.00023	0.000034	0.00008
Calcium ^a	0.22	0.24	0.21	0.21	0.14	1.2	0.28	0.15	0.22	0.22	0.23	0.26
Chromium ^b	<0.0019	<0.0021	0.0028	0.0026	<0.0019	0.0021	<0.0019	<0.0021	0.003	0.0055	<0.0019	<0.0021
Copper ^a	0.029	0.028	0.026	0.022	0.024	0.025	0.0076	0.0067	0.0031	0.004	0.014	0.014
Iron ^a	0.013	0.011	0.025	0.0035	0.0044	0.0084	0.035	0.014	0.026	0.0064	0.0082	0.017
Lead ^c	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029
Magnesium ^a	0.06	0.069	0.075	0.07	0.029	0.082	0.12	0.076	0.084	0.073	0.063	0.093
Manganese ^b	<0.00042	0.0005	0.0012	0.0016	<0.00042	0.0018	0.0007	<0.00042	0.0011	0.0009	0.0005	0.0005
Mercury ^c	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017
Molybdenum ^c	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062	<0.0062
Nickel ^c	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066
Selenium ^c	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.00062	<0.0015	<0.0015	<0.0015	<0.0015	<0.00062	<0.00062
Silver ^c	<0.000047	<0.000047	<0.000069	<0.000069	<0.000069	<0.000069	<0.000047	<0.000047	<0.000069	<0.000069	<0.000069	<0.000069
Sodium ^b	<0.058	<0.058	0.12	0.08	0.072	0.060	<0.058	0.06	0.13	0.13	<0.089	<0.058
Strontium ^c	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.0031	<0.003	<0.003
Sulfate ^a	2.7		2		2.7		2.7		2.1		2.6	
Thallium ^c	<0.0011	<0.0011	<0.00062	<0.00062	<0.0011	<0.0011	<0.0011	<0.0011	<0.00062	<0.00062	<0.0011	<0.0011
Vanadium ^c	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021	<0.0021
Zinc ^a	0.022	0.021	0.0200	0.016	0.018	0.043	0.0016	0.011	0.015	0.012	0.034	0.036

^aDetected in all samples of unused (control) runoff water.^bDetected in one or more unused runoff water samples.^cBRL in all unused runoff water samples.

Table 2. Summary of Analytical Results for Recirculated Runoff Water for Stabilized Clay under Various Test Simulations

Analyte	Concentration in runoff (mg/L)					
	28-day total	28-day dissolved	56-day total	56-day dissolved	84-day total	84-day dissolved
Aluminum ^a	1.2	0.7	0.66	0.37	0.55	0.38
Antimony ^b	0.023	0.055	<0.00093	<0.00093	<0.00093	<0.00093
Arsenic ^b	<0.00054	0.00071	<0.00054	0.0019	<0.0012	0.0009
Barium ^a	0.18	0.17	0.15	0.16	0.1	0.11
Beryllium ^c	<0.00018	<0.00018	<0.000065	<0.000065	<0.00018	<0.00018
Boron ^a	0.69	0.69	0.62	0.66	0.46	0.48
Cadmium ^b	0.00002	<0.00002	<0.00002	<0.00002	0.0001	0.000053
Calcium ^a	18	17	17	18	14	14
Chromium ^a	0.029	0.028	0.036	0.038	0.032	0.033
Copper ^a	0.0062	0.0036	0.004	0.002	0.0078	0.0053
Iron ^a	0.3	0.0093	0.16	0.07	0.11	0.043
Lead ^c	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029
Magnesium ^a	6.2	6	5.3	5.6	3.4	3.4
Manganese ^a	0.0046	0.001	0.0033	0.0053	0.0029	0.0015
Mercury ^c	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017
Molybdenum ^a	0.029	0.041	0.057	0.058	0.071	0.068
Nickel ^c	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066	<0.0066
Selenium ^b	<0.0015	0.003	0.0027	0.0025	0.002	0.0019
Silver ^c	<0.000047	<0.000047	<0.000069	<0.000069	<0.00069	<0.000069
Sodium ^c	25	25	42	45	40	42
Strontium ^a	0.51	0.51	0.55	0.58	0.45	0.46
Sulfate ^a	42		26		27	
Thallium ^c	<0.0011	<0.0011	<0.00062	<0.00062	<0.0011	<0.0011
Vanadium ^a	0.0053	0.0048	0.0055	0.0057	0.0058	0.0043
Zinc ^b	0.0068	<0.0016	0.0056	<0.0016	0.012	0.0058

^aDetected in all samples of stabilized clay runoff water.

^bDetected in one or more stabilized clay runoff water samples.

^cBRL in all stabilized clay runoff water samples.

test pads consisted of a perforated PVC discharging pipe at the high end of the test pads, a collection trough constructed of split PVC piping at the low end of the pads, and a holding tank with a pump-driven recirculation system with a flow meter. The pump capacity in the recirculation system had a fixed capacity of 0.05 m³ per hour, designed to simulate a rainfall event equivalent to 5.1 cm per hour of run time, given the surface area of the test pads. The components and configuration of the testing apparatus are illustrated in Figs. 1 and 2.

Application Times for Simulated Rainfall Events

It is recognized that the surface area contacted by runoff water in the field will be much greater than that of the test pads used in this bench-scale simulation. As such, there may be a potential for additional mobilization and concentration of contaminants in the runoff water as it would pass over the surface of the matrix in an operational roadbed during storm events. To account for this possibility, multiple simulations using the test pads were run over an 84-day testing period using recirculated runoff water during each simulated storm event.

