ABSTRACT

Title of Thesis:	SOLUBLE SALTS REDUCTION AND METALS BEHAVIOR OF DREDGED SEDIMENT FOR REUSE IN HIGHWAY SLOPE APPLICATIONS
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Waterways are dredged routinely to maintain navigation channels, resulting in large quantities of dredged materials (DM) that require disposal. This study examines the innovative reuse of DM as a topsoil alternative in highway slopes. The dredged material met Maryland Department of Transportation, State Highway Administration (MDOT SHA) topsoil requirements for pH, organic matter, and particle size distribution, and required 122 cm (48 inches) of rainwater to leach soluble salts to below limits. Column leach tests were performed on DM and topsoil to evaluate metal leaching behavior; extractions were performed to determine total and potentially mobile metals content. DM leached metals concentrations below drinking water maximum contaminant levels (MCLs) for >95% of the samples tested, and passed a toxicity characteristic leaching procedure (TCLP). Extraction data showed higher total concentrations of arsenic, chromium, and lead as compared to topsoil, but similar concentrations in the EDTA-extracted fractions indicating that metals are strongly bound.

SOLUBLE SALTS REDUCTION AND METALS BEHAVIOR OF DREDGED SEDIMENT FOR REUSE IN HIGHWAY SLOPE APPLICATIONS

by

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Chapter 1

Introduction

There is a persistent need to dredge waterways such as ports and rivers for maintenance and environmental considerations throughout the United States. Dredged materials contain organic contaminants as well as trace metals, and are typically stored in dredged material containment facilities (DMCF). According to the Maryland Port Authority (MPA), approximately 5 million cubic yards of sediment is dredged annually in the Maryland portion of the Chesapeake Bay ("Innovative Reuse and Beneficial Use of Dredged Material Guidance Document" 2017). This sediment is transported to and stored in one of the three DMCF sites in Maryland, one of which is Cox Creek, which is located in Curtis Bay, Maryland (Grubb et al. 2011). This facility has a total capacity of 6 million cubic yards, with an annual capacity of 500,000 cubic yards, and has a plan for expansion in the next few years to increase their capacity. In order to reduce the amount of dredged material (DM) stored in containment facilities, the MPA is exploring innovative reuse to develop commercial outlets in the Baltimore area for 500,000 cubic yards of DM annually. Innovative reuse refers to on-land applications of DM as an alternative to conventional disposal, and can have environmental benefits and reduce resource waste. As of 2017, authorized innovative reuses of dredged material included: landfill daily, intermediate, and final cover; landfill closure caps; or soil and fill material, including soil amendments ("Innovative Reuse and Beneficial Use of Dredged Material Guidance Document" 2017). In the hopes of expanding the authorized reuses, the Maryland Dredge Material Management Program proposed six ways to beneficially

and economically reuse the DM: (i) Landfilling, (ii) Landscaping, (iii) Agriculture, (iv) Land reclamation, (v) Engineering Fill, and (vi) Building Materials ("Innovative Reuse and Beneficial Use of Dredged Material Guidance Document" 2017)).

Topsoil is the uppermost layer of soil that contains nutrients and microorganisms, which is able to stabilize vegetation cover in disturbed areas. However, topsoil shortage is a widespread problem and poses an obstacle for land reclamation in a variety of uses, including road embankments and mineland reclamation (Bekele et al. 2015). Topsoil is vital for highway slope applications because infrastructure creates areas with nutrient-poor soils and little vegetation cover, making them vulnerable to erosion and leading to high environmental costs (Peco et al. 2017). Alternatives to conventional topsoil such as manure and fly ash are potential solutions to this issue; however, concerns such as erodibility and organic matter content prevent them from being ideal candidates. Although manure has similar soil physical properties to topsoil and high concentrations of nutrients, such as nitrogen and phosphorus, that are important for plant growth, the organic matter content resulted in lower performance than that of topsoil (Peco et al. 2017). Fly ash has also been used as a topsoil substitute, specifically in disturbed mine sites; however, its higher fines content causes higher erodibility and surface crust formation, which reduces infiltration rates (Gorman et al. 2000).

A possible solution to both the reuse of dredged material and alternative to conventional topsoil is the reuse of DM as a manufactured topsoil. The feasibility of using dredged material in lieu of topsoil has been evaluated through bench-scale screening tests and extended plant growth tests performed on DM from the New

York/New Jersey Harbor, Pearl Harbor, and Toledo Harbor. These evaluations showed that treated DM has similar physical and chemical properties similar to a manufactured topsoil product and can be used for landscaping purposes (Jones et al. 2001; Hue et al. 2002; Sturgis et al. 2002).

Dredged material often has certain physical characteristics that need to be improved through stabilizing it with an additive. DM has high gravimetric water content (40-100%) which makes it undesirable for geotechnical uses. DM typically has low organic matter (0-6%), and high pH and salinity as measured by electrical conductivity (EC). The particle size distribution depends on the source of the dredged material, and is typically a mixture of silt and sand. All these factors have prevented widespread use of DM as a topsoil material on highway slopes.

One method to reduce the moisture and salt contents of DM is a combination of dewatering and desalination, and is generally achieved by exposing the DM to sunlight until acceptable and steady moisture contents and salinity levels are reached. Sheehan et al. (2010) has applied this approach on sediments dredged from Port Waterfort, Ireland, which involved sampling the sediments at two locations that were sources of fine and coarse material, and mixing the DM to give a particle size distribution similar to that of topsoil that allowed for drainage as well as nutrient and water retention. Several mixes were created using different mix ratios, and compared to topsoil. The 200-mm thick DM samples were exposed to sunlight and monitored for 3-4 weeks until they reached stable moisture contents. The desalination process was done similarly, monitoring rainfall levels to determine if irrigation would be needed to boost desalination. Desalination to the target level of 2 mS/cm took 2-3

months, with coarser mixes requiring less time. This process was simple and low cost; however, the requirement of a large area for material placement and time-intensive nature of the dewatering process were the main barriers (Sheehan et al. 2010).

The study by Sheehan et al. (2010) also showed that addition of compost to DM may be needed to increase the organic matter content and another amendment, such as aluminum sulfate ($Al_2(SO_4)_3$) could be useful to decrease the pH to acceptable levels. All these efforts significantly increased the capacity of DM to promote plant growth.

Pearl Harbor DM was also used to create a successful topsoil using soil amendments and phytoremediation. The free water in DM was decanted, DM was crushed to pass through 2-mm sieve, and mixed with soil and two different types of compost (biosolids and manure). The soil used had a high calcium content to dampen the effect of sodium from the dredged material. The EC of the mixtures were measured, and it was determined that the mixtures had lower EC compared to the dredged material as a result of dilution of the dredged material in the blend (Hue et al. 2002). The salinity was reduced between 34.4 to 64.2% after 3 months as a result of uptake of salt by seashore paspalum grass, beach pea, and Bermuda grass. The manure compost was shown to make the DM mixture suitable for plant growth, which could then reduce salt concentrations in the mixture and degrade pollutants such as PAHs (Hue et al. 2002).

The U.S. Army Engineer Research and Development Center has evaluated dredged material blends using DM from the Toledo Harbor, Ohio as well as Confined

Placement Facilities in Mobile, Alabama. Optimal blends were created using dredged material, cellulose, and N-Viro® biosolids, a biosolids compost with a pH of 7.0, without pretreatment of DM to account for pH or salinity issues. The Toledo blends were further used in a field demonstration that produced fertile topsoil used to landscape the University of Toledo and the Toledo Botanical Gardens (Sturgis et al. 2002). However, the bench-scale screening tests showed that as the amount of cellulose increased, a calcium amendment was required to improve plant growth. Cellulose also was shown to increase salinity levels to 2-12 ppt. The reason for the lack of growth was inconclusive, but could be attributed to pH and nutrient deficiency (Sturgis et al. 2002).

An obstacle to the use of dredged material in applications such as landscaping is the presence of acid volatile sulfides (AVS) and simultaneously extracted metals. Materials dredged from waterways are typically faced with a change in conditions when moving from anoxic to oxic conditions. Dredged material usually does not contain oxygen, so when it experiences a change in environment and becomes oxidized, there are changes in the redox potential, microbial community, and metal availability that can potentially be hazardous to surrounding ecosystems (DeLaune and Smith 1985).

