ABSTRACT

Title of Thesis:	Geoenvironmental Behavior of Lime Amended Dredged Materials
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Several hundred million cubic yards of sediment are dredged from various U.S. ports, harbors, and waterways annually to maintain and improve the nation's navigation system for commercial, national defense, and recreational purposes. The United States Environmental Protection Agency mandated containment of dredged sediments in designated containment facilities. For several years, the Maryland Environmental Service is building and operating dredged material confinement facilities. Due to high operation and maintenance costs, Maryland Dredged Material Management Program aims to repurpose the material for various uses. The current study aims to explore the use of sediments dredged from Chesapeake Bay as a potential highway embankment material. Geotechnical analysis is coupled with environmental assessment in order to ensure satisfactory performance of the dredged materials as an embankment fill attributed with no potential environmental ramifications. It is essential to quantify performance and environmental impacts before initiating large scale construction using dredged materials and this study aims to explore these requirements.

GEOENVIRONMENTAL BEHAVIOR OF LIME-AMENDED DREDGED MATERIALS

by

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1. Introduction

Prior to the year 1996, dredged materials (DM) acceptable for ocean disposal were placed at the USEPA designated ocean disposal sites (UDMCRE, 2001). Over 5 million of tons of dredged sediments were produced in the United States between 2008 and 2014 (USACE, 2015) and development of safe and sustainable applications is an important societal challenge (Figure 1.1).

Maryland Port Authority estimates that 500,000 cubic yards of material is dredged annually in Maryland. The material has been stored and contained at Hart – Miller Island until it reached its maximum capacity in the year 2009. In accordance with the Maryland state law, the material cannot be placed outside the harbor area and all unconfined placement of the material was ceased by the end of year 2010 (IRC, 2009). This material has been stored at Cox Creek Dredged Material Containment Facility, located south of Scott Key Bridge, on the western shore of Patapsco River. The facility has a total projected capacity of 6 million cubic yards, and the forecast of the volume of material dredged from the Bay demands a plan of action to repurpose it as the running cost of containment is increasing with time.

The Maryland Dredged Material Management Program plans to repurpose the DM for six primary purposes: (i) Landfilling, (ii) Landscaping, (iii) Agriculture, (iv) Land reclamation, (v) Engineering Fill, and (vi) Building Materials. After several rounds of life-cycle cost and analysis, the most attractive approach has been identified as using the material as a borrow fill in highway embankment construction (IRDM, 2007). Using DM as an embankment fill material entails

problems like workability, low strength, and leaching of contaminants into nearby waters.

Past studies showed that the material is classified as a silty soil and the granular nature of material makes it possible to blend it with cementitious additives (Malasavage et al. 2011). The use of stabilized dredged material for roadway projects does not pose a significant environmental concern, however screening analysis of percolated water indicated that some of the metals and chloride may exceed the groundwater quality standards (UDMCRE, 2001).

A series of laboratory and field tests have been conducted as part of previous work to assess the performance of DM as a highway embankment fill (Grubb et al. 2011, Landris 2007). A two-phase field demonstration project involved construction of a 3.5 m (12 ft.) high-trial, single-lane highway embankment made of DM blended with steel slag fines (Malasavage et al. 2012). Embankments were also built with DM-crushed glass blends, which doubled and tripled in strength within 2 years due to aging under self-weight (Grubb et al. 2008). There is a plethora of literature on geomechanical and environmental behavior of pure and treated dredged sediments (Grubb et al. 2011, Malasavage et al. 2010, Gaffney et al. 2008). However, material properties vary significantly depending on the location they are dredged from and the way they are stored, and there is a need to produce additional data on mechanical and environmental properties of sediments dredged from Annapolis and Baltimore Harbors in Chesapeake Bay for their possible use in highway applications. In order to respond to this need, a series of laboratory tests were conducted on pure and lime-treated sediments

dredged from the Bay. The current study followed the methodology mentioned below:

- Stabilization options were explored to improve dry unit weight and strength characteristics of the pure DM to satisfy Maryland State Highway Administration (SHA) highway embankment fill material criteria.
- Lime-based additives were selected considering the soil properties and embankment fill material requirements. Extensive tests were conducted to quantify the lime-to-dredged material ratios to meet the compaction limits and record strength improvement.
- Long-term leaching properties of the material and its blends were determined via column leach tests. Surface water and groundwater models were used to predict impact of contaminants in soil to surface and groundwater.
- A series of recommendations based on mechanical and leaching properties of treated and pure DM were made for their potential use as highway embankment fill materials.

Section 2 discusses the mechanical properties and how addition of lime changes the compaction and strength characteristics of DM. Section 3 provides and analysis of the leaching properties of DM. Section 4 is a summary of the results and a set of recommendations.



Figure 1.1 Annual dredged material production across United States of America (U.S. Army Corps of Engineers, 2015)

2. Mechanical Properties of Treated Dredged Material

2.1. Introduction

Lime stabilization of soils and sediments is widely used in several structures, such as highways, airports, embankments and slope protection (Anon 1990, Wilkinson et al. 2010). Prevalent use of lime is primary because of its overall economy and ease of construction, which provides an added attraction for engineers (Dash et al. 2012). Addition of lime has an advantage of physical stabilization as well as chemical modification of the dredged material. Utilization of dredged materials in highway embankment has been documented in earlier studies (Malasavage et al. 2012, Grubb et al. 2015). New Jersey Department of Transport (NJDOT) conducted several test embankments and test roadway projects using dredged sediments at OENJ Redevelopment Site in Elizabeth, New Jersey. The investigation from NJDOT of the test embankments revealed that engineering fill was susceptible to settlement and freeze-thaw effects. The current study intends to explore the mechanical effects of lime-based additives (quick lime and lime kiln dust) blended with bottom-sea sediments dredged from Chesapeake Bay in Maryland.

2.2. Materials

DM used in the study was sampled from a containment facility at Cox Creek, Maryland. The dredged material is pumped into the containment facility as a mixture of soil and water, therefore samples were collected from four different locations (Figure 2.1), and labeled based on their sampling locations, e.g., DM1 for sample collected from Cell 1. Top 0.5 to 1 ft. of soil was removed before sampling the dredged materials. The samples DM1 and DM2 were found to have lower natural water content than DM3 due to presence of higher amount of water in Cell 3 at the time of sampling. The material in Cell 4 was stacked at that location for over 10 years as various studies of DM were carried out over time by different agencies.

The DM was collected in air-tight buckets to preserve natural water content of the samples. Debris and foreign materials were removed by hand, or by sieving through the 19-mm sieve upon transporting the buckets to the laboratory. Due to existence of appreciable amount of fines (~36-65% by weight) in the samples, lime kiln dust and quick lime were added to improve their strength parameters. Quick lime (≈85% CaO) was provided by Carmeuse Lime & Stone, and lime kiln dust (≈20-80% CaO) was purchased from Mintek Resources, Inc. Chemical composition of LKD and QL provided by their respective suppliers have been provided in appendix C. Both quick lime (QL) and lime kiln dust (LKD) were used to enhance cementation characteristics of the dredged sediments. Four different dredged sediments (DM1–DM4) and two additives (quick lime and lime kiln dust) were tested at different proportions. A clayey soil, commonly used in highway embankment construction by the local Department of Transportation, was also included in the testing program. This soil is often placed beneath the industrial byproducts used in the embankments, per construction guidelines of the local highway agency. The embankment soil (ES named herein) was classified as low plasticity clay (CL), according to Unified Soil Classification System (USCS). Gravel

(4.75 mm-19 mm) procured from Laney Materials, LLC, was used in this study to improve compaction characteristics of the select dredged materials.



Figure 2.1 Location of Cox Creek Dredged Material Containment Facility and sampling locations.