By using a pump capacity of 0.05 m³ per hour to simulate a 5.1 cm per hour rainfall event on each test pad, the contact time of water particles with the surface of the test pads at this rate of application would be approximately 0.6 min for each pass of the recirculated runoff water. Simulation of this rainfall event in the field on a typical 61 m section of roadbed with a 3% grade would

require 2.2 min of actual contact time of a particle of runoff water with the roadbed surface. Under the said field condition, contact time will be about 3.6 times longer than under experimental conditions. To make the bench-scale laboratory simulations equivalent to field conditions in terms of time of concentration, the same runoff water was recirculated 3.6 times (0.16 m³ of flow) for each test or simulation.

A total of three simulations were performed on each of the two test pads constructed. Simulations were run at intervals of 28, 56, and 84 days postconstruction. This allowed time for the compacted matrix to set properly and for the surface to dry to a degree that would maximize the potential for physical disturbance of the matrix surface (and subsequent mobilization of matrix particles) due to water droplet impacts.

The six separate simulations performed included the following procedures:

1. As a control or baseline condition and as an added quality assurance/quality control practice, a sample of nonrecirculated (clean) synthetic precipitation was collected directly from the storage vessel in which it was formulated immediately prior to its use in each simulation.
2. To approximate a prolonged storm event, recirculated synthetic precipitation was applied to test pads with nonstabilized and fly ash-stabilized clay during each of the three time intervals. Fresh (clean) synthetic precipitation was applied at the initiation of each event.

Table 3. Summary of Analytical Results for Recirculated Runoff Water for Nonstabilized Clay under Various Test Simulations

Analyte	Concentration in runoff (mg/L)					
	28-day total	28-day dissolved	56-day total	56-day dissolved	84-day total	84-day dissolved
Aluminum ^a	0.45	0.056	5.2	0.082	0.56	0.031
Antimony ^b	0.028	0.037	<0.00093	<0.00093	<0.00093	<0.00093
Arsenic ^b	<0.00054	<0.00054	0.0012	<0.00049	<0.0012	<0.00049
Barium ^a	0.012	0.01	0.034	0.01	0.0067	0.0052
Beryllium ^b	<0.00018	<0.00018	0.00035	<0.000065	<0.00018	<0.00018
Boron ^b	0.012	0.01	0.026	0.016	<0.0077	<0.0077
Cadmium ^b	<0.00002	<0.00002	0.00015	<0.00002	0.00012	0.00017
Calcium ^a	26	26	65	58	28	29
Chromium ^a	0.0068	0.005	0.015	0.0055	0.0043	0.0035
Copper ^a	0.012	0.0066	0.015	0.0046	0.012	0.0037
Iron ^a	0.4	0.016	5.4	0.043	0.54	0.0063
Lead ^c	<0.029	<0.029	<0.029	<0.029	<0.029	<0.029
Magnesium ^a	14	14	27	23	5	4.7
Manganese ^a	0.0094	0.01	0.066	0.017	0.018	0.011
Mercury ^a	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017	<0.00017
Molybdenum ^b	<0.0062	0.011	0.0097	0.0065	<0.0062	0.0067
Nickel ^b	<0.0066	<0.0066	0.0092	<0.0066	<0.0066	<0.0066
Selenium ^b	0.0017	0.0016	<0.0015	<0.0015	<0.0015	<0.00062
Silver ^c	<0.000047	<0.000047	<0.000069	<0.000069	<0.000069	<0.000069
Sodium ^a	22	22	33	32	2.9	3.1
Strontium ^a	0.073	0.074	0.13	0.12	0.041	0.04
Sulfate ^a	61		160		69	
Thallium ^c	<0.0011	<0.0011	<0.00062	<0.00062	<0.0011	<0.0011
Vanadium ^b	<0.0021	<0.0021	0.0099	<0.0021	<0.0021	<0.0021
Zinc ^b	0.009	0.0067	0.031	<0.0016	0.0089	0.0016

^aDetected in all samples of nonstabilized clay runoff water.

^bDetected in one or more nonstabilized clay runoff water samples.

^cBRL in all nonstabilized clay runoff water samples.

Sample Collection and Analysis Procedures

Clean, sealed, labeled, and preserved plastic sample bottles were supplied to the testing laboratory directly from We Energies environmental laboratory. Zero headspace samples were collected directly from the holding tanks after each simulation, following a 5-min manual mixing of the water in the tank to ensure uniform resuspension of particulates. Care was taken to avoid metal surface-runoff water contact during mixing and sample collection. As noted above, field blanks of fresh synthetic precipitation were collected immediately before, and target samples collected after each sampling event. At the conclusion of sampling for each simulation from each test pad, the holding tank, collection and dispersing pipes, and the pump were properly decontaminated, and the tubing used for recirculating runoff water was replaced. Samples were shipped at 4°C for analysis.

Laboratory quality assurance procedures, sample preparation, and analytical testing for total and dissolved constituents in the runoff water samples for each simulation were performed. All analyses were done using U.S. EPA SW-846 methods (U.S. EPA 2007). Samples for total metals analysis were prepared using EPA Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Flame Atomic Absorption (FLAA) Spectrophotometry or Inductively Coupled Plasma (ICP) Spectroscopy" and EPA Method 3020A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by Graphite Furnace Atomic Absorption (GFAA) Spectroscopy." Samples for dissolved analysis were prepared by filtering through

a 0.45- μ m membrane filter prior to preservation and analysis. Metals analysis was completed using both ICP spectroscopy and GFAA spectroscopy depending on the analyte and the required method of detection. Mercury was measured using cold-vapor atomic absorption spectroscopy and sulfate by ion chromatography.