In anaerobic conditions, microbes require an electron source other than oxygen, and a common electron acceptor is sulfate, which is transformed into sulfides. When geomedia which were previously anoxic become exposed to oxygen, microbes use the oxygen instead of sulfate because it has a higher reduction potential. As a result, the sulfides are oxidized. The most dominant form of reduced sulfide in

soils is pyrite (FeS_2), which is stable under anaerobic conditions. However, when exposed to oxygen, the pyrite oxidizes which leads to soil acidification. The extent of this acidification depends on the pyrite content and for how long oxidation occurs (DeLaune and Smith 1985).

In addition to lowering the pH of the sediment, acid volatile sulfides are hazardous because of the increase in metal leaching from the dredged material. The oxidation of soils promotes the growth of aerobic bacteria such as *Acidithiobacillus* that can contribute to mobilizing metals (Pía Di Nanno et al. 2007). Also with a decreasing pH, H^+ ions are in competition with dissolved metals for adsorption sites, which decreases the ability of metals to adsorb and increases their mobility (Peng et al. 2009). In particular, the leaching behavior of cadmium, copper, lead and zinc are of importance when looking at dredged sediments (Lors et al. 2004).

In order to determine the suitability of Chesapeake Bay dredged sediments as a manufactured topsoil, a series of laboratory tests were conducted in this study to define physical, geotechnical, and environmental performance of these materials. The objective of this research study was to create a dredged material blend that can be used in place of natural topsoil on highway slopes, and evaluate its environmental and geotechnical behavior. The environmental behavior of the dredged material will specifically look at metal leaching in comparison to EPA's drinking water maximum contaminant levels (MCLs) due to the DM's potential use as a topsoil. This reuse could put the dredged material close to groundwater that potentially supplies drinking water, so metals leaching needs to be compared to drinking water limits.

The study consisted of the following tasks:

1. Evaluation of particle size distribution, pH, organic matter and soluble salts content of the dredged materials and compare them to Maryland Department of Transportation State Highway Administration (MDOT SHA) topsoil specifications.
2. Evaluation of long-term metal leaching of DM through column leach tests.
3. Assessment of shear parameters of DM and compare to topsoil under varying moisture conditions.

Chapter 2

Materials and Methods

2.1 Materials

Dredged material stockpiled from the Baltimore and Annapolis Harbors was used in the study. Eight buckets of dredged sediment were collected from Stockpile 1B in the Cox Creek DMCF in Curtis Bay, Maryland. An excavator was used to collect material from different depths of the stockpile (Figure 1), and then the material gathered was mixed and placed in airtight 5-gallon plastic buckets (Figure 2), which were stored at room temperature at the University of Maryland. In order for the dredged material to be used as a topsoil on highway slopes, it must meet State Highway Administration specifications for furnished topsoil, so the properties listed in those specifications (Table 1) were tested. If the dredged material alone did not meet the criteria, a series of amendments were added based on the properties that needed to be met. This testing and amending procedure is outlined in Figure 3.

Soil pH was consistent across the buckets of DM, with an average pH of 6.80 ± 0.19 per ASTM D4972 and organic matter content of 5.24 ± 0.08% per ASTM D2216. The pH and organic matter for the buckets ranged from 6.57 to 7.12 and 5.12 to 5.35% range, respectively, staying within the acceptable limits of MDOT SHA for furnished topsoil (6.1 to 7.2 for pH and 4 to 8% for organic matter).

Soluble salts content measured as conductivity was determined using a 10 mL mixed, wet sample of DM, which was added to a 50 mL centrifuge tube. A soil:water ratio of 1:4 was used, then the centrifuge tube was tumbled for 24 hours. The sample was then allowed to settle for 1 hour, and the conductivity was measured using a

Figure 1: Excavator collecting dredged material from Stockpile 1B, December 20, 2017.

Figure 2: Buckets of DM filled at Cox Creek DMCF, December 20, 2017.

Table 1: Maryland Department of Transportation State Highway Administration specifications for furnished topsoil *(*"Special Provision Insert 920-Landscaping Materials; Section 920.01.02 Furnished Topsoil" 2018).

<table>
<tr><th colspan="6">Composition - Furnished Topsoil</th></tr>
<tr><th>Test Property</th><th>Test [1] Method</th><th colspan="4">Test Value and Amendment</th></tr>
<tr><td>Prohibited Weeds</td><td>—</td><td colspan="4">Free of live stems and roots of species in 920.01.01 as well as live stems and roots of Bermudagrass, Quackgrass, and Yellow Nutsedge.</td></tr>
<tr><td>Debris</td><td>—</td><td colspan="4">920.01.01</td></tr>
<tr><td>Grading Analysis</td><td>R-58</td><td colspan="4">920.01.01</td></tr>
<tr><td rowspan="5">Textural Analysis</td><td rowspan="5">T-88</td><td colspan="2">Particle</td><td colspan="2">% Passing by Weight</td></tr>
<tr><td>Size</td><td>mm</td><td>Minimum</td><td>Maximum</td></tr>
<tr><td>Sand</td><td>2.0 – 0.050</td><td>20</td><td>75</td></tr>
<tr><td>Silt</td><td>0.050 – 0.002</td><td rowspan="2">Combined Silt and Clay
25</td><td>75</td></tr>
<tr><td>Clay</td><td>less than 0.002</td><td>30</td></tr>
<tr><td>Soil pH</td><td>ASTM D 4972</td><td colspan="4">pH 6.1 to pH 7.2</td></tr>
<tr><td>Organic Matter</td><td>T-267</td><td colspan="4">4.0 to 8.0% OM by weight</td></tr>
<tr><td>Nutrient Content</td><td>—</td><td colspan="4">920.01.01</td></tr>
<tr><td>Soluble Salts</td><td>EC 1:2 (V:V)</td><td colspan="4">500 ppm (0.78 mmhos/cm) or less.</td></tr>
<tr><td>Harmful Materials</td><td>—</td><td colspan="4">920.01.01</td></tr>
<tr><td colspan="6">Note:
[1] Materials Standards and Materials Testing 356 (MSMT 356) has been superseded by OMT Landscaping Soils Eligibility List. Test methods not defined herein shall be as per visual inspection or methods defined by the Landscape Operations Division.</td></tr>
</table>