Figure 2.2 Grain size distributions of the dredged materials

Sample	Moisture	Specific	Gravel	Sand	Fines	Liquid	Plastic	Plasticity	USCS Soil
Number	Content	Gravity		(%)	(%)	Limit	Limit	Index	Classification
	(%)		(%)			(%)	(%)	(%)	
DM1	10.9	2.63	9.9	45.3	44.8	24.9	21.3	3.53	SM (Silty sand)
DM2	10.4	2.58	19.9	56.5	36.6	26.5	23.3	3.29	SM (Silty sand)
DM3	98.3	2.46	17.8	27.8	54.4	61.6	49.2	12.4	MH (High plastic silt)
DM4	23.8	2.63	3.7	31.4	64.9	51.5	36.9	14.6	MH (High plastic silt)
ES	17.2	2.66	1.6	27.2	71.2	50	28	22	CL – CH (High plastic clay)

 Table 2.1 Properties of materials used in the testing program

2.3. Methods

Atterberg limit tests (ASTM D 4318) and sieve analysis (ASTM C 136) were performed to classify soil and establish compatibility of additives for the soil. Grain size distributions of the dredged sediments are given in Figure 2.2. DM1 and DM2 were classified as silty sand (SM) while DM3 and DM4 were classified as high plastic silt (MH) per USCS. Sample passing through U.S. Sieve No. 40 was used in the liquid limit and plastic limit tests. Properties of dredged materials and embankment soil (ES) are presented in Table 2.1.

Pocket penetrometer tests were carried on all DM samples and their mixtures prepared with two lime-based additives at varying percentages by weight. The results of these screening tests were compiled to get an initial understanding of the relation between strength of DM and percentage of lime additives added by weight. The screening for the mixtures were made by blending 2.5%, 5%, 7.5%, and 10% by weight of quick lime (QL) and lime kiln dust (LKD) with DM. All samples were cured at 20^o C and 95% relative humidity for 1 day and 7 days before testing.

Standard Proctor compaction tests (ASTM D698) were carried out to determine compaction characteristics of the four different DM amended with LKD or QL at 5% by weight. This percentage was chosen based on initial screening made by the pocket penetrometer measurements (Section 2.4). DM and their blends were mixed at their corresponding natural moisture contents before the compaction test. Compaction characteristics of the blends are shown in Figures 2.3-2.6.

California Bearing ratio (CBR) tests were performed in order to assess the bearing capacity of pure and treated dredged sediments for their possible use in highway systems. Samples were compacted at their corresponding optimum moisture contents in the CBR mold. All CBR tests were conducted by following methods outlined in AASHTO T-193 and ASTM D1883 and at 1.27 mm/min strain rate using Geotest Instrument S5840 Multi-Loader frame. The equipment had a maximum loading capacity of 44.8 kN. The undrained shear strength (cu) for the specimens was predicted from CBR using an empirical model developed for cohesive soils by Gregory and Cross (2007). The model assumes the CBR plunger penetrating in the soil as a circular foundation, in turn supporting the correlation of CBR values to the bearing capacity of soil.

CBR = 0.09 x c_u (2.1)

2.4. Results

A significant decrease in dry unit weight of most of the dredged materials was observed upon addition of LKD and QL (Table 2.2). Addition of lime brings about the colloidal reactions and minor flocculation or aggregation occurs in the sample. Due to addition of lime, pH of soil increases substantially. The workability of soil ameliorates with increase in lime, although the lime addition must be below lime fixation point (Dash and Hussain, 2015). 5% gravel and 50% sand have been added to DM3 and DM4 to increase the maximum dry unit weights due to original dry unit weights of these two dredged materials being lower than 15.7 kN/m³, a limit generally used by the local highway agency in constructing highway embankments. However, DM3 was dropped out of the further study as no



Figure 2.3 Compaction characteristics of DM1



Figure 2.4 Compaction characteristics of DM2



Figure 2.5 Compaction characteristics of DM3



Figure 2.6 Compaction characteristics of DM4

Note: LKD-A = DM+30% sand + LKD; LKD-B = DM+50% sand + LKD;

QL-A=DM+30% sand+ QL; QL-B = DM+50% sand + QL; considerable improvement in its maximum dry unit weight was observed upon addition of QL or LKD.

The DM has a slender compaction curve due to plasticity limits and finegrained characteristics of the dredged materials (Figure 2.3 to Figure 2.6). Due to high fines content of the DM, the compaction is very sensitive to change in water content. The maximum dry unit weight of the dredged sediments ranges from 11.9 kN/m³ to 18.5 kN/m³, and lower dry unit weights are attributed to higher fines content in the samples. Workability of the material increases because lime additives make the compaction curve flatter, which makes achieving the required dry unit weight possible over a wider range of water content. Sweeney et al. (1988) reported that short-term reactions take place before compaction of soil, which results in cementation of particles into a loose structure and cementation developed at the points of contact between the particles which offers higher resistance to compaction and decreases dry unit weight of soil.

The CBR values presented in Table 2.2 conform to the range of CBR and material properties and classification by Yoder and Witczak (1975). Increase in strength is observed in all the samples after addition of lime-based additives. Quick lime-amended samples display higher strength compared to LKD-amended samples due to higher free calcium present in QL.

The pocket penetrometer data in Figures 2.7-2.10 show that the undrained shear strength of DM does not change significantly after stabilization when the additive is blended at 2.5% by weight with the DM and the curing period is kept at 1 day. The 5% and 7.5% blends yield similar strength characteristics. DM with 10% LKD or quick lime exhibits the maximum improvement in strength although a steep decrease in its workability characteristics can be observed after 7 days of curing. The 5% blends exhibit a considerable increase in strength over 7 days and can be considered as the optimal mixtures or future environmental testing.

CBR results show considerable increase in strength after addition of limebased additives (Table 2.2). Addition of lime additives to soil forms a matrix that directly affects strength. The matrix transforms the soil from a granular, sandy-silty material to a hard, relatively impermeable material with significant bearing capacity (NLA, 2004). QL based blends produced slightly higher strength as compared to LKD amended ones due to higher free calcium content (Figure 2.11). The cu values predicted from the CBR for DM samples and their respective blends are shown in

Table 2.2. c_u of the samples increased between 0.5 – 38% of their original strengths.



Figure 2.7 Comparison of pocket penetrometer test values for DM1



Figure 2.8 Comparison of pocket penetrometer test values for DM 2



Figure 2.9 Comparison of pocket penetrometer test values for DM3



Figure 2.10 Comparison of pocket penetrometer test values for DM4



Figure 2.11 Undrained shear strength of pure and treated DM

Sample	Maximum Dry Unit Weight	Wopt (%)	CBR	Undrained Shear Strength
	(kN/m ³)		(70)	(kPa)
DM1	18.5	13.1	15	165
DM1 + 5% LKD	16.7	10.5	15	170
DM1 + 5% QL	16.3	12.1	16	173
DM2	17.7	18	10	113
DM2 + 5% LKD	16.8	13.1	12	130
DM2 + 5% QL	16.6	17.7	12	132
DM3	13	27	13	143
DM3 + 5% LKD	12.4	33	13	144
DM3 + 5% QL	11.9	29.2	13	147
DM4	13.7	32.1	11	117
DM4 Blend ¹ LKD	14.7	24	13	148
DM4 Blend ² QL	14.3	20	15	162
Embankment Soil (ES)	16.4	26	-	-

 Table 2.2 Summary of compaction and strength parameters

All proportions based on dry weights

¹ DM4 + 50% Sand + 5% Gravel + 5% LKD

² DM4 + 50% Sand + 5% Gravel + 5% QL

2.5. Conclusions

A series of geomechanical tests was conducted to improve the strength properties of Chesapeake Bay sediments for their potential use as a highway embankment fill. A small (0.5-25%) improvement in undrained shear strength was observed upon LKD addition (average CaO%=20-80%) while the increase was 2.5 to 38% for QL treated DMs (CaO%=85%). Even though relative compaction is the main parameter used in constructing highway embankments, $\gamma_{dry max} = 15.7$ kN/m³ is another unit weight limit for embankment materials constructed by the SHA. The results of the tests showed that DM1, DM2, and their respective blends exceeded this limit (Table 2.2). A satisfactory performance of these blends deemed these samples competent for investigating leaching behavior, which will be covered in Chapter 3.