Results and Discussion

Table 1 presents the results for analyses performed on the unused (control) synthetic precipitation samples collected immediately prior to each simulation. Analytical results for all parameters included in the recirculated runoff water analyses are presented for all simulations using stabilized and nonstabilized clay in Tables 2 and 3, respectively. In addition, a comparison between the most recent results for OCPP composite fly ash leachate testing and the maximum dissolved concentration measured in runoff water from stabilized clay is also provided in Table 4 (ASTM 2001).

Unused (Control) Synthetic Precipitation

The synthetic precipitation was analyzed for total and dissolved metal concentrations prior to its use in the simulations. Six analytes (calcium, copper, iron, magnesium, sulfate, and zinc) were detected at concentrations above reporting limits in all control samples. Another six analytes (aluminum, barium, cadmium,

Table 4. Summary Results (mg/L) for 2005 Leachate Test of OCPP Bulk Fly Ash

Parameter	Natural Resources (NR)		OCPP flyash leachate	Maximum concentration (Max. conc.) in stabilized clay runoff water ^a
	538 category 1 standard	NR 538 category 2 standard		
Dissolved aluminum	1.5	15	34	0.7
Dissolved antimony	0.0012	0.012	<0.0014	0.055
Dissolved arsenic	0.005	0.05	<0.0013	0.0019
Dissolved barium	0.4	4	32	0.17
Dissolved beryllium	0.0004	0.004	0.000097	<0.00018
Dissolved boron	0.19	1.9	4.5	0.69
Dissolved cadmium	0.0005	0.005	0.000058	0.000053
Chloride	125		0.83	NA
Dissolved chromium	0.01	0.1	0.0065	0.038
Dissolved copper	0.13		<0.0025	0.0053
Dissolved iron	0.15		0.016	0.07
Dissolved lead	0.0015	0.015	0.002	<0.029
Dissolved manganese	0.025	0.25	0.0012	0.0053
Mercury	0.0002	0.002	0.0000016	<0.00017
Dissolved molybdenum	0.05		0.031	0.068
Dissolved nickel	0.02		0.034	<0.0066
Nitrate-nitrite as N	2		<0.02	NA
Dissolved selenium	0.01	0.1	0.0033	0.003
Dissolved silver	0.01	0.1	<0.000069	<0.000069
Sulfate	125	1250	<0.20	NA
Dissolved thallium	0.0004	0.004	<0.00062	<0.0011
Dissolved vanadium			<0.0018	0.0057
Dissolved zinc	2.5		<0.0036	0.0058

Note: Bolded values exceed the NR 538 Category 1 or 2 standard, and/or represent a significant (>10×) increase from the extractant blank; blank cells indicate no standard for this analyte; test results obtained through standard ASTM methods (ASTM 2001); NA=not analyzed.

^aSee Table 1.

chromium, manganese, and sodium) were detected in one or more control samples at low concentrations, generally at or near the reporting limit. The analytes detected and the concentrations measured were generally consistent with naturally occurring levels of trace inorganic constituents in natural waters, indicating that the synthetic precipitation utilized in the tests appropriately simulated field conditions.

A comparison of results of the analysis of control water used for stabilized versus nonstabilized simulations indicates very low variability in the constituent make up of the runoff water used in the test simulations, further suggesting that the synthetic precipitation formulated for use in the runoff simulations did not constitute a significant source of bias in the results for constituents potentially associated with the leachable fraction of fly ash-stabilized soil.

With the exception of copper, none of the positive results documented for the control samples contributed appreciably to the comparisons of results for the runoff water samples to potentially applicable water quality benchmark values. Results for copper in control runoff water indicated that measured concentrations in eight of the 12 samples exceeded the lowest (i.e., most conservative) potentially applicable benchmark value. However, as copper is not present in the leachable fraction of OCPP fly ash (Table 4), these results should not constitute a significant source of bias with regard to the conclusions of this analysis.

Recirculated Runoff Water—Stabilized Clay

Six of the target analytes (beryllium, lead, mercury, nickel, silver, and thallium) were not detected in any samples of recirculated

runoff water collected from the stabilized clay test simulations. Five analytes (antimony, arsenic, cadmium, selenium, and zinc) were detected in one or more samples of recirculated runoff water collected from the stabilized clay test simulations. The remaining 14 target analytes (aluminum, barium, boron, calcium, chromium, copper, iron, magnesium, manganese, molybdenum, sodium, strontium, sulfate, and vanadium) were detected in all samples collected from the stabilized clay simulations.

Results for the stabilized clay samples generally exhibited a very high degree of consistency between dissolved and total analyses for each simulation. This indicates that trace metals are generally present as dissolved constituents in runoff water and are not significantly associated with suspended solids or colloidal matter in the water.

Recirculated Runoff Water—Nonstabilized Clay

Four of the target analytes (lead, mercury, silver, and thallium) were not detected in any samples of recirculated runoff water collected from the nonstabilized clay test simulations. Ten analytes (antimony, arsenic, beryllium, boron, cadmium, molybdenum, nickel, selenium, vanadium, and zinc) were detected in one or more samples of recirculated runoff water collected from the nonstabilized clay test simulations. The remaining 11 analytes (aluminum, barium, calcium, chromium, copper, iron, magnesium, manganese, sodium, strontium, and sulfate) were detected at concentrations above reporting limits in all target samples of recirculated runoff water from the nonstabilized clay test simulations.