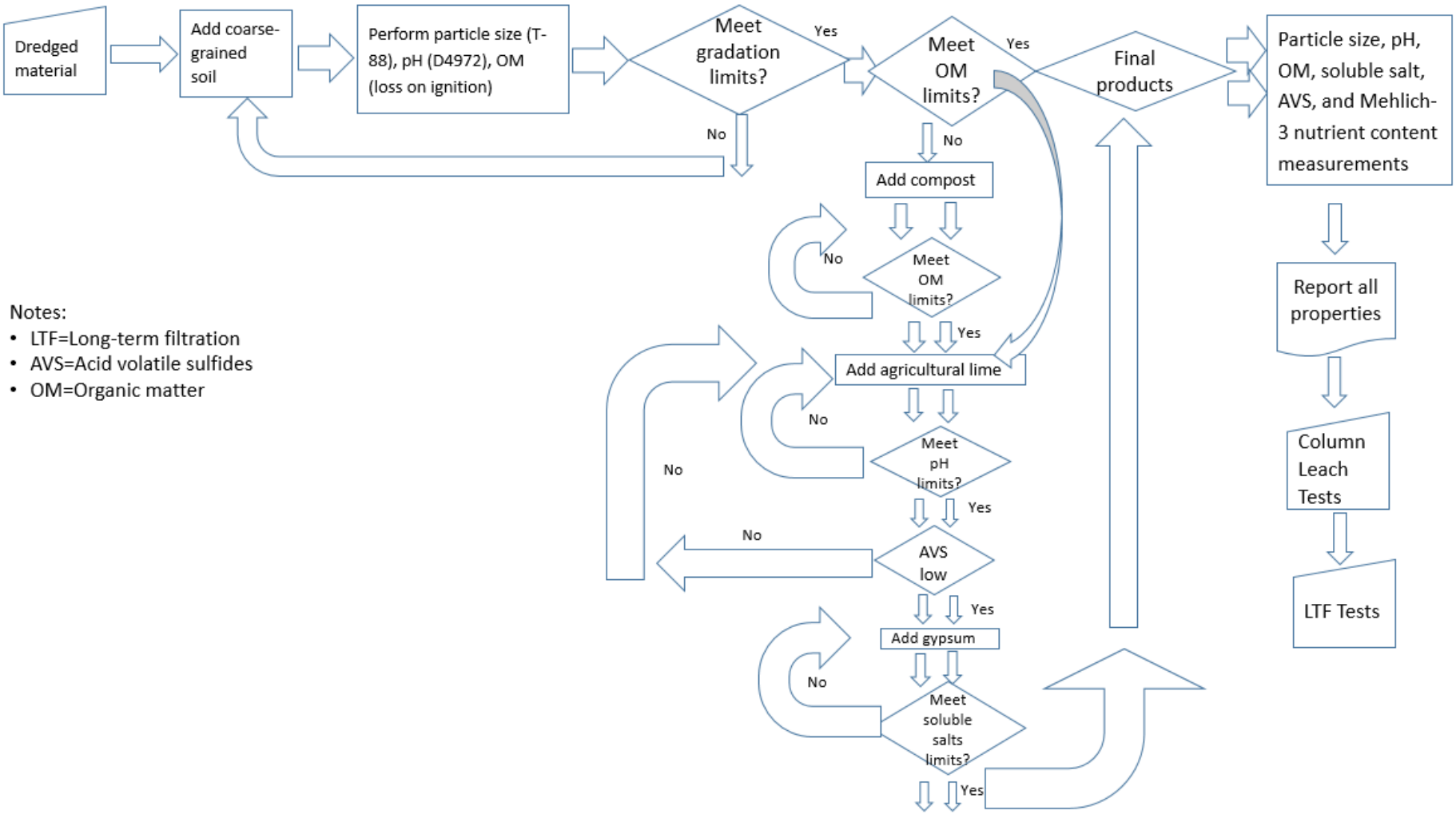

Figure 3: Flowchart illustrating research objectives.

calibrated conductivity probe. The soluble salts were much higher than the maximum limit of 500 ppm, with samples ranging from 1736 to 2359 ppm, with an average of 1970 ± 189 ppm. As a result, gypsum was added to the dredged material in order to meet the MDOT SHA requirements.

The particle size distribution was determined using the AASHTO T-88 method, and showed that the DM contained 53% sand, 26% silt, and 1.6% clay (Figure 4), which complied with MDOT SHA specifications of 20-75% sand, a minimum of 25% combined silt and clay, a maximum of 75% silt, and a maximum of 30% clay. The soil was classified as sandy loam, A-7-5, and silty sand per U.S. Department of Agriculture (USDA), American Association of State Highway and Transportation Officials (AASHTO) and Unified Soil Classification Systems (USCS), respectively. Specific gravity of DM ranged from 2.612-2.704 per ASTM D854. The average liquid and plastic limits were determined to be 41 and 27, respectively, per ASTM D4318, and the average plasticity index was determined to be 14.9.

Soil pH, soluble salts, organic matter, and gradation were also measured for a topsoil control, collected from The Stone Store in Hanover, Maryland. The topsoil had an average pH of 5.21 ± 0.09, soluble salts of 1286 ± 73 ppm, and organic matter of 15.48 ± 0.622%. The topsoil contained 70% sand, 17% silt, and 0% clay, and classified as a loamy fine sand per USDA classification. Table 2 summarizes DM and topsoil properties in comparison to SHA topsoil specifications.

Direct shear testing was performed on the DM and topsoil per ASTM D3080 using GEOTAC's DigiShear™ system to determine the angle of internal friction. The peak friction angles were similar for the topsoil (39.8°) and DM (37.9°), indicating

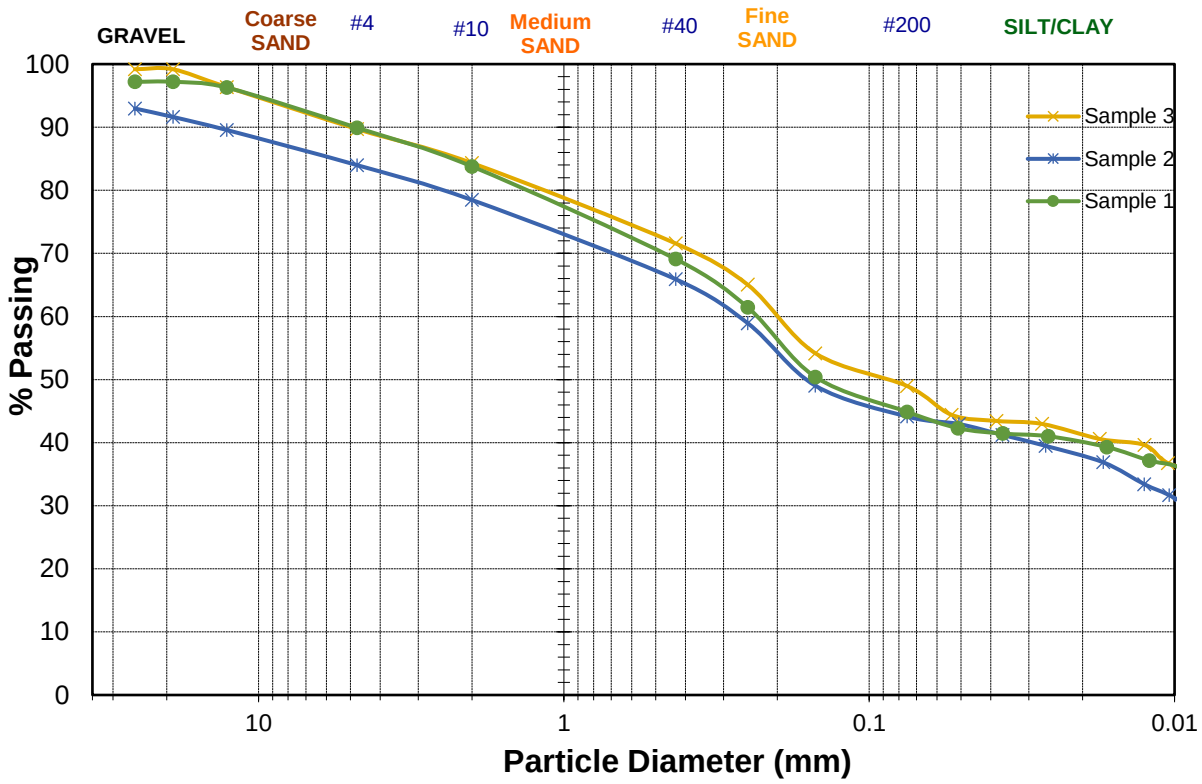

Figure 4: Particle size distribution for DM.

Table 2: Material characterization summary.

Parameter	**DM Measured Value**		**SHA Specification**				**Meets Requirements?**	**Topsoil Measured Value**		**Meets Requirements?**
Gradation	**Particle**	**% Passing by Weight**	**Particle**		**% Passing by Weight**		Yes	**Particle**	**% Passing by Weight**	No
	Sand	52.71	**Size**	**mm**	**Minimum**	**Maximum**		Sand	69.65	
			Sand	2.0-0.05	20	75				
	Silt	26.10	Silt	0.05-0.002	Combined silt and clay 25	75		Silt	17.25	
	Clay	1.63	Clay	Less than 0.002		30		Clay	0	
pH	6.80 ± 0.19		6.1-7.2				Yes	5.21 ± 0.09		No
Organic Matter (%)	5.240 ± 0.084		4-8				Yes	15.483 ± 0.622		No
Soluble Salts (ppm)	1970± 189		500 ppm or less				No	1286± 73		No
AVS (µmol/g dry weight)	<0.01		-				-	-		-

that the materials should have similar geotechnical performance and stability on highway slopes. Mouazen (2002) found that sandy loam soil similar to the sediments tested in this study had angles of internal friction ranging from 24.9 to 36.9° at varying bulk densities, with the internal friction angle increasing with bulk density. The higher internal friction angle of the DM and topsoil could be due to lower clay contents (1.6 and 0%, respectively, as compared to 13.4%). A study by Kim et al. (2018) determined that internal friction angle of a clay-sand mixture increases with up to 10% clay content, but decreases with clay contents above 10% due to the variations in the voids between clay and sand particles. This study also found internal friction angles ranging from 34.0 to 38.7° for sand-clay mixtures, which supports the findings of this study. The residual friction angle was 37.3° for topsoil and 35.3° for DM, indicating that after peak shear stress the particles are not able to interlock as well, but would still be stable long-term when exposed to stresses.