DM3 was dropped out of the study due to no considerable increase in maximum dry unit weight and strength after addition of gravel, sand and lime-based additives.

DM4 showed similar index properties as DM3; however, notable increase in compaction characteristics ($\gamma dry max \sim 15$ kN/m³ for its blends) and strength was observed after adding sand and gravel (Table 2.1). Accordingly, DM4 and its blend with 50% sand, 5% gravel and 5% lime-based additives were also included in the environmental testing program.

3. Experimental Evaluation of Trace Metal Leaching from Dredged Material to Surface and Groundwater

3.1. Introduction

Even though lime-amended DM has favorable mechanical properties, one key issue that has prevented its use in embankments is the surface water impacts caused by leaching of metals from DM. Rain water percolates through the embankment profile, making its way to surface water and groundwater, potentially transporting trace elements into these systems. Furthermore, pH conditions and pollutant leaching potential are highly influenced by the intended DM application. Limited studies aimed at pollutant characteristics in surface water during construction of highway embankments have been carried out (Boyer 1994, Banks et al. 2006, Mayer et al. 2008). Use of Chesapeake Bay dredged sediments for construction can impact the ecosystem by leaching chemical contaminants, thus a comprehensive study of leaching behavior is carried out by conducting a series of column leach tests. Contaminant transport into surface water and groundwater was simulated via two numerical models developed in earlier studies.

3.2. Methods

3.2.1. Sequential Column Leach Test (SCLT)

In order to simulate flow through a highway embankment constructed with pure or treated DM and a thin layer of embankment soil (ES), a series of sequential column leach tests (SCLTs) were conducted. The SCLT setup is shown in Figure 3.1, and the conceptual flow model for surface water and groundwater contamination is

given in Figure 3.2. Maryland SHA construction guidelines require all recycled materials to be encapsulated by a material specified by the agency. The encapsulating material is also expected to carry properties that is suitable for highway construction. Accordingly, a clayey soil, commonly used in highway embankment construction by the SHA and named embankment soil (ES) herein, was included in the testing program. Upon removal of larger particles through a No. 4 (4.75-mm) sieve, the specimens were compacted at their optimum moisture contents in a PVC column with 101.6-mm diameter and 116.4-mm height using standard Proctor effort (ASTM D698).

The columns were operated in an up-flow mode using a peristaltic pump on the influent line. The polypropylene influent lines were connected to a polyethylene reservoir tank, which was filled with the 0.02 M NaCl solution prepared with ASTM Type II water (resistivity > 1 Megaohm-cm, ASTM D1193) at near-neutral pH (pH 6-7). On the effluent end of the column, polypropylene tubing transferred the effluent solution into the sampling tubes. An inflow rate of 15 mL/hr was used in both columns, considering the relatively lower hydraulic conductivity of the embankment soil. In these tests, the effluent tubing of the first column, which contains pure or treated DM, is connected to the second column that houses the embankment soil. Effluent samples were collected from both columns in order to compare the pH, EC and metal concentrations. The suspended solids in the collected leachate were filtered through 0.2 micrometer pore size, 25 mm membrane disc filters fitted in a 25-mm easy pressure syringe filter holder by using

60 mL plastic syringe. A series of falling head hydraulic conductivity tests were conducted on specimens before the columns were dismantled.



Figure 3.1 Sequential Column Leach Test (SCLT) setup



Figure 3.2 Conceptual model of groundwater and surface water contamination

3.2.2 Chemical Analysis

The total elemental analysis (TEA) of the materials was performed using an ICP-OES (Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometer). First the samples and 5 mL of HNO₃ were placed in 50 mL digestion tubes. The caps of the tubes were loosely placed, and the tubes were put on a digestion block where they were heated at 120°C for 16 hours before being removed from the block to cool down. After cooling, 1 mL of Hydrogen-Peroxide (H_2O_2) was added to each digestion tube and the tubes were heated on the digestion block for another 30 min. This step was repeated, and samples were left to cool down. Afterwards, the samples were diluted to 50 mL and left to sit before the ICP-OES analysis was performed. For ICP-OEP analysis, the samples were diluted further at 1:1 ratio. All the equipment was triple acid-washed and stored in clean bags before use. Every 20 samples, a blank sample was run, and a spiked sample was run every 10 samples to check the calibration curve. Minimum detection limits (MDLs) for ICP-OES were determined for each metal and the calibration standards in accordance with the U.S. Code of Federal Regulations Title 40. The chemical composition of the materials is provided in Table 3.1. The pH values of the leachates collected from SWLTs and both columns of SCLTs were measured in accordance with ASTM D 1293, whereas the material pH's of DM and ES were determined in accordance with EPA SW-846 Method 9045.
Table 3.1 Total element analysis of the dredged materials and the embankment soil

Analyt e	DM1 (mg/Kg)	DM2 (mg/Kg)	DM3 (mg/Kg)	DM4 (mg/Kg)	ES (mg/Kg)	MDL (mg/Kg)
Мо	<2	<2	<2	4	<2	2
Cu	88	45	149	344	61.7	2
Pb	40	69	69	142	<5	5
Zn	81	98	264	194	142	2
Ag	<0.5	<0.5	<0.5	0.8	461	0.5
Ni	17	15	47	117	17.4	2
Со	7	6	23	14	29.1	2
Mn	378	279	1407	572	885	5
Fe	21,800	37,400	45,900	65,700	53,700	0.01
As	11	12	17	53	3.24	5
U	<20	<20	<20	<20	<20	20
Th	7	6	11	13	N/A	2
Sr	56	33	104	109	N/A	2
Cd	<0.4	<0.4	0.5	<0.4	<0.4	0.4
Sb	<5	<5	<5	6	N/A	5
Bi	<5	<5	<5	<5	N/A	5
V	52	68	120	155	138	2
Ca	5300	1700	10,200	6500	1940	0.01
Р	0.03	0.031	0.098	0.112	262	0.002
La	22	18	47	43	N/A	2
Cr	78	88	162	205	37	2
Mg	3100	3700	9800	7000	6300	0.01
Ва	200	141	355	327	98.6	1
Ti	2500	2100	3600	3400	N/A	0.01
AI	26,400	20,600	67,400	67,200	47,700	0.01
Na	2900	1300	9100	3400	106	0.01
К	7300	11,900	18,000	20,300	2350	0.01
Zr	47	34	88	84	N/A	2
Sn	5	4	11	9	N/A	2
Y	11	7	25	19	N/A	2
Nb	5	5	15	10	N/A	2
Be	<1	1	3	2	N/A	1
Sc	6	5	15	16	N/A	1
S	5000	1000	8000	9000	110	0.1

SCLT results were analyzed for aluminum (AI), arsenic (As), boron (B), calcium (Ca), chromium (Cr), cobalt (Co), iron (Fe), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), silver (Ag), vanadium (V) and zinc (Zn) for all dredged materials and the embankment soil. Based on their elevated concentrations in leachates, the differences in their leaching patterns, as well as their potential risk to the environment the five metals selected for further discussion were: aluminum (Al), arsenic (As), cobalt (Co), nickel (Ni), and zinc (Zn). Elution curves of the remaining 9 metals are given in Appendix A. These metals do not present any serious environmental concern as no EPA Water Quality Limit (WQL) is available for them or no significant leaching is observed from the test.

Exposure to high levels of AI can have adverse effects to humans and animals. Aluminum can easily transit from solid to solution phase at low pH values, and is very easily mobilized by acid rain. Mobility of this element can inhibit cell division in plants due to exposure, and produce chromosomal aberrations and color changes due to phosphate deficiency (Manna and Parida 1965, Barabasz et al. 2002).