With few exceptions, results for the nonstabilized clay samples

Table 5. Screening of Analytes for Identification of Indicator Parameters

Screening criteria	Analyte																										
	Al ^a	Sb ^a	As ^b	Ba ^a	Be ^b	Bo ^a	Cd ^a	Ca ^c	Cr ^a	Cu ^d	Fe ^a	Pb ^b	Mg ^a	Mn ^c	Hg ^b	Mo ^a	Ni ^b	Se ^a	Ag ^b	Na ^c	Sr ^a	(SO ₄ ²⁻) ^a	Ti ^b	V ^a	Zn ^a		
Nondetect in all target (stabilized) runoff samples					X							X			X		X		X								
Concentration in stabilized runoff < nonstabilized runoff or BRL in all simulations					X		X					X	X		X		X		X					X	X		
Not present at significant concentration in flyash leachate		X		X	X	X	NA	X	X	X	X		NA	X	X				X	NA	NA		X	X	X	X	X
If detected, maximum concentration in control (unused) runoff samples > minimum potentially applicable benchmark										X								X									
Potentially comparable environmental quality benchmark criteria unavailable							X							X													X

Note: NA=not analyzed.

^aRetained for further indicator parameter screening.

^bEliminated as indicator parameter based on frequency of detection in stabilized clay runoff samples.

^cEliminated as indicator parameter based on absence of potentially applicable benchmark criteria for comparison.

^dEliminated as indicator parameter based on occurrence in control samples.

generally exhibited a very high degree of consistency between dissolved and total analyses for each simulation. This indicates that trace metals are generally present as dissolved constituents in runoff water and not associated with suspended solids or colloidal matter in the water. As noted above, this same relationship was exhibited by the stabilized clay samples, suggesting that the addition of fly ash had little effect on the dissolution chemistry for the trace metals from the soil matrix.

Comparison of Analytical Results for Recirculated Runoff Water

Tables 2 and 3 present the results of analyte concentrations in recirculated runoff water from stabilized and nonstabilized clay for each test simulation, respectively. Ten analytes (beryllium, calcium, lead, magnesium, manganese, mercury, nickel, silver, sulfate, and thallium) were either not detected in any sample or exhibited lower concentrations in runoff water from stabilized clay versus that from nonstabilized clay in all cases. Nine analytes (aluminum, antimony, arsenic, cadmium, copper, iron, selenium, vanadium, and zinc) exhibited mixed results with the difference in concentrations in runoff water from stabilized clay versus nonstabilized clay being lower in some corresponding simulations and higher in others.

Only six analytes (barium, boron, chromium, molybdenum, sodium, and strontium) had higher concentrations in runoff water from stabilized clay for all simulations. For barium and boron, this difference exceeded a factor of 10 in virtually all simulations.

Analysis of OCPP Fly Ash Leachate

For comparison purposes, results of leachate testing of bulk fly ash from the OCPP are summarized in Table 4. These results show the soluble fractions of the fly ash in the absence of any other material in the matrix. This testing is performed annually in support of the beneficial reuse permitting for fly ash required under WNDR regulations (WNDR 2005), and is conducted in accordance with standard ASTM protocol (ASTM 2001). The OCPP fly ash was the sole soil amendment used in the stabilized clay test pad. Six analytes (aluminum, barium, boron, chloride, lead, and nickel) detected in fly ash leachate exhibited a significant increase from the extractant blank and exceeded one or more of the applicable WNDR standards (WNDR 2005) developed for the protection of groundwater quality.

Screening of Target Analytes for Inclusion as Indicator Parameters

Several criteria were considered using a “weight-of-evidence” approach in selecting target analytes for inclusion as indicator parameters for the evaluation of potential water quality impacts from runoff water. These criteria included:

1. Whether the analyte was detected in one or more samples collected from stabilized runoff water in any simulation;
2. If detected, whether the concentration of an analyte in stabilized runoff water was less than that detected in nonstabilized runoff water or was below reporting limit (BRL) in all samples;
3. Whether an analyte was shown to be present at significant concentrations in OCPP fly ash leachate versus that in an extractant blank (Table 4);

Table 6. Potentially Applicable Water Quality Criteria and Benchmarks (mg/L) for Comparison to Runoff Water Results

Analyte	WI NR 105 acute toxicity criteria (WDNR 2004) ^a	U.S. EPA ambient water quality criteria (AWQC)-freshwater criterion maximum concentration (CMC) (U.S. EPA 1999) ^a	NOAA freshwater screening guideline [National Oceanic and Atmospheric Administration (NOAA) 1994] ^a	Oak Ridge National Laboratory (ORNL) (1996) ecotox screening values (mg/L)	
				Tier II acute values	EPA region IV acute screening values
Aluminum					0.75
Antimony			0.088	0.18	1.3
Arsenic		0.34	0.36		0.36
Barium				0.11	
Beryllium			0.13	0.035	0.016
Boron				0.03	
Cadmium	0.00436	0.0043	0.0039		0.00179
Calcium					
Chromium	1.803	0.57	1.7		0.98432
Copper	0.01682	0.013	0.018		0.00922
Iron					
Lead	0.10692	0.065	0.083		0.03378
Magnesium					
Manganese				2.3	
Mercury		0.0014	0.0024		0.0024
Molybdenum				16	
Nickel	1.361	0.47	1.4		0.789
Selenium			0.02		0.02
Silver		0.0034	0.0041		0.00123
Sodium					
Strontium				15	
Sulfate					
Thallium			1.4	0.11	0.14
Vanadium				0.28	
Zinc	0.1204	0.12	0.12		0.06504

Note: NR 538 standards were also considered a benchmark criteria for comparison (see Table 4); blank cells indicate no benchmark or criteria available for that analyte.

^aAssumes hardness of 100 mg/L.

- If an analyte was detected in any stabilized runoff samples, whether the concentration of that analyte in control water was greater than any potentially applicable water quality benchmark; and
- Whether any potentially applicable water quality benchmark criteria had been promulgated for the analyte.