Acid volatile sulfides (AVS) concentration was determined using Brouwer and Murphy's modified diffusion method (Brouwer and Murphy 1994). A standard curve was created using reagent grade sodium sulfide nonahydrate crystals, with concentrations ranging from 10^{-2} M to 10^{-6} M. The sulfides were volatilized using hydrochloric acid, and trapped in a sulfide antioxidant buffer (2 M NaOH, 0.1 M EDTA, 0.1 M ascorbic acid) which was then measured using a sulfide ion selective electrode (ThermoFisher Scientific Cat. No. 9416BN) and reference electrode (ThermoFisher Scientific Cat. No. 900200). All chemical sources are listed in Table 3.

Table 3: Chemical name and manufacturer.

Chemical	**Manufacturer**
Calcium chloride	Fisher Scientific
Sulfide nonahydrate crystals	Carolina Biological Supply
Hydrochloric acid	Fisher Chemical
Sodium hydroxide	Fisher Chemical
EDTA	Fisher BioReagents
Ascorbic acid	Acros Organics
Sulfuric acid	VWR
Nitric acid	Fisher Chemical
Sodium chloride	VWR
Glacial acetic acid	Fisher Chemical
Ammonium nitrate	Acros Organics
Ammonium fluoride	Fisher Chemical
Hydrogen peroxide	Fisher Chemical
Potassium chloride	VWR
pH buffer solutions	Oakton

2.2 Methods

2.2.1 Soluble Salts Reduction

Gypsum Treatment of Dredged Materials

Screening experiments were conducted to test the effect of gypsum (Espoma Organic Garden Gypsum) addition to reduce soluble salts content in DM through an ion exchange process where the calcium in the gypsum may be exchanged with the sodium in DM and the sodium can then be flushed out when rinsed with water (Abdel-Fattah 2012). The amount of gypsum added to each column was 4, 8, and 12 grams of gypsum (crushed with mortar and pestle into a fine powder) into 70 grams (dry weight) of DM following mass balance calculation with the amount of calcium in the gypsum, the known amount of soluble salts in the DM, and per recommendations from Amezketa et al. (2005) and Wong et al. (2009). Columns 25 mm in diameter were set up in triplicate and each consisted of 70 grams (dry weight) of DM. Synthetic rainwater composed of 18 µM H_2SO_4, 18 µM HNO_3, and 23 µM NaCl (Davis et al. 2001) was pumped through columns at 25 mm/hour using a peristaltic pump and Masterflex tubing. A single 6-hour storm, which consisted of 150 mm of rainwater, was run through each of the columns.

Dredged Material Washing

Gypsum treatment of DM was initially performed in 25-mm diameter columns; however, the amount of DM required for future testing was estimated to be approximately 2 kg so a larger system was used for dredged material washing. This was accomplished by using an 18.9 liter plastic bucket with a 1.6-mm hole drilled in the bottom, a single layer of geotextile (permittivity, $\Psi = 1.5\ s^{-1}$), and 150 mm of DM

placed inside. A peristaltic pump and Netafim fogger was used to apply the water evenly across the bucket at the equivalent of 25 mm/h.

In order to obtain a better understanding of the effect of washing on the dredged material, additional batches were washed with 305 and 610 mm of rainwater.

2.2.2. Acid Digestion of Sediments

Acid digestion of sediments was performed according to EPA Method 3050B using an Environmental Express 36-Well 50 mL HotBlock™. A 1.5-g sieved (No. 10) sample was placed in a 50-mL polypropylene digestion vessel. 5 mL (1:1) HNO_3 and DI water were added to the vessel and swirled. The sample was covered with a ribbed watch glass and heated in a HotBlock™ at 95°C for 15 minutes. The sample was cooled, and 2.5 mL HNO_3 was added. The sample was refluxed for 30 minutes, and this process was repeated until no brown fumes were given off by the sample. The sample was then heated at 95°C for 2 hours, and cooled completely. 1 mL DI water and 1.5 mL of 30% H_2O_2 was added to the sample slowly. After 5-10 minutes, the sample was placed on the HotBlock™ with watch glass in place. 0.5 mL of H_2O_2 was added until the sample remained unchanged in color. The sample was heated for 2 hours, then 5 mL concentrated HCl was added. The sample was refluxed for 15 minutes, then cooled and diluted to 50 mL with DI water. Samples were filtered with a 0.2 µm filter (MilliporeSigma) and stored at 4°C.

2.2.3. EDTA Extraction

An EDTA extraction was performed using the procedure described in Quevauviller et al. (1996). A 5-g soil sample sieved through a number 10 sieve was placed in a 50 mL polypropylene centrifuge tube. 50 mL of 0.05 M EDTA was added to the centrifuge

tube, and the sample was tumbled at 30 rpm for 1 hour. The sample was filtered with a 0.2 µm filter (MilliporeSigma) and stored at 4°C.

2.2.4 Toxicity Characteristic Leaching Procedure

The toxicity characteristic leaching procedure followed EPA Method 1311 to determine the mobility of heavy metals in the dredged sediments. The dredged material was sieved with a number 10 (2-mm) sieve, and extracted with extraction fluid #1 (5.7 mL glacial CH_3CH_2OOH, 64.3 mL 1 N NaOH into 1 L, pH 4.89) . A 2.5-g sample with a 20:1 liquid-to-solid ratio was used and rotated at 30 rpm for 18 hours. The sample was filtered through a 0.7 µm glass fiber filter (Whatman), and acidified with nitric acid to pH<2. Samples were stored at 4°C.

2.2.5. Mehlich 3 Extraction

A 2-g soil sample sieved through a number 10 sieve was placed in a 50 mL polypropylene centrifuge tube. 20 mL of Mehlich 3 extracting solution (0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3, 0.001 M EDTA) was added to the tube, and tubes were shaken at 200 rpm for five minutes. Extracts were filtered through a 0.2 µm filter (MilliporeSigma).

2.2.6 Column Leach Test

Glass columns with a 25-mm inside diameter and 200-mm height (Kimble Kontes Flex-Column 420400-2520) were filled with DM (washed with 0, 305, 610, and 1219 millimeters of rainwater) or topsoil. The material was not compacted but lightly tapped by hand until columns were full. 0.01 M NaCl in deionized water was used as influent to simulate a rainfall event, and was pumped in an upflow direction (Masterflex L/S 13). The flow rate was 25 mm/hr, which corresponds to 12 mL/min for the column volume. pH and EC of the effluent were recorded to evaluate

relationships to metal leaching behavior. Samples were acidified with nitric acid to pH<2 and stored at 4°C.

2.2.7. Analytical Techniques

Leachate pH and EC were measured using a VWR SymPHony meter (model B40PCID) equipped with a Thermo Scientific Model Sure-Flow pH probe and VWR conductivity probe (Cat. No. 89231-618). The conductivity probe was calibrated with a 1411 mS/cm KCl solution and the pH probe was calibrated using standard buffer solutions at pH 4.01, 7.0 and 10.01.

An inductively coupled plasma emission spectrophotometer (Shimadzu Model ICPE-9000) was used to measure elemental concentrations of Ag, Ba, Cr, Cu, and Zn. Due to the low MCLs for As, Cd, Hg, Pb and Se (0.01, 0.005, 0.002, 0.015 and 0.05 mg/L respectively), several types of instrumentation were applied to achieve detection limits lower than these levels.

For approximately the first half of testing, a hydride generator system (Elemental Scientific's hydrideICP) was used in conjunction with the ICP-OES in order to achieve detection limits below 0.05 mg/L for selenium. The hydride generator converts hydride-generating elements such as selenium and arsenic to gas, which increases signal intensity and improves sensitivity. The peristaltic pump that moves solution through the generator broke in February 2019 and was unable to be used for the remaining samples.