Arsenic (As), which is found in several different species and oxidation states, has been observed to cause chronic health effects including cancer (Hughes, 2012). Arsenic is toxic to the majority of organ systems, and its sensitivity to organs like the kidney makes it dangerous for human beings (Cohen et al. 2006). While chronic arsenic exposure directly affects the vascular system, it causes hypetension and cardiovascular disabilities (Jomova et al. 2010).

Cobalt is an element that is not easily found in free form in the environment, but is known for being introduced into the food chain due to its absorption by plants in the form of fertilizers and industrial pollutants (Punsar et. al 1975, Delpeux et. al 2002). Exposure to cobalt can cause damage to respiratory organs, heart and thyroid (Coates 1971, Bucher et. al 1990).

Nickel (Ni) has found to be carcinogenic (Rathor et al. 2014) (Anderson et a. 1996). Elevated lung and nasal cavity risks were observed with workers exposed to high levels of nickel. Laryngeal, kidney and prostate cancer have been recorded in previous studies from people working in mining and nickel refinery industry (Menzel, 1987). USEPA regulates nickel concentration in natural waters due to its potential acute and chronic effects to human health.

Zinc (Zn) is naturally present in natural waters. Average zinc concentration in seawater is 0 - 6.5 ppb and 5 - 10 ppb in fresh water. Zinc enters the environment also due to human activity of burning waste, discharging waste water from manufacturing industries. Zinc contamination in natural water can impact human health (Maroulakis, 2009). Consumption of zinc-rich water can cause acute stomach cramps, nausea and vomiting. Prolonged exposure to zinc can cause chronic disorders like anemia, kidney and pancreatic damage, decreased levels of high density lipoprotein (ATSDR, 2005).

3.2.3. Modeling of Contaminant Transport in Surface Water

Contamination of surface water may be of concern for embankments constructed by dredged materials. The current study tries to simulate contamination by a

combination of column leach test and computer aided models. Analytical solutions of advection- dispersion equation (ADE) based models are used to simulate contaminant transport processes in streams and rivers. The ADE distinguishes two transport models: advective transport and as a result of passive movement along with water, and dispersive transport to account for diffusion and small-scale variations in flow velocity, as well as any other process that contribute to solute movement.

Solutions based on equations developed by van Genuchten (2013) were used to define advective, dispersive, longitudinal transport, and lateral dispersion. These equations were developed in a numerical model, namely UMDSurf, to compute concentration distributions as a function of distance. For one-dimensional transport, solute flux, J_s , can be written as

$$J_s = uC - D_x \frac{\partial C}{\partial x}$$
(3.1)

where u is the longitudinal fluid flow velocity, solute concentration expressed in mass per unit volume of solution, D_s is the longitudinal dispersion coefficient accounting for combined effects of ionic diffusion and hydrodynamic dispersion, and x accounts for longitudinal coordinate.

The mass balance equation is formulated by considering the accumulation of solute in the control volume over time as a result of divergence of the flux (i.e. outflow).

$$\frac{\partial c}{\partial t} = -\nabla X J_s - R_s + R_w C_e \tag{3.2}$$

where t is time and R_s represents arbitrary sinks/sources of solute. R_s <0 means consumption, and greater than zero signifies feeding of solute. The last term in the expression denotes injection if it is greater than zero. In order to approximate ADE without producing major error in the solution, C_e and R_w terms can be ignored. This makes the expression:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x}$$
(3.3)

Natural processes like biodegradation, inactivation and radioactive decay may affect the concentration of contaminants. These processes can be aggregated in the term R_s (Eq. 3.2). In order to solve for the solution analytically, these terms need to be limited to linear expressions. Governing differential equation can be represented in the following form:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} - \mu C + \gamma$$
(3.4)

Three major initial and boundary condition components were used to analyze the governing differential equation, which are stated below:

$$C(x,0) = f(x) \tag{3.5}$$

$$(uC - \omega D_x \frac{\partial C}{\partial x})_{x=0} = u g(t)$$
(3.6)

$$\frac{\partial c}{\partial x}(\infty,t) = 0 \text{ or } \frac{\partial c}{\partial x}(L,t) = 0$$
(3.7)

Production decay for the semi-infinite domain is assumed to be zero to compute a conservative solution. A Heaviside step function with initial concentration C_{\circ} is expressed as:

$$g(t) = \begin{cases} C_0, 0 < t \le t_0 \\ 0, t \ge t_0 \end{cases}$$
(3.8)

The solution for Equation 3.4 will be:

$$C(x,t) = \begin{cases} C_i + (C_0 - C_i)A(x,t), & 0 < t \le t_0 \\ C_i + (C_0 - C_i)A(x,t) - C_0A(x,t-t_0), t \ge t_0 \end{cases}$$

(3.9)

where,

$$A(x,t) = \frac{1}{2} erfc \left[\frac{x - ut}{\sqrt{4D_x t}} \right]$$
(3.9.1)

$$\sqrt{\frac{u^2 t}{\pi D_x}} \exp\left[\frac{-(x-ut)^2}{4D_x t}\right] = \frac{1}{2} \left(1 + \frac{ux}{D_x} + \frac{u^2 t}{D_x}\right) \exp\left(\frac{ux}{D_x}\right) \operatorname{erfc}\left[\frac{x-ut}{\sqrt{4D_x t}}\right]$$
(3.9.2)

Surface runoff and evaporation from the pavement surface, the shoulders, and the surrounding ground are not considered in the model. Infiltration of runoff along the edges of the pavement structure is ignored. The retardation factors for each metal were obtained by fitting van Genuchten (1981) analytical leaching model to the metal concentrations in the effluent of the Br tracer column leaching tests (Dayioglu, 2016) and incorporated into the model to simulate the retardation of the solute in natural soils located between the embankment corner and the surface waters.

3.2.4. Groundwater Contamination Modelling

A computer-aided groundwater contamination model (WiscLEACH) was employed to analyze metal transport from the embankment to groundwater. Three analytical solutions for advection-dispersion-reaction equation (ADRE) were combined in WiscLEACH to develop a method for assessing impacts to groundwater caused by leaching of trace elements from DM used in highway embankment. WiscLEACH simulations were conducted to study concentration profiles in soil vadose zones and in groundwater. Contours of trace metal were developed at different years as a function of depth to groundwater, thickness of base layer and hydraulic conductivity. The model also approximates material profile as homogeneous and isotropic. Water in the system (highway embankment) due to precipitation on road pavement percolates into groundwater or surface runoff (Li et al. 2007). As water percolates down through the profile, trace elements leach from the DM and migrate downward through the subgrade soils until they reach the groundwater table. Flow in the DM and subgrade is assumed to occur only in the vertical direction. Steady one-dimensional (1D) flow is assumed to occur in the pavement layer and the vadose zone, with net infiltration rate controlled by a combination of least permeable layer and annual precipitation rate. Surface runoff and evaporation are not considered to make the analysis conservative.

Transport in the vadose zone is assumed to follow ADRE for 1D steady vertical flow with 2D dispersion and a linear, instantaneous and reversible adsorption. Trace elements that reach the groundwater table are transported horizontally and vertically. The flow of groundwater is assumed to be a steady

state, saturated and horizontal flow. Chemical and biological reactions that may transform trace elements are assumed to be absent. Further information on WiscLEACH is provided by Li et al. (2007).

Transport and hydraulic conductivity parameters of soil were determined from laboratory Br tracer and falling head hydraulic conductivity tests (BS 1377-6) respectively (Table 3.2). Effective porosities and dispersion coefficients for each material and metal were determined by fitting the Ogata-Banks (1961) equation to the effluent Br concentrations in tracer tests. van Genuchten (1981) equation was used to compute retardation factors for individual metals with dispersion coefficients and effective porosities from Ogata-Banks equations. Annual precipitation rate of 1 m/yr was selected as average annual rainfall in the State of Maryland is 0.98 to 1.3 m/yr according to the United States Geological Survey (NWIS, 2017).