The results of the screening process described above are summarized for all original target analytes in Table 5. In general, if an analyte was detected in stabilized clay runoff water at levels greater than those measured from nonstabilized clay, and it was shown to be associated with fly ash leachate from previous testing, and potentially applicable water quality benchmark criteria were available, it was retained for further screening. Fourteen of the original 25 target analytes met these criteria, as summarized in Table 5.

To facilitate indicator parameter selection and assess the potential environmental significance of the fly ash runoff testing results, benchmark values were compiled from existing literature sources and represent the range of ambient freshwater concentrations that are associated with protection of acute (first flush) effects to aquatic life. The ranges of potentially applicable surface water benchmark values for all analytes measured in runoff water are summarized in Table 6. For several common and ubiquitous analytes with low inherent toxicity (i.e., calcium, manganese, and sodium), no environmental quality benchmark values were avail-

able from the literature sources consulted and these three analytes were therefore excluded for consideration as indicator parameters partially on this basis.

Further screening of the remaining 11 analytes for inclusion as indicator parameters was performed. Their measured concentrations from all simulations for both stabilized and nonstabilized soils were compared with ranges of the potentially applicable water quality benchmarks summarized in Table 6.

Tables 7 and 8 summarize the results of the numeric comparisons between runoff water concentrations and water quality benchmark values for the 12 simulations included in the tests. If a benchmark or criteria value existed for a given analyte and the test result exceeded that value, it is indicated in bold in the tables.

Table 9 summarizes the results for analytes exceeding one or more of the benchmark value in runoff water from either stabilized or nonstabilized clay simulations. Three analytes (barium, boron, and molybdenum) were detected above one or more benchmark values only in runoff water from stabilized clay simulations. On this basis, these analytes were included as indicator parameters for the purposes of assessing potential water quality impacts.

Four additional analytes (aluminum, antimony, chromium, and iron) were detected above one or more benchmarks in runoff water in simulations from both stabilized and nonstabilized clay. However, the results for iron and antimony clearly indicate that

Table 7. Comparison of Runoff Water Concentrations (Total and Dissolved) (See Table 2) from Stabilized Clay Simulations to Potentially Applicable Benchmarks and Criteria

Analyte	Exceedence of comparison benchmark or criteria														
	WI NR 105 acute			U.S. EPA fresh water (FW) acute AWQC			NOAA FW acute guideline			ORNL tier II acute			U.S. EPA reg. VI acute		
	28-day	56-day	84-day	28-day	56-day	84-day	28-day	56-day	84-day	28-day	56-day	84-day	28-day	56-day	84-day
Aluminum													Y-N	N-N	N-N
Antimony							N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N
Arsenic				N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Barium										Y-Y	Y-Y	N-N			
Beryllium							N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N
Boron										Y-Y	Y-Y	Y-Y			
Cadmium	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Calcium															
Chromium	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Copper	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Iron															
Lead	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Magnesium															
Manganese										N-N	N-N	N-N			
Mercury				N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Molybdenum										N-N	N-N	N-N			
Nickel	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Selenium							N-N	N-N	N-N				N-N	N-N	N-N
Silver				N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Sodium															
Strontium										N-N	N-N	N-N			
Sulfate															
Thallium							N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N
Vanadium										N-N	N-N	N-N			
Zinc	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N

Note: Y= YES, N=NO; the first and second letter represents TOTAL and DISSOLVED concentrations, respectively; blank cells indicate benchmark or criteria unavailable for that analyte.

their presence in the runoff water is associated with the clay matrix as they are present in nonstabilized samples at levels at or above those in stabilized samples. The relationship between stabilized and nonstabilized samples with respect to chromium and aluminum is less clear and therefore they were also retained as indicator parameters. One additional analyte (sulfate) was detected above one or more benchmark values only in runoff water from one nonstabilized clay simulation. This analyte was not included as an indicator parameter.

Figs. 3 and 4 illustrate the relationship between the measured concentrations of the indicator parameters in runoff water selected through the weight-of-evidence approach (i.e., aluminum, barium, boron, chromium, and molybdenum) and the range of reported water quality criteria for nonstabilized and stabilized simulations, respectively.

Conclusions

The results discussed above indicate that a relatively small number of analytes are likely to be present in runoff water generated from the surface of clay soils stabilized with OCPP fly ash. In general, several important observations can be made regarding the results for the analytes measured in stabilized clay runoff water and selected as indicator parameters. First, there is very little variation between results for samples collected over the time-

frame covered by the simulations (i.e., 28–84 days after pad construction). Second, results for samples analyzed for total (i.e., unfiltered) and dissolved (i.e., filtered) metals were consistent indicating that the dissolution of fly ash constituents from the matrix was largely confined to the dissolved phase. Third, the indicator parameters are consistent with parameters shown to be extractable from bulk OCPP fly ash through leachate testing. Consequently, the selection and evaluation of these analytes as indicator parameters is appropriate and representative of fly ash-stabilized clay for the purpose of assessing the potential for water quality impacts due to surface water runoff.