An ICP-MS (ThermoScientific Element 2) was used to analyze arsenic, cadmium, lead and selenium in column leach effluent. Samples were filtered with a 0.2 µm filter (MilliporeSigma) and diluted 9:1 with DI water to prevent the salts in

the samples from clogging the instrument. 1 mL of 100 ppm Indium was added to 9 mL of diluted sample as a tracer to indicate if clogging occurred. Although samples tested with the ICP-MS were filtered, which deviates from previous methodology, a comparison of eight random filtered and unfiltered samples determined that filtering did not reduce the metals concentration (Table 4).

A direct mercury analyzer (Milestone DMA-80) at the United States Department of Agriculture's Beltsville Agricultural Research Center (USDA BARC) was used to analyze mercury in samples. Some samples were held longer than the recommended holding time of 28 days for mercury; however, concentrations were similar to those measured within the recommended holding time. All standards prepared for metal analysis were prepared in a four percent nitric acid matrix. Detection limits and instrumentation used for each metal are listed in Table 5.

Table 4: Comparison of zinc concentrations of filtered and unfiltered samples measured by ICP-OES.

Sample	**Zinc concentration (µg/L)**	**Percent Difference**
24A-E34	407	9.95
24A-E34 filtered	452	
0C-E36	330	5.71
0C-E36 filtered	1400	
24A-E32	108	8.47
24A-E32 filtered	118	
0C-E13	10.3	54.4
0C-E13 filtered	22.6	
24A-E23	32	11.4
24A-E23 filtered	36.1	
24A-E34	455	6.19
24A-E34 filtered	485	
24C-E19	57.2	3.54
24C-E19 filtered	59.3	
12C-E21	17.4	62.3
12C-E21 filtered	46.1	
Average Percent Difference		**20.2**

Table 5: Instrumentation and detection limits for metals analysis.

Metal	**Instrumentation**	**Detection Limit (mg/L)**	**Maximum Contaminant Level (MCL) (mg/L)**
Silver	ICP-OES	0.0025	0.1
Arsenic	ICP-MS	0.0023	0.01
Barium	ICP-OES	0.01	2
Cadmium	ICP-MS	0.001	0.005
Chromium	ICP-OES	0.01	0.1
Copper	ICP-OES	0.01	1
Mercury	DMA-80	0.002	0.002
Selenium	ICP-MS	0.0052	0.05
Lead	ICP-MS	0.042	0.015
Zinc	ICP-OES	0.02	5

Chapter 3

Results and Discussion

3.1 Acid Volatile Sulfides

Acid volatile sulfides (AVS) of the dredged material were determined to be below the detection limit of 10^{-6} M, equal to approximately 0.01 µmol/g dry weight. A range of dredged material masses (1-2 g) was used in accordance with Brouwer and Murphy (1994) in an attempt to reach values within the standard curve; however, even at the top of the range, the values were under the standard curve. Sand was used as a blank to compare to samples, and values were similar (-605 ± 36 mV for a blank as compared to -610 ± 5 mV for DM), indicating the absence of AVS in the dredged material. AVS becomes problematic, causing changes in pH and metal leachability, when values are 5 µmol/g or higher (Di Toro et al. 1992). The absence of AVS in the dredged material is expected as the material had been exposed to oxidizing conditions prior to sample collection. The stockpile where the DM was placed was open to the atmosphere and mixed routinely, so any sulfides might have been oxidized between the time the material was dredged and when it was stockpiled.

3.2 Soluble Salts Reduction

3.2.1 Gypsum Treatment of Dredged Materials

As seen in Table 6, the soluble salts content of DM decreased from an initial volume of 2359 ppm (0% gypsum) to 1407-1425 ppm under a single 8-hour synthetic rain event upon gypsum addition; however, no clear trend could be observed between the amount of gypsum added and reduction in soluble salts. Due to the lack of a trend, the

Table 6: Soluble salts in 25-mm diameter columns with 4, 8, and 12 g gypsum added to 70 g DM after washing with synthetic rainwater (Davis et al. 2000) at 25 mm/hr for a single 8-hour rain event and three 8-hour rain events.

Grams gypsum added	**Rain event**	**Soluble Salts (ppm)**
-	None	2359
4	One 8-hour	1418
8	One 8-hour	1407
12	One 8-hour	1425
0	Three 8-hour	262.3 ± 30.00
4	Three 8-hour	1275.87 ± 25.55
12	Three 8-hour	1310.87 ± 41.32

next series of tests were under three 8-hour synthetic rain events. The columns consisted of 70 g of DM treated with 0, 4, and 12 g of gypsum. The DM was removed from the columns and tested for soluble salts after the rain simulations. The control column (no gypsum added) showed significant reduction from 2359 ppm to 262 ± 30 ppm; however, the columns with gypsum added had soluble salts of approximately 1310 ppm, with little difference between 4 and 12 grams of gypsum added (Table 6). Tests completed from this point on included columns with 0 and 12 g of gypsum added, as it was determined that the amount of gypsum added did not decrease the soluble salts of the DM. The MDOT SHA topsoil limit for soluble salts is 500 ppm, so additional testing was conducted to determine the amount of synthetic rainwater through one consecutive event needed to reach the limit.

A series of destructive tests were performed with increasing amounts of synthetic rainwater run through the columns. A column was dismantled at certain time intervals (hours 1, 4, 6 and 8 for 8-hour rain event; hours 2, 10, 14 and 18 for 18-hour rain event; hours 2, 10, 18, 24, 30 and 36 for 36-hour rain event) and the DM with 0 and 12 g gypsum was measured for soluble salts in order to determine when the limit was reached. Rain events started at 8 hours, then increased to 18 hours and 36 hours, with the reduction to 500 ppm estimated at 32 hours for 0% gypsum (Figure 5). Soluble salts in columns with gypsum added did not reduce below 1500 ppm for the 36-hour rain event (Figure 6). There was a large amount of variability in the values due to the fact that the test was destructive, so 32 hours was determined to be a conservative estimate for washing without gypsum addition. Assuming a porosity of 0.4, the 813 mm of synthetic rainwater through 150 mm of DM equates to

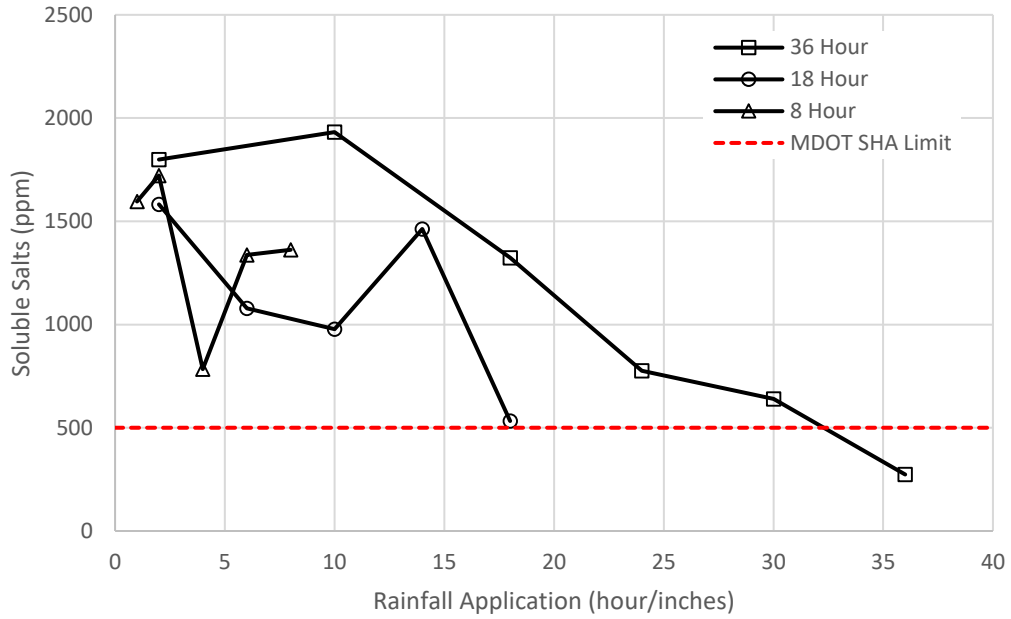

Figure 5*:* Soluble salts as EC (ppm) of DM as a function of synthetic rainfall application at 25 mm/hr for 70 g pure DM (0% gypsum) added for 8-, 18-, and 36-hour rain events.