Material	K, (m/year)	K, (cm/s)	n _e	i	α _∟ (m)	α _T (m)	R _d for Al	R _d for As	R _d for Co	R _d for Ni	R _d for Zn
DM1	4.81	1.52 x 10 ⁻ ⁵	0.521	0.001	5.6 x 10 ⁻ 4	0.565	2	4.5	2.7	2.6	3.6
DM2	4.72	1.49 x 10 ⁻ ⁵	0.524	0.001	5.4 x 10 ⁻ 4	0.366	1.6	-	1.5	1.6	2.4
DM2LKD	4.85	1.53 x 10 ⁻ ₅	0.525	0.001	1.8 x 10 ⁻ 4	0.450	4.2	-	-	-	-
DM2QL	4.81	1.52 x 10 ⁻ ⁵	0.525	0.001	7.7 x 10 ⁻ ⁵	0.772	5.3	-	-	-	-
DM4QL	4.44	1.40 x 10 ⁻ ⁵	0.515	0.001	9.6 x 10 ⁻ ⁵	0.711	-	-	-	3.6	-
Subgrade	0.36	1.14 x 10 ⁻ 6	0.27	0.001	0.147	0.015	7.3	7.3	7.3	7.3	7.3
ES	0.32	1.01 x 10 ⁻ 6	0.25	0.001	0.1	0.01	7.2	7.2	7.2	7.2	7.2
Pavement	18.29	5.79 x 10 ⁻ ⁵	0.35	0.001	0.1	0.01	1	1	1	1	1
Aquifer	3784	1.19 x 10 ⁻ 2	0.30	0.001	0.1	0.01	1	1	1	1	1

 Table 3.2 Hydraulic transport input parameters for pavement, embankment, subgrade and aquifer structure

Table 3.3 Input s	ite parameters
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WPOC	WP	Ws	Zgwt	Annual	TMAX	Т	Side Slope
(m)	(m)	(m)	(m)	Precipitation	(yrs)	(m)	(H : V)
				rate			
				(m/yr)			
30	6	2	5	1	200	7	2:1

Notes: W_{POC} = Point of compliance, W_P = Pavement width, W_S = Shoulder width, Z_{GWT} = Dept to groundwater table,

 T_{MAX} = time in years, T = Thickness of embankment structure

3.3. Results

3.3.1. Sequential Column Leach Tests (SCLTs)

Figure 3.3 shows temporal characteristics of effluent pH for pure and treated DM. Considering low hydraulic conductivity of DM (1.40×10^{-5} to 1.53×10^{-5} cm/s) and ES (1.01×10^{-6} cm/s), all tests were continued until 20-25 pore volumes (PV) on an average. The pH of effluent solution from pure DM indicates acidic behavior (pH 3.5-6) whereas highly alkaline pH (pH 6.5-11.5) is observed for the column that contained a lime-amended DM. pH characteristic of the effluent originating from the sequential column (effluent from ES) exhibit near-neutral behavior (pH 6.5). These results also show that pH of the effluent decreases after passing through clayey ES due to buffering capacity of this embankment soil (Table 3.1).

The pH of effluent solution from lime-amended DM remained between 10.5 and 13 and presented an alkaline behavior (Figure 3.3). There are several factors contributing to the changes in pH of the effluent. Addition of lime-based additives increase the free calcium content Ca²⁺ ions and cause formation of Ca(OH)₂, which may be the primary factor. pH in all the columns fluctuated 1-2 pH units throughout the tests due to dynamic characteristic of column leach testing.

Three distinct leaching patterns can generally be observed in the trace metal leaching from recycled materials, namely first-flush, lagged response and steady-state leaching (Bin-Shafique 2002, Komonweeraket et al. 2015). First-flush leaching is characterized by a high initial concentration followed decrease in concentration with increase in pore volume. First-flush pattern occurs due to release of metals from water



5 10 15 20 Pore Volume of Flow

Figure 3.3 Effluent pH in SCLT

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soluble fraction as well as from the sites with low adsorption energies (Bin-Shafique et al. 2006, Morar 2008). Materials with high CaO content typically exhibit a first-flush leaching pattern (Sauer et al. 2012). Edil et al. (1992) indicated that these patterns are governed by changes in solubility as a function of changing pH. Lagged response is characterized by peak concentrations of trace metals after flushing the soil for a few pore volumes, whereas steady-state leaching pattern does not exhibit any significant changes throughout the test (Bin-Shafique et al. 2002).

Figures 3.4-3.8 present a series of CLT elution curves for AI, As, Co, Ni, and Zn. Effluent from DM1, DM2 and DM4 shows acidic behavior, thus pH conditions and the presence of high levels of AI in the material (Table 3.1) mobilized AI ions into the effluent. First-flush pattern is observed from DM1 and DM2 with a distinct peak initially and concentrations falling below the reported EPA WQL of 0.75mg/L. Effluent from DM4 does not include any AI concentrations initially (<0.2 mg/L). At ~10PV, steady state leaching of AI is observed. This can be attributed to a sudden drop of pH at ~5 PV. The observed trend is reasonable as AI is reported to mobilize under acidic and alkaline conditions, i.e., amphoteric behavior (Langmuir 1997, Kenkel 2003). Moreover, high levels of aluminum in DM measured in TEA (20, 600-67, 400 mg/L, Table 3.1) can be responsible for the elevated AI concentrations in SCLTs.

Effluent from lime-amended DM shows alkaline behavior (pH10-12.5). Al is expected to leach from lime-amended DM due to amphoteric characteristics of the metal. Effluents from DM2LKD and DM2QL show first-flush pattern of leaching with

peak concentrations of 1.17 mg/L and 0.78 mg/L, respectively, and the concentrations from these two blends are significantly lower than the ones from pure DM samples (Table 3.3). It is suspected that addition of LKD and QL increases pH but retards the mobility of AI, thus leaching significantly lower AI. DM4LKD exhibits a steady-state leaching behavior (Figure 3.4) but the peak AI concentrations are consistently lower than those from DM4 (Table 3.3).

Effluent from sequential columns (effluent percolating from ES) shows nearneutral pH. Al concentrations from all the sequential columns, except DM2-LKD are found to be below the reported EPA WQL. It is important to note that DM2LKDES results in a peak Al concentration that is very close to EPA WQL (0.8 mg/L versus 0.75 mg/L). Near-neutral pH conditions and buffering capacity of the material significantly reduced the mobility of Al leaching from the materials.

Effluents from DM1, DM2 and DM4 show acidic behavior, thus pH conditions and the presence of As in the material may have mobilized As ions into the effluent. Al-Abed et.al (2007) also showed that As is mobilized under acidic and alkaline conditions, i.e., amphoteric behavior. A first-flush pattern is observed from DM1 and a lagged response is observed from DM2 with a distinct peak at 2.4 PV, after which concentrations falling below the reported EPA WQL of 0.34 mg/L. DM4 shows As concentrations consistently below the reported EPA WQL (Table 3.3).

Arsenic leaching from lime-amended DM shows alkaline behavior (pH 10-12.5). Effluent from all the lime-amended DM columns consistently shows As leaching below detection limit (0.2 mg/L), since addition of lime decreases As

mobility in soils (Camacho et al. 2008). It is suspected that addition of LKD and QL increases the pH but significantly retards the mobility of As, resulting in leaching less of As compared to pure DM. Similar observations were made by Grubb et al. (2011) when arsenic-contaminated dredged sediments were mixed with alkaline steel-slag fines.