It should be emphasized that the comparison of indicator parameter concentrations in recirculated runoff water to ambient surface water quality criteria is a highly conservative approach for evaluating the potential for environmental impacts for several reasons. First, the potential for constituents to desorb or dissolve in a given particle or volume of runoff water is vastly increased by repeatedly passing the same water over the surface of the matrix. Second, in a field application, fresh or unimpacted rainwater would continually be added to the flow over the matrix surface during the course of each precipitation event, diluting dissolved concentrations in proportion to the surface area of the roadbed, and reducing constituent loads in runoff water that would occur due to the addition of unimpacted rainwater at points further down gradient. Third, under actual field conditions, constituent concentrations in runoff water would typically be attenuated by

Table 8. Comparison of Runoff Water Concentrations (Total and Dissolved) (See Table 3) from Nonstabilized Clay Simulations to Potentially Applicable Benchmarks and Criteria

Analyte	Exceedence of comparison benchmark or criteria														
	WI NR 105 acute			U.S. EPA FW acute AWQC			NOAA FW acute guideline			ORNL tier II acute			U.S. EPA reg. VI acute		
	28-day	56-day	84-day	28-day	56-day	84-day	28-day	56-day	84-day	28-day	56-day	84-day	28-day	56-day	84-day
Aluminum													N-N	Y-N	N-N
Antimony							N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N
Arsenic				N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Barium										N-N	N-N	N-N			
Beryllium							N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N
Boron										N-N	N-N	N-N			
Cadmium	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Calcium															
Chromium	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Copper	N-N	N-N	N-N	N-N	Y-N	N-N	N-N	N-N	N-N				Y-N	Y-N	Y-N
Iron															
Lead	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Magnesium															
Manganese										N-N	N-N	N-N			
Mercury				N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Molybdenum										N-N	N-N	N-N			
Nickel	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Selenium							N-N	N-N	N-N				N-N	N-N	N-N
Silver				N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N
Sodium															
Strontium										N-N	N-N	N-N			
Sulfate															
Thallium							N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N
Vanadium										N-N	N-N	N-N			
Zinc	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N	N-N				N-N	N-N	N-N

Note: Y=YES, N=NO; the first and second letters represent TOTAL and DISSOLVED concentrations, respectively; blank cells indicate benchmark or criteria unavailable for that analyte.

Table 9. Indicator Parameters Exceeding One or More Potentially Applicable Benchmark Criteria in Runoff Water under Various Test Simulations

Test simulation	Test material	Potential indicator parameter													
		Al ^a	Sb ^b	Ba ^a	Bo ^a	Cd ^c	Cr ^a	Fe ^b	Mg ^c	Mo ^a	Se ^c	Sr ^c	(SO ₄ ²⁻) ^c	V ^c	Zn ^c
28 day—total	Stabilized clay	X	X	X	X		X	X							
	Nonstabilized clay		X					X							
28 day—dissolved	Stabilized clay		X	X	X		X								
	Nonstabilized clay		X												
56 day—total	Stabilized clay			X	X		X	X							
	Nonstabilized clay	X					X	X				X			
56 day—dissolved	Stabilized clay			X	X		X			X					
	Nonstabilized clay														
84 day—total	Stabilized clay				X						X				
	Nonstabilized clay							X							
84 day—dissolved	Stabilized clay				X		X			X					
	Nonstabilized clay														

^aIncluded as final indicator parameter for stabilized clay simulations.

^bEliminated as indicator parameter based on exceedence of potentially applicable benchmarks in nonstabilized clay simulations.

^cEliminated as indicator parameter based on lack of exceedence of potentially applicable benchmarks in all stabilized clay simulations.