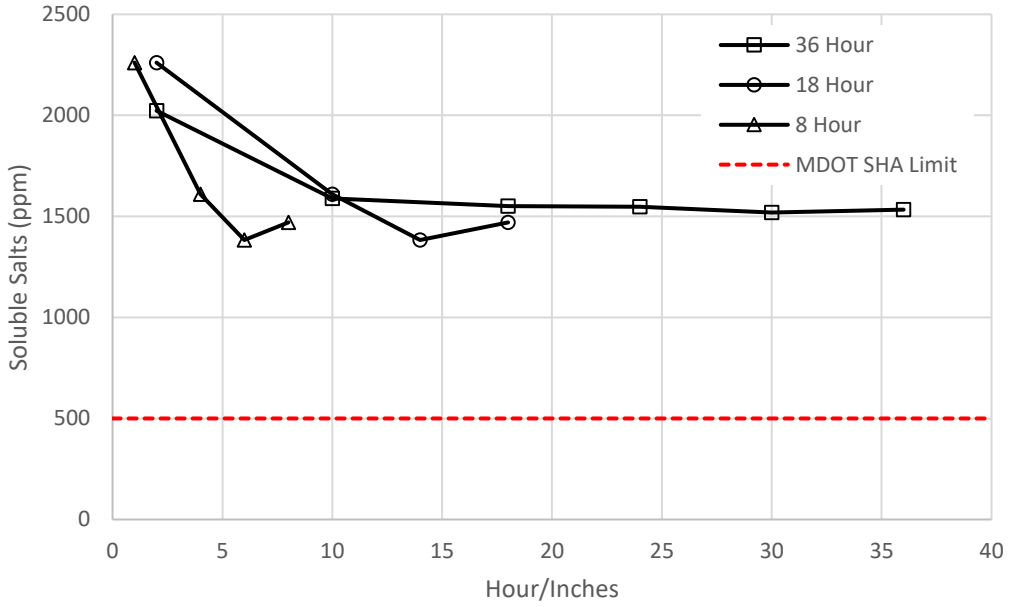

Figure 6: Soluble salts as EC (ppm) of DM as a function of synthetic rainfall application at 25 mm/hr for 12 g gypsum added to 70 g DM for 8-, 18-, and 36-hour rain events.

approximately 14 pore volumes of synthetic rainwater in order to reach below the 500 ppm soluble salts limit. Figure 7 shows the soluble salts in the leachate collected from the 18-hour synthetic rain event comparing DM with 0 and 12 g gypsum added. The leachate from the columns with gypsum added had higher initial salts, indicating that the calcium in the gypsum did exchange with sodium in the soil and flush it out, however the calcium contributes to soluble salts as measured by electrical conductivity.

A study conducted by Abdel-Fattah (2012) using gypsum and two different types of compost depicted a similar leachate trend, with the gypsum amended compost having a higher initial leachate EC than untreated soil. During the beginning of leaching, the mobile ions, such as Cl^- and Na^+ were leached in both amended and unamended soil in the form of NaCl and Na_2SO_4, and, in subsequent leaching less mobile compounds such as $NaHCO_4$ and Na_2CO_3 were leached from amended soils. The slightly soluble salts $CaSO_4$ and $CaCO_3$ dissociated, and sodium ions replaced the calcium and were subsequently leached from the soil. Abdel-Fattah (2012) found that the leachate EC stabilized to similar values among amended and unamended soils after a period of leaching, similar to a trend from this study, shown in Figure 7, and demonstrates the capability of gypsum to replace sodium ions in amended soils.

The initial higher effluent EC from columns with gypsum in the current study demonstrates the flushing out of sodium through the exchange of calcium on adsorption sites. From the results of Abdel-Fattah (2012), it can be estimated that, while the amount of sodium in the DM decreased due to ion exchange, the amount of soluble salts as measured by electrical conductivity remained the same because

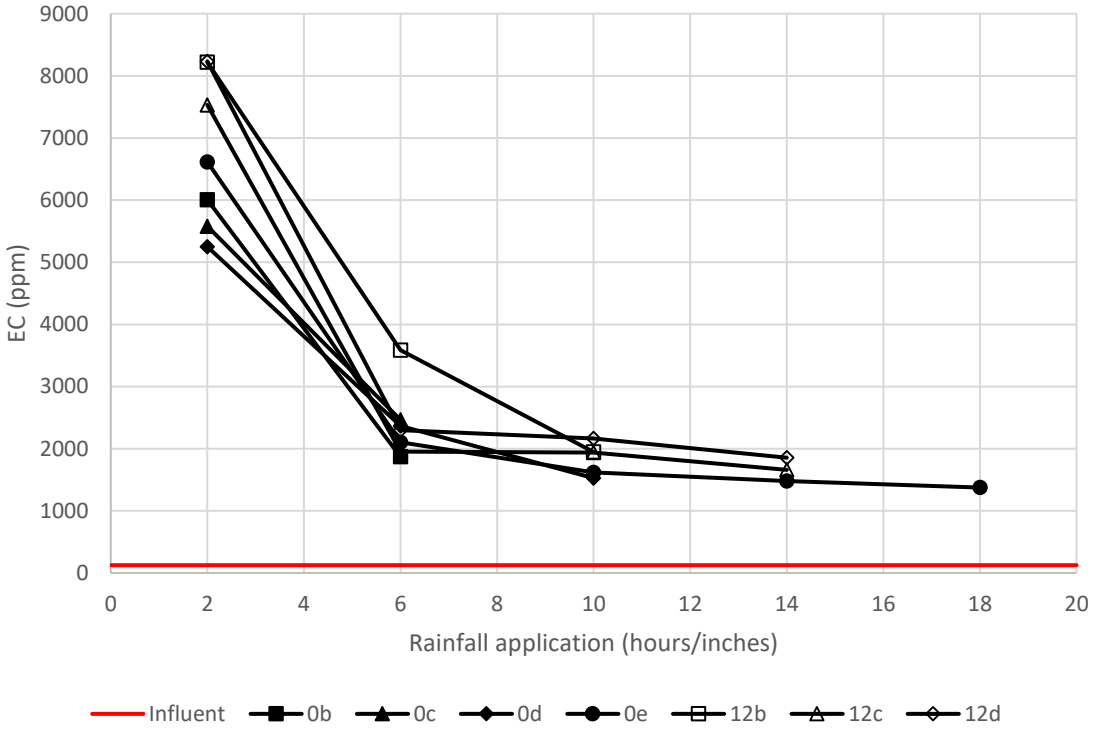

Figure 7: Soluble salts as EC (ppm) in leachate from columns of 70 g DM with 0 and 12 g gypsum as a function of synthetic rainfall application at 25 mm/hr for 18-hour rain event.

conductivity is a measurement of ions including calcium. Although exchangeable sodium percentage (ESP) and sodium adsorption ratio were not measured in the current study, it is expected that the ESP would decrease as the sodium is leached and replaced with calcium. Gypsum treatment is typically recommended for saline sodic soils used for agriculture in order to improve soil structure and infiltration (Abdel-Fattah 2012). These soils generally have EC $\geq$ 4 dS/m compared to the DM average of 1.97 dS/m, and sodic soils have an ESP $\geq$ 6 (Isbell 1996). Sodic soils can show soil crusting and have low hydraulic conductivity, which affects crop production and erosion (Amezketa et al. 2005). Gypsum is used as an amendment in sodic soils to prevent soil crusting and improve infiltration by lowering the ESP but contributes to conductivity as it is introducing more calcium ions into the soil.

Gypsum treatment of the DM demonstrated that the addition of gypsum as a soil amendment to the DM was not effective in reducing soluble salts concentrations of the material below the MDOT SHA limit. Synthetic rainwater flowing through the DM reduced the soluble salts in the material by washing out the salts; however, a large amount of water, approximately 14 pore volumes, was necessary to meet MDOT SHA limits.