Effluent from sequential columns (effluent percolating from ES) shows nearneutral pH. First-flush leaching pattern is observed from DM2ES. This is expected due to As leaching from DM2 (Table 3.4 and Figure 3.5). As concentrations in DM1LKDES, DM2LKDES and DM2QLES peak after 4, 2.5 and 2.6 PV respectively and then rapidly decreased. Lagged behavior of As has been observed in previous studies (Becker et al. 2013) due to changing speciation of As(III) and As(V) which can have an effect on leaching characteristics. Peak As concentrations were lower for sequential columns when compared to pure DM (<1.25 mg/L versus <2.65 mg/L) due to pH and buffering capacity of the material.

Sample	рН	AI	As	В	Со	Cu	Fe	Mg	Mn	Ni	Zn
DM1	4.5-6	14.5	2.65	3.37	2.91	2.43	28.2	187	21	2.19	44.6
DM1ES	6.5-7.5	< 0.2	1.25	0.49	0.343	< 0.2	< 0.2	318	< 0.2	0.2	0.87
DM1LKD	11-11.5	< 0.2	0.2	< 0.2	<0.2	3.01	< 0.2	243	2.43	0.2	0.27
DM1LKDES	6.5-8	< 0.2	1.56	0.61	< 0.2	< 0.2	< 0.2	472	< 0.2	0.2	0.71
DM1QL	11-12.5	< 0.2	< 0.2	< 0.2	< 0.2	4.09	< 0.2	290	0.28	0.23	0.29
DM1QLES	7-7.5	< 0.2	1.36	0.25	0.23	< 0.2	< 0.2	380	< 0.2	< 0.2	0.63
DM2	3.5-4.5	68.7	2.59	4.65	3.78	1.34	37.9	366	30.9	4.2	63.6
DM2ES	5.5-6.5	1.36	2.39	1.21	0.35	< 0.2	3.62	329	55.2	0.38	9.47
DM2LKD	6.5-7	1.17	< 0.2	< 0.2	< 0.2	< 0.2	1.88	180	15.6	< 0.2	0.45
DM2LKDES	6-7	0.80	0.612	< 0.2	< 0.2	< 0.2	< 0.2	301	42.5	< 0.2	<0.05
DM2QL	10.5-11.5	0.78	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	19	< 0.2	< 0.2	< 0.05
DM2QLES	6-7	0.662	0.251	< 0.2	< 0.2	0.22	< 0.2	220	24.6	< 0.2	< 0.05
DM4	3.5-4.5	2.2	< 0.2	< 0.2	< 0.2	4.2	28	256	81.6	< 0.2	< 0.05
DM4ES	6-6.5	< 0.2	< 0.2	< 0.2	<0.2	< 0.2	< 0.2	306	73.6	1.37	< 0.05
DM4LKD	10-11	0.78	< 0.2	< 0.2	< 0.2	1.13	< 0.2	246	< 0.2	< 0.2	< 0.05
DM4LKDES	6-7	< 0.2	1.84	< 0.2	< 0.2	< 0.2	10.7	198	65	< 0.2	< 0.05
DM4QL	12-13	< 0.2	< 0.2	< 0.2	< 0.2	1.91	< 0.2	221	< 0.2	0.58	< 0.05
DM4QLES	6.5-7	< 0.2	< 0.2	< 0.2	< 0.2	0.33	4.07	110	35.6	< 0.2	< 0.05
EPA WQL	6.5-9	0.75	0.34	N/A	N/A	0.013	N/A	N/A	N/A	0.47	0.12
MDL	N/A	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.05

Table 3.4 Peak effluent concentrations from SCLT. Concentrations exceeding EPA WQL are in bold.

Notes: EPA WQL= Environmental Protection Agency Water Quality Limits for protection of aquatic life and human health in fresh water; MDL = Minimum detection limit





Figure 3.4 SCLT elution curves for Aluminum



Figure 3.5 SCLT elution curves for Arsenic

Although EPA WQL has not been prescribed for cobalt (Co), it is known that this metal can be highly toxic to living organisms (Linna et al. 2004). A limit of 1.5 mg/L has been proposed in past studies (Valdez-Vega, 2011) due to its harmful effects to living organisms. First-flush pattern is observed from DM1 and DM2 with a distinct peak initially (PV=0), and concentrations rapidly decreasing as a function of pore volume. Effluent from DM4 shows Co concentrations consistently below the detection limit of 0.2 mg/L.

Effluent from all columns of lime-amended DM consistently show Co concentrations below the detection limit of 0.2 mg/L (Table 3.3 and Figure 3.6). Elution of Co increases with increase in acidity and iron content, while manganese reduces the mobility of cobalt (Greinert et al. 2011). Considerable concentrations of manganese and iron can be observed in pure DM compared to lime-amended DM (Appendix A), which may have potentially influenced the leaching behavior of Co.

Peak Co concentrations from sequential columns are significantly lower than pure and lime-amended columns (Table 3.3). Co leaching from pure and lime-amended DM falls below 1.5 mg/L, a limit proposed by Valdez-Vega (2011), after 2-3 pore volumes of flow and use of ES in highway construction significantly reduce the risk of Co leaching (Figure 3.6). First-flush pattern is observed from DM2ES due to significant amount of Co leaching from DM2 column (up to 3.78 mg/L). A steady-state response is observed from DM1ES due to DM1 leaching Co, although the pattern is not evident from the graph as the concentrations are found to be very close to the detection limit. Buffering capacity of ES significantly affects

the mobilization of Co due to adsorption on the surface of ES, thus reducing concentrations of Co in the effluent.



Figure 3.6 SCLT elution curves for Cobalt

Nickel (Ni) commonly occurs as M²⁺ cation and is generally more mobile under acidic conditions as it tends to get adsorbed strongly to minerals at neutral and alkaline pH (Lockwood et al. 2015). Ni is expected to leach from DM columns due to concentrations between 15-117 mg/L observed in TEA. Effluents from DM1, DM2 and DM4 show acidic behavior, thus pH conditions and presence of Ni in the material mobilized Ni ions into the effluent. First-flush pattern is observed for DM1 and DM2 with a distinct peak initially and concentrations falling below the reported EPA WQL of 0.47 mg/L after 2-5 pore volumes of flow.

Effluent from lime-amended DM showed alkaline behavior (pH 10-12.5). Lower concentrations of Ni leach from lime-amended DM, since Ni forms insoluble hydroxides, such as Ni(OH)₂, at pH>9 due to a decrease in solubility of Ni (Richter and Theis 1980, Bradbury and Baeyens 2009). Ni can also form strong complexes with organic molecules (Ashworth and Alloway 2004, Baken et al. 2011) and can therefore have a strong impact on concentrations of trace metals in circumneutral and alkaline pore waters in soil (Davis 1984, Ashworth and Alloway 2004) despite the tendency of metal cations to be adsorbed to minerals present at neutral and alkaline conditions (Wu et al. 2001, 2002).

First-flush pattern is observed from DM4QL and the concentrations drop rapidly to below EPA WQL after 2-3 PV. All the other lime-amended DM columns show Ni leaching below the detection limit of 0.2 mg/L. Addition of LKD and QL increases the pH and significantly retards the mobility of Ni, thus leaching significantly lower Ni compared to pure DM.

Effluent from sequential columns (effluent percolating from ES) shows nearneutral pH, and Ni concentrations for all the sequential columns are found to be below the reported EPA WQL except DM4ES. Ni leaching from DM4 presents a lagged response pattern; a peak is observed after 17 pore volumes of flow followed by a drop in the concentrations below the reported EPA WQL. The laggedresponse may be attributed to relatively lower hydraulic conductivity of DM4 (9.8 x 10^{-6} cm/s) compared to that of DM1 and DM2 (1.52 x 10^{-5} and 1.49×10^{-5} cm/s).