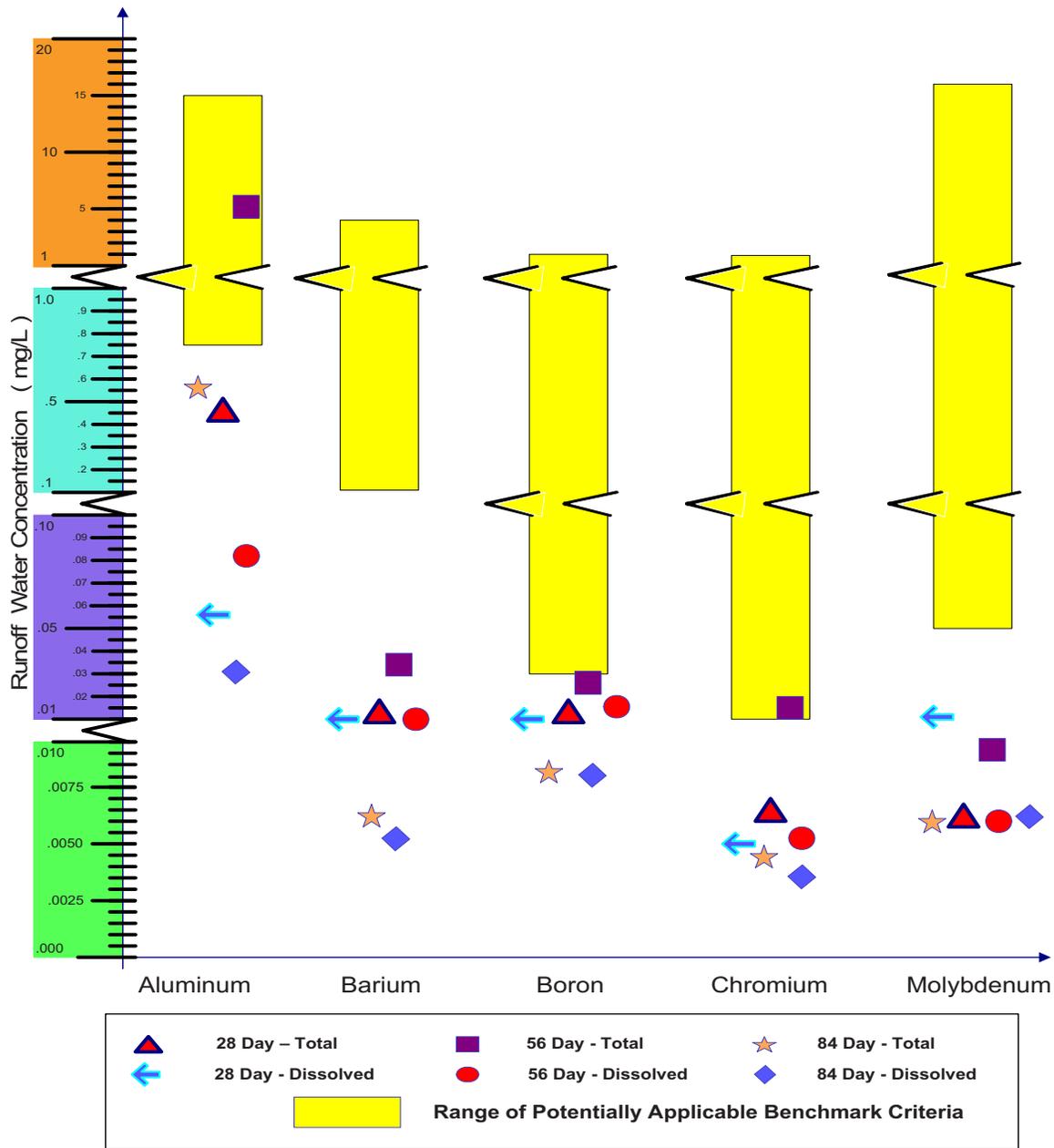


Fig. 3. Comparison of dissolved and total concentrations of indicator parameters in runoff water to range of potentially applicable water quality benchmark criteria for nonstabilized clay simulations

lateral and vertical flow of runoff through soil, humus, and other organic material in ditches and roadside areas prior to migration to surface waters. Finally, concentrations in recirculated runoff water would be far higher than and not representative of those in ambient receiving waters due to dilution and mixing.

Aluminum

Out of the six simulations, the 28-day simulation had the highest total aluminum concentration in runoff water from stabilized clay. In nonstabilized clay, the 28-day simulation was over 10 times lower than the highest reported value from other simulations. However, the total aluminum concentration measured during the

56-day simulation (Table 3) from nonstabilized clay was approximately five times higher than the 28-day simulation (Table 2) concentration from stabilized clay. This suggests that the clay matrix (having naturally elevated aluminum levels relative to other soil types) may be a significant source of aluminum in runoff water. In addition, since aluminum appears to leach readily from bulk fly ash (Table 4), it is possible that the clay matrix is attenuating dissolution potential, especially as the stabilized clay cures over time. This is supported by the fact that results for stabilized runoff water from the 56- and 84-day simulations showed no concentrations above benchmark criteria. In light of these considerations, the potential for adverse aquatic impacts due to aluminum levels in stabilized clay runoff water may be considered insignificant.