3.2.2 Dredged Material Washing

The results of the dredged material washing tests are presented in Figure 8. Addition of 813 mm of synthetic rainwater (corresponding to 32 hours of washing under 25 mm/hr flow rate) yielded EC values above the MDOT SHA limit of 500 ppm set for topsoil. Upon application of an additional 203 mm of synthetic rainwater (i.e., a total

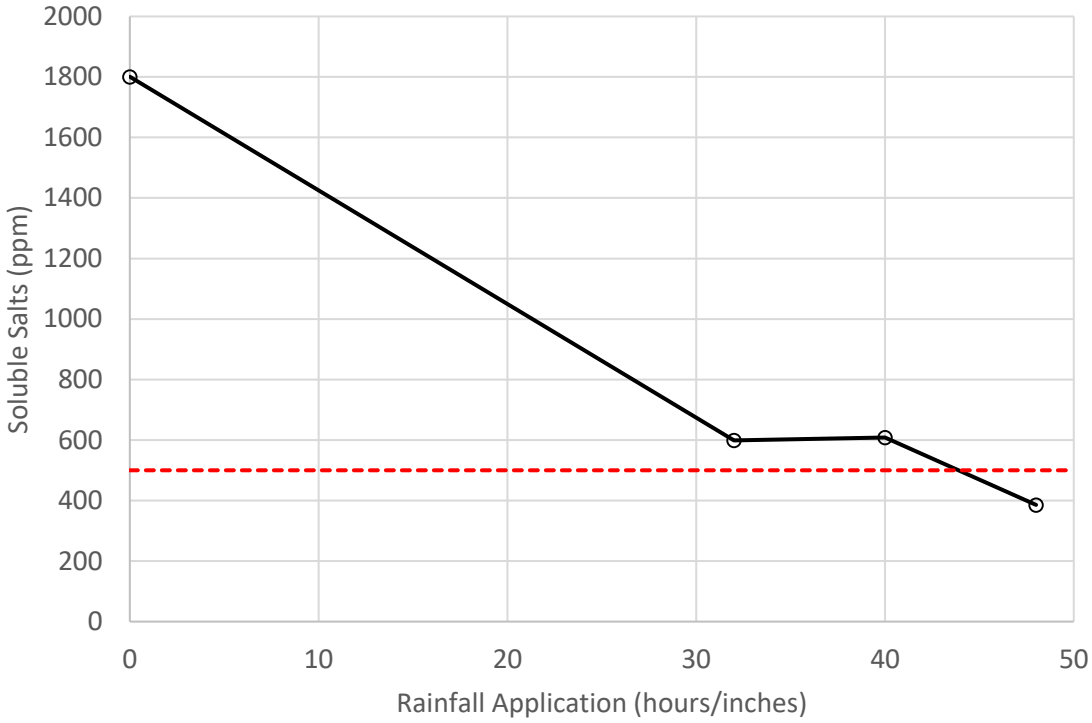

Figure 8: Soluble salts as EC (ppm) of DM as a function of synthetic rainfall application at 25 mm/hr for washing of sediments in 300-mm diameter bucket.

of 40 hours at 25 mm/hr), the salt concentrations were still above 500 ppm, and another 203 mm of synthetic rainwater (i.e., a total of 48 hours at 25 mm/hr) were applied to achieve values below the limit (Figure 8). The pH of the leached DM was measured to ensure that the DM still met the other requirements, and it was unchanged at an average of 6.80 ± 0.21.

Effluent samples from dredged material washing were analyzed for metals and showed a lagged response for certain metals (Figures 9-12). The leachate from the dredged material washed with 305 and 610 mm of synthetic rainwater had values below the detection limits given in Table 5. Barium, chromium, copper, and zinc appear in effluent when the DM was washed with 1219 mm of synthetic rainwater. The curve for all four metals looks similar, with concentrations increasing slightly at 31 and 33 hours, and a large rise at hour 41, then increasing slightly again at hour 47.

Concentrations in these effluent samples are shown in Table 7. Zinc had the highest effluent concentrations, at 612 µg/L at hour 47. Barium concentrations increased above detection limits at hour 33, as compared to hour 31 when the other metals increased. Barium was present at lower concentrations than chromium, copper, and zinc throughout the sediment washing process.

Dredged material washing of 10 kg versus 70 g of material demonstrated that although the depth of the DM layer being washed was the same (152 mm), on a larger scale, a larger volume of water is required to reduce soluble salts in the material. In addition to salts, metals are washed from the sediments during this process, with concentrations of copper and zinc above 400 µg/L and lower levels (less than 200 µg/L) of barium and chromium eluted towards the end of the process. This could

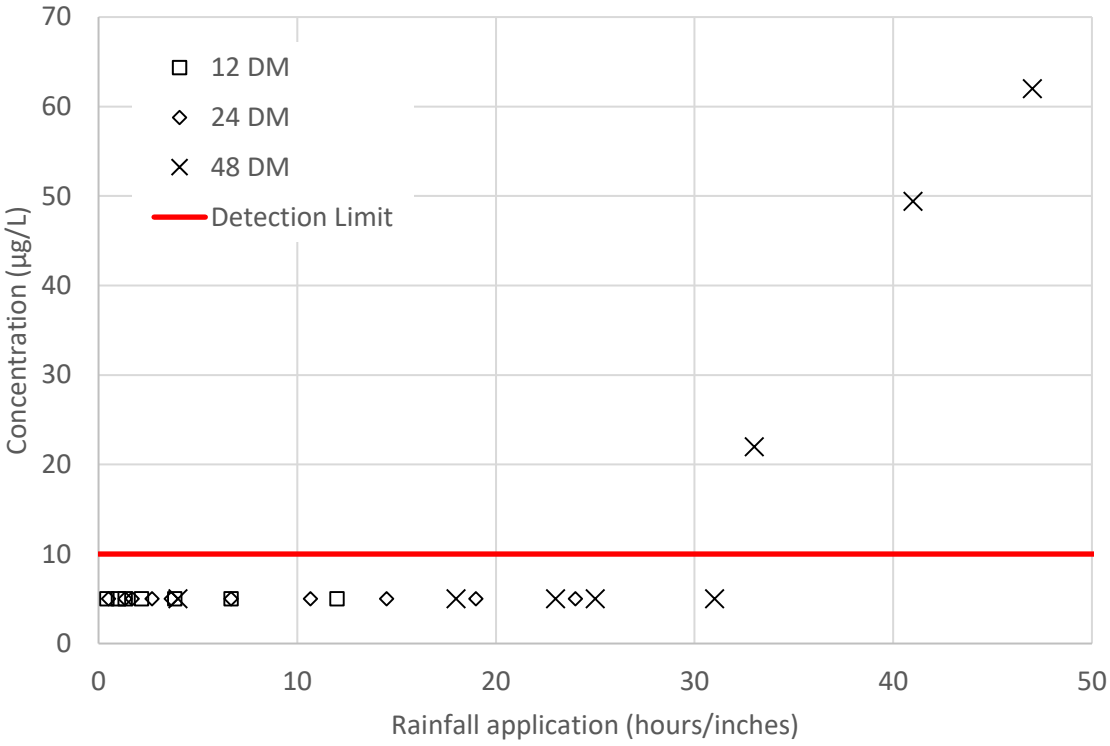

Figure 9: Barium concentrations in sediment washing effluent for 10 kg DM washed with synthetic rainwater at 25 mm/hr. Concentrations less than the detection limit are plotted as half the detection limit.