Acidic conditions (pH 3.5-6) and the presence of high levels of Zn in the dredged material (81-264 mg/L, Table 3.1) mobilized Zn ions into the effluents of DM1, DM2 and DM4 (Figure 3.6). Cetin et al. (2012) also showed that Zn can be mobilized under acidic and alkaline conditions. First-flush pattern is observed from DM1 and DM2 with a distinct initial peak and concentrations fall below the reported EPA WQL of 0.12 mg/L. Effluent from DM4 did not have any Zn concentrations above the detection limit of 0.05 mg/L.

Effluents from lime-amended DMs show alkaline behavior (pH 10-12.5), and Zn leaching is expected due to amphoteric characteristic of Zn. First-flush leaching pattern is observed from DM2LKD with a peak concentration of 0.45 mg/L, although it is not clear from Figure 3.8 as the temporal changes in concentrations are minor. It has been observed that Zn transforms from residual fraction to manganese oxides bound complexes after addition of lime (Saha et al. 1999). It is suspected that addition of LKD and quick lime increases the pH but retards the mobility of Zn, thus resulting in leaching significantly lower amounts of Zn.

Effluent from sequential columns (effluent percolating from ES) shows nearneutral conditions (pH 5.5-7.5). First-flush pattern is observed from DM2ES as a result of Zn leaching from DM2. Due to buffering by the ES at near-neutral pH, the peak concentrations are found to be lower than pure DM (<0.05-63.6 mg/L versus <0.05-9.47 mg/L). A lagged response is observed for DM1QLES, with a peak concentration of 0.63 mg/L after nearly 2 pore volumes of flow. The concentration of Zn falls below the reported EPA WQL after 8 pore volumes of flow. It is suspected that Zn in DM1QLES was mainly mobilized from the embankment soil as the effluent from DM1QL column has lower Zn concentrations (C_{peak}=0.29 mg/L).



Figure 3.7 SCLT elution curves for Nickel



Figure 3.8 SCLT elution curves for Zinc

3.3.2. Chemical Transport Modeling Surface Water (UMDSurf)

Figures 3.9 and 3.10 show the UMDSurf-predicted concentrations of AI, Ni, and Zn in the stream at 20, 50, 100, 500, and 1000 m away from the source (from the entrance point into the stream). The results are obtained based on the assumptions of an instantaneous injection (t=10 s) of 1 kg (2.2 lb.) solute in the main channel of a river having a cross section of 10 m² (107 ft²), an average velocity of 1 m/s (3.3 ft/s) and a dispersion coefficient of 5 m²/sec (54 ft²/sec) as per De Smedt et al. (2005) and van Genuchten (2013). Either peak or stabilized concentrations can be used for surface water modeling. Peak concentrations obtained by the column leach test played a role for surface water modelling to keep the analysis conservative. Concentration of metals modeled at t = 0 (initial point) are much lower than peak concentration of the metals observed in SCLTs. As the leachate passes through the subgrade and natural soil to reach surface water, the metal concentrations are retarded. Two different subgrade soils were assumed to exist below the highway embankment:

- CL similar to embankment soil commonly used by SHA with pH of 5.9 and retardation factors of 7 for AI, Cu, Ni and Zn.
- CL-ML similar to a typical subgrade soil encountered in Maryland with a pH of 6.3 and retardation factors 50, 44,7, and 16 for Al, Cu, Ni and Zn respectively.

Metal concentrations decrease significantly with time and horizontal distance from the surface of the DM-ES system. Concentrations of all metals decrease by 50% at 20 meters away from the entrance point. Al, Ni and Zn concentrations drop significantly below EPA WQL for respective metals at around 100 meters. The concentration trends continue to stay below EPA WQL after the 100-meter threshold. For instance, AI concentrations of DM1 at the point of entrance to the surface water are 5.6 mg/L and 0.68 mg/L for CL and CL-ML soil, respectively. The same concentrations are reduced by approximately 4-5 times at a horizontal distance of 100 m, and fall below the reported EPA WQL for CL type soil at 100 m and at 0 m for CL-ML type soil. High concentrations of Zn are observed to leach into surface water (C=0.27 - 63.6 mg/L), and after being buffered in the natural soil formation, 2.5 - 6 mg/L of Zn is observed at the initial point of entry. Simulations show that concentrations of Zn for pure and lime-amended DM fall below the reported EPA WQL at a horizontal distance of ≈1000 m for CL type formation and ≈750 m for CL-ML formation.

It can also be observed from Figures 3.9 and 3.10 that the rate of decrease is greater, for higher initial concentrations as indicated by steeper slopes. It should also be emphasized that percolation of leachate through the DM-ES system as well as the natural soil absorb metals, thus decreasing the risk of metals entering into surface waters.



Figure 3.9 Surface water contamination of a) Aluminum b) Nickel c) Zinc as a function of horizontal distance (CL type subgrade soil)



Figure 3.10 Surface water concentration of a) Aluminum b) Nickel c) Zinc as a function of horizontal distance (CL-ML type subgrade)

3.3.3. Chemical Transport Modeling Groundwater (WiscLEACH)

Figures 3.11-3.15 show the contour plots of the predicted concentrations of Al in the soil vadose zone and groundwater for 5, 20, 50, and 100-year time periods after completion of construction. For brevity, plots for Al and As for a CL-ML type subgrade are provided, the concentration profiles for rest of the metals and subgrades are given in Appendix B.

Addition of lime-based additives reduce the risk of groundwater contamination (Figures 3.11-3.14). A comparison of the 5-year contours of DM1, DM2, DM2LKD and DM2QL shows that Al originating from lime-amended DM does not leach into the groundwater. The majority of Al stays in the vadose zone whereas for the pure DM embankment, 3 mg/L and 2 mg/L Al is leached out into groundwater for DM1 and DM2, respectively. Al concentrations reduce as a function of distance from the POC (e.g., at the centerline of pavement structure, at the point of compliance). Retardation factors for pure DM (Table 3.2) are lower than the ones for lime-amended DM. Al concentrations for all the samples simulated on WiscLEACH were found to be consistently below the reported EPA WQL of 750 μ g/L.

Results from WiscLEACH also show low concentrations of As leaching into groundwater. Simulations of 5-year time period show no As entering the groundwater, and low concentrations of As, ranging from 1 to 5 μ g/L, enter into groundwater after 20, 50, and 100 years (Figure 3.15). All arsenic concentrations in groundwater remain below the EPA WQL of 340 μ g/L. Similarly, Ni and Zn concentrations are below their respective EPA WQLs (Appendix B).



Figure 3.11 Predicted AI concentrations in vadose zone and groundwater for simulating flow of DM1 leachate through CL-ML subgrade



through CL-ML subgrade



through CL-ML subgrade



Figure 3.14 Predicted AI concentrations in vadose zone and groundwater for simulating flow of DM2QL leachate through CL-ML subgrade



Figure 3.15 Predicted As concentrations in vadose zone and groundwater for simulating flow of DM1 leachate through CL-ML subgrade
3.4. Conclusions

A research study was undertaken to investigate the environmental impacts associated with pure and lime-treated DM on highway embankments and underlying subgrades in Maryland. A battery of laboratory sequential column leach tests (SCLTs) were conducted to determine the environmental suitability of DM. Embankment soil (ES), a soil commonly used in highway embankment construction in Maryland and recommended by the local highway agency to be placed adjacent to recycled materials during embankment constructions, was also included in the testing program. Numerical analyses were conducted to determine the possible contamination of surface waters and groundwater with trace metals originating from DM. The following conclusions can be made:

- pH of effluent from lime-amended DM is alkaline (pH 10-11) and higher than pure dredged material (pH 3-4). It is observed that addition of lime-based additives increases the pH of the material by 5-6 pH units.
- Three leaching patterns namely, first flush, lagged response, and steadystate flow were observed during the testing of samples employed in the current study.
- Aluminum (AI) generally showed first-flush pattern except for DM4, which exhibited a steady-state leaching pattern. Most of the AI leaching was observed from DM. Lower leaching of AI was observed from DMLKD and DMQL. Thus, addition of lime-based additives decreased AI leaching from DM.