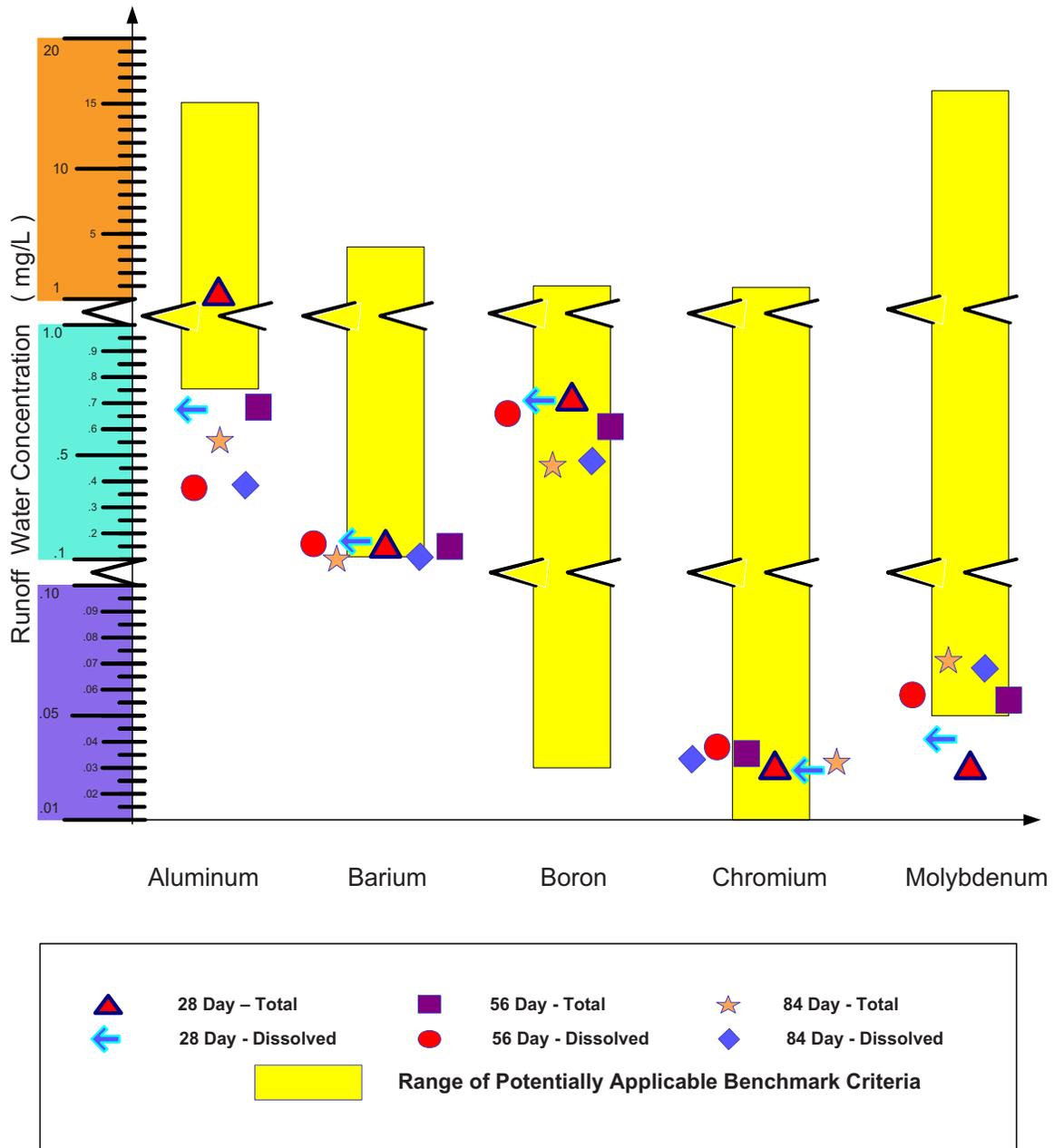


Fig. 4. Comparison of dissolved and total concentrations of indicator parameters in runoff water to range of potentially applicable water quality benchmark criteria for stabilized clay simulations

Barium

Total and dissolved concentrations of barium in stabilized clay runoff were at or slightly above the lowest benchmark criteria in all the six simulations. The highest measured concentration was in the 28-day total simulation (0.18 mg/L), but the measured concentrations were highly consistent in all simulations. This concentration is more than 20 times lower than the highest benchmark value (the NR 538 Category 2 Standard of 4 mg/L). As noted in Table 4, barium has been shown to leach readily from bulk OCPP fly ash, with measured concentrations in leachate of 32 mg/L. While the fly ash may be a source of barium in the stabilized clay runoff water, the fact that measured concentrations are over two orders of magnitude lower than those from bulk leachate suggests that, like aluminum, the clay matrix may also be attenuating the

dissolution potential of barium. Likewise, the absence of barium concentrations above benchmarks in stabilized clay runoff from the 84-day simulation indicates that the dissolution potential may decrease as the matrix cures over time. Consequently, the potential for adverse aquatic impacts due to barium levels in stabilized clay runoff water is highly unlikely.

Boron

Boron was measured above the two lowest reported benchmark values in stabilized clay runoff in all six simulations. The measured concentrations were very consistent in all cases (0.46–0.69 mg/L). These concentrations are between three and five times lower than the highest reported benchmark value for boron (NR

Category 2 Standard of 1.9 mg/L). As noted in Table 4, boron has been shown to leach readily from bulk OCPP fly ash, with measured concentrations in leachate of 4.5 mg/L. While the fly ash is a likely source of boron in the stabilized clay runoff water, the fact that measured concentrations are approximately 10 times lower than those from bulk leachate suggests that the clay matrix may be attenuating the dissolution potential of boron. However, the reduced boron concentrations in stabilized clay runoff from the 84-day simulation indicate that the dissolution potential may further decrease as the matrix cures over time. In light of these considerations and the conservatism inherent in the analysis, the potential for adverse aquatic impacts due to boron levels in stabilized clay runoff water would be very low.

Chromium

Chromium concentrations measured in runoff water from stabilized clay range from 0.028–0.038 mg/L, and slightly exceeded the lowest reported benchmark criteria (NR 538 Category 1 Standard of 0.01 mg/L) in all six simulations. However, they are approximately 60 times lower than the highest reported benchmark of 1.8 mg/L. As noted in Table 4, chromium does not typically leach readily from bulk OCPP fly ash. However, the concentration of chromium measured in runoff from nonstabilized clay averaged about one order of magnitude lower than that in stabilized clay. This suggests that the fly ash may be a source of chromium in the runoff water. However, due to the low concentrations measured relative to the range of applicable criteria, the potential for adverse aquatic impact due to chromium levels in stabilized clay runoff water would be very low.

Molybdenum

Molybdenum concentrations in runoff water from stabilized clay exceeded the lowest reported benchmark criteria (NR 538 Category 1 Standard of 0.05 mg/L) in four (56- and 84-day) of the six simulations. The measured concentrations ranged from 0.029 to 0.071 mg/L. The 56- and 84-day simulation concentrations are 200 times lower than the highest reported benchmark of 16 mg/L (Table 6). The concentrations of molybdenum measured in stabilized clay runoff were similar to those measured from bulk OCPP fly ash leachate (0.031 mg/L), indicating that fly ash may be a source of molybdenum in runoff. However, the low concentrations observed and the conservatism inherent in the analysis, indicate that the potential for adverse aquatic impacts due to molybdenum levels in stabilized clay runoff water would be insignificant.

Recommendations

The results of this study suggest that the use of uncovered fly ash–stabilized clay on surfaces having light traffic would have insignificant adverse effects on water quality due to surface water runoff. While low levels of fly ash constituents may be mobilized from the matrix surface, these concentrations would have little potential to cause adverse impacts in receiving waters under typical field conditions, particularly for the soils that were tested. Consequently, the application of fly ash–stabilized clay on exposed surfaces is a safe, viable, and cost effective alternative to concrete, asphalt, or aggregate overlay.

Future environmental research possibilities related to this topic may include:

1. The use of alternative sources of fly ash and soil-to-fly ash mixture ratios;
2. The use of alternative soil types in the mixture;
3. Testing under varying degrees of use and vehicular traffic;
4. Testing varying degrees of slope and potential for erosion resistance; and
5. Pilot-scale field simulations with larger exposed surface areas (minimum 61-meter length with 3% cross slope) natural rainfall and sampling and analysis of receiving waters.

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