- Arsenic (As) showed a lagged-response leaching pattern, except for DM1.
 Distinct peaks were observed at 2-5 pore volumes followed by a drop of concentrations below detection limits. The peaks analyzed for the materials tested show that peak concentrations of As leaching from DM (2.59 2.6 mg/L) were higher than peaks for the lime-amended DM (0.6 1.8 mg/L). Thus, addition of lime based additives decreased As leaching from DM.
- Nickel (Ni) showed first-flush pattern of leaching, except for DM4ES. A lagged-response was observed for DM4ES, which might be attributed to relatively lower hydraulic conductivity of the material as compared to others (9.8 x 10⁻⁶ cm/s versus 1.52 x 10⁻⁵ and 1.49 x 10⁻⁵ cm/s, Table 3.2).
- Zinc (Zn) showed a first-flush leaching pattern. An initial distinct peak was followed by a drop in concentrations below the EPA WQL at 25-30 pore volumes. Due to lower EPA WQL (0.12 mg/L) imposed on Zn, it takes more time for Zn concentrations to fall below the required limits.
- First-flush and lagged response of the metals were attributed to release of metals into the effluent from the water-soluble fraction. The concentrations of all metals that exhibited either first-flush or lagged response stabilized after 12-15 pore volumes.
- Due to dynamic conditions of leaching, pH of the effluent changed over time.
 However, the change was small, and pH did not fluctuate more than 1-1.5 pH units.
- Analysis of effluent from ES columns showed that pH stayed in a nearneutral range. Trace metal leaching at near-neutral conditions was found to

be consistently below the reported EPA WQL, with few exceptions. Majority of the metal was adsorbed on the ES surface, thus leaching very low concentrations of metals.

- Surface water simulations (UMDSurf) showed that all metal concentrations in the DM effluents fell significantly below their respective EPA WQLs at 100 m in the surface water, except for Zn, which fell below EPA WQL at 1000 m.
- WiscLEACH simulations show that groundwater metal concentrations were significantly below the reported EPA WQLs. It is concluded that lime amended DM perform better than pure DM embankments.
- Even though peak concentrations of metals leaching out from the material are higher than their respective EPA WQL's, groundwater contaminations are found to be consistently lower than the regulated concentrations (USEPA WQL).

Use of recycled materials in construction always poses a number of geotechnical and environmental challenges, such as low unit weight, low shear strength, and metal leaching. Environmental assessment conducted in the current study shows that DM may leach metals; and addition of quick lime and lime kiln dust can decrease the leaching potential. Further, use of ES between the natural formation and DM can decrease metal leaching by adsorbing metals and stabilizing pH of the material to near-neutral levels (pH 6 - 7.5). Thus, embankments constructed with lime-treated DM underlain by ES leach lower trace metals relative to the ones constructed with pure DM.

4. Conclusions and Recommendations

4.1. Conclusions

Dredging operations all around the world are throttling up due to increasing need of maintaining waterways over time. Repurposing dredged materials (DM) for highway embankment use is a potentially promising solution to decrease the cost of containment of the material as well as decreasing the cost of highway construction. Highway embankment construction requires high volume of material, which can be fulfilled by massive volume of DM stored in a number of dredged material containment facilities as well as periodic dredging of the material.

Past studies suggest that DM (Grubb et al. 2015, Malasavage et al. 2010) is generally a fine-grained material, which has several design and construction considerations for highway embankments. High plasticity, low unit weight, low strength and poor workability are the characteristics that can be observed for dredged sediments, which may relate to swelling, slope stability failure, and difficulty in construction (USACE, 2015). In order to enhance the engineering performance of dredged materials, they are typically mixed with lime or cement-based binders. Lime adhere particles together and increase overall strength characteristics (Chan, 2014).

DM may leach trace metals into the environment, and it would be a precarious assumption to use DM as an embankment material without investigating potential leaching of metals into surface water and groundwater. A research study was undertaken to investigate the environmental impacts associated with pure and treated Chesapeake Bay DM on highway embankments

and underlying subgrades in Maryland. A battery of laboratory sequential column leach tests (SCLTs) were conducted to determine the environmental suitability of DM. Numerical analyses were conducted to determine the possible contamination of surface waters and groundwater with trace metals originating from DM. The following conclusions can be made:

- Addition of lime-based additives to Chesapeake Bay DM decreased the unit weight of the material and increased the overall strength. 5% addition of quick lime or lime kiln dust (by weight) to the material yielded favorable mechanical properties of the material. 10-20% decrease in unit weights was observed due to addition of lime-based additives but strength of DM increased by 0.5 - 38% with LKD/QL.
- 2. It has been observed from long-term leaching tests that aluminum, arsenic, nickel, cobalt, and zinc leached from DM, but the metal concentrations quickly decreased to EPA water quality limits (WQLs) for protection of aquatic life and human health in freshwaters. Addition of LKD and quick lime lowered the amount of metals leaching from the material. Placement of embankment soil (ES) adjacent to DM decreased the concentrations 2-10 times and stabilized pH to near-neutral conditions.
- Metal concentrations in the effluents originated from lime-amended DM were lower than those in pure DM effluents. Addition of lime actively decreased metal leaching into surface and groundwater.
- 4. In surface waters, the concentrations of metals leached from DM or limeamended DM were below the EPA WQLs. The transport of metals was

significantly retarded by the natural formation located between the DMamended highway embankment and the body of surface water. The metal concentrations were further reduced by 40% in CL type formation and 50% in CL-ML type formation, at locations in the surface waters 40-50-m away from the natural formation. Surface water simulations also showed that metal concentrations fall below the reported EPA WQLs at 100 m from initial point of contamination of surface water.

5. Addition of LKD and quick lime decreased groundwater contamination with Al during a 5-year time period. It is evident from groundwater modeling that contamination transport to groundwater is sufficiently dispersed in the vadose zone and metal concentrations may even decrease further with time.

4.2. Recommendations

Based on limited number of laboratory tests, it can be recommended that DM can be amended with different lime-based additives to achieve physical as well as chemical improvement.

Even though lime-amended Maryland DMs can be deemed as environmentally sound materials for the construction of highway embankments, the effect of aging on environmental suitability of DMs was not considered in the current study. Moreover, the influent solution for the column leach tests did not simulate the runoff from highway travel lanes, but rather precipitates typical for Maryland regions. In order to model the highway runoff as the additional source of

pollution, it is recommended that the influent solution in a future study is spiked with different metals.

Field tests can be carried out to simulate field conditions and assessment of mechanical as well as environmental performance as the temperature, rainfall patterns and field geotechnical properties (e.g., Υ_{dmax} , S) can actively influence the analysis and a comparison to laboratory data can be made. In order to introspect field performance, a slope stability analysis as well as seismic analysis can be conducted for the proposed embankments constructed with pure or lime-amended DM. APPENDICES

APPENDIX A:

TRACE METAL CONCENTRATIONS OF SEQUENTIAL COLUMN LEACH TEST













Mn









APPENDIX B: WISCLEACH ANALYSIS RESULTS















APPENDIX C: LIME COMPOSITION

Lime kiln dust composition		
Component	Formula	% by weight
Calcium Carbonate	CaCO₃	0 - 30
Calcium Oxide	CaO	20 - 80
Calcium Hydroxide	Ca(OH)₂	0 - 10
Calcium Magnesium Carbonate	CaMg(CO ₃) ₂	0 - 30
Aluminum Oxide	Al ₂ O ₃	0 - 15
Ferric Oxide	Fe ₂ O ₃	0 - 5
Magnesium Oxide	MgO	0 - 60
Sulfur	SO ₃	0 - 10

Quick lime composition		
Component	Formula	% by weight
Calcium Oxide	CaO	> 85
Aluminum Oxide	Al ₂ O ₃	< 1.5
Magnesium Oxide	MgO	< 15
Silica (total)		< 5

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