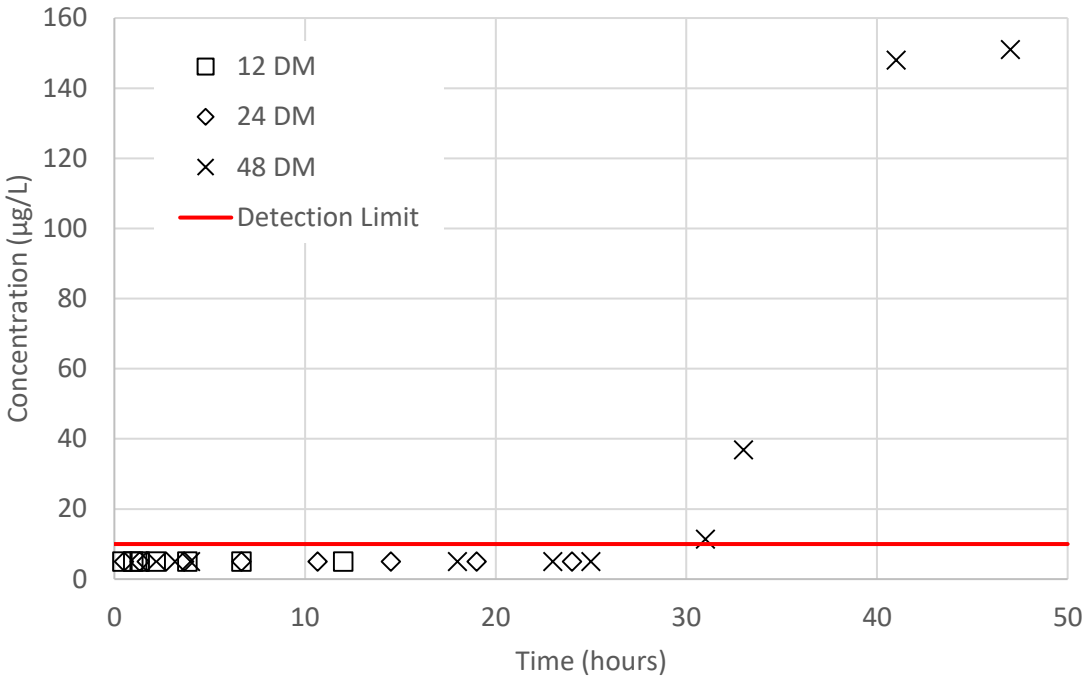

Figure 10: Chromium concentrations in sediment washing effluent for 10 kg DM washed with synthetic rainwater at 25 mm/hr. Concentrations less than the detection limit are plotted as half the detection limit.

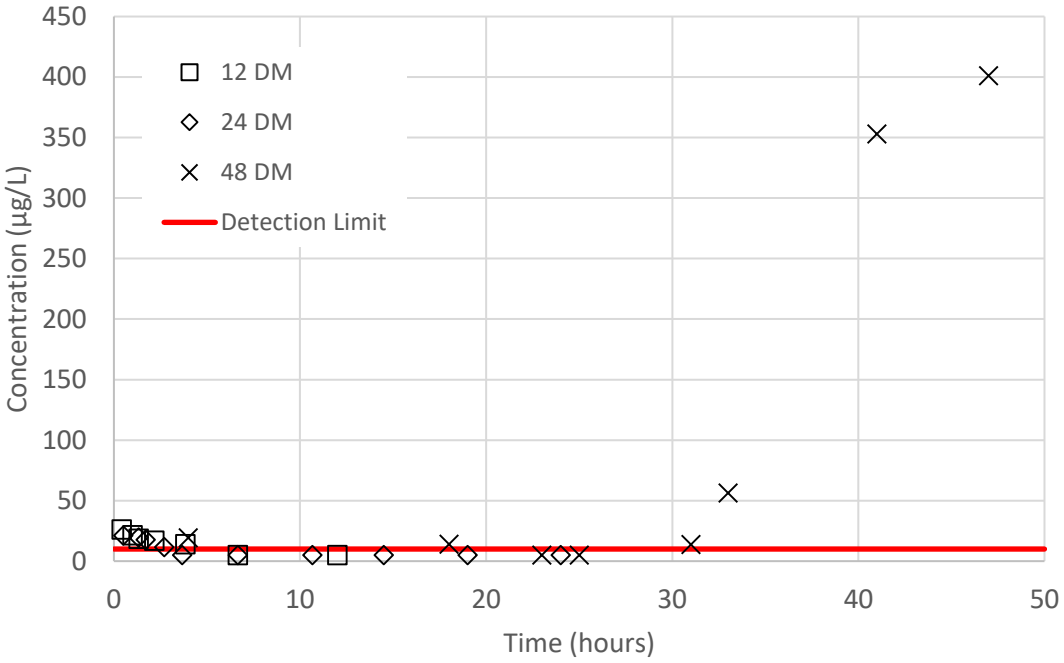

Figure 11: Copper concentrations in sediment washing effluent for 10 kg DM washed with synthetic rainwater at 25 mm/hr. Concentrations less than the detection limit are plotted as half the detection limit.

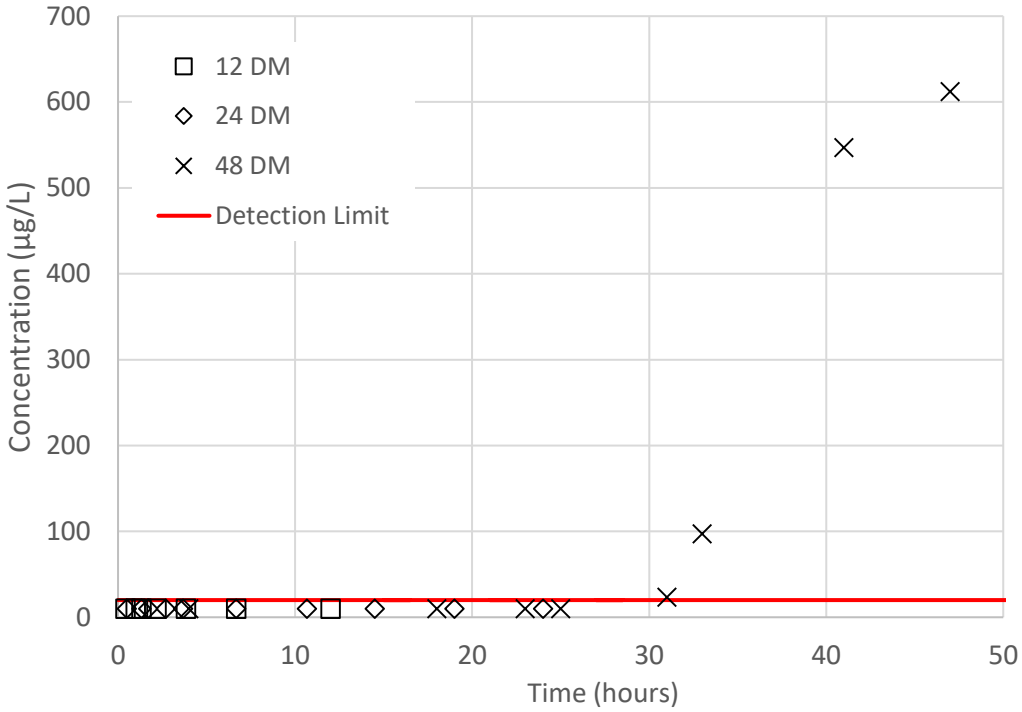

Figure 12: Zinc concentrations in sediment washing effluent for 10 kg DM washed with synthetic rainwater at 25 mm/hr. Concentrations less than the detection limit are plotted as half the detection limit.

Table 7: Metal concentrations in leachate collected from the dredged material washing process (at a rate of 25 mm/hr).

Midpoint time (hour)	**Metal Concentration (µg/L)**			
	Barium	**Chromium**	**Copper**	**Zinc**
4	<10	<10	19.2	<20
18	<10	<10	14	<20
23	<10	<10	<10	<20
25	<10	<10	<10	<20
31	<10	11.4	13.6	23.4
33	22	36.8	56.4	97.1
41	49.4	148	353	547
47	62	151	401	612

potentially impact the handling of the washing process, as metals leaching would need to be monitored to ensure that nearby water sources are not contaminated with metals.

3.3 Total Metals Concentrations in Sediments

Acid digestion of sediments (EPA Method 3050B) provides information on the total concentrations of the elements measured in this study. Although the method does not dissolve elements bound to silicates, it determines metals that could be mobile under different environmental conditions. Table 8 and Figure 13 provide information on metals concentrations in both topsoil and dredged material, both washed and unwashed, and the materials that had been subjected to column leach testing (TS-C and 48DM-C). Arsenic was present in all dredged materials measured, at concentrations around 7 mg/kg. Barium, copper and zinc had much higher concentrations in topsoil than the dredged material, while chromium and lead were present in higher concentrations in the dredged material than in topsoil. There were no detectable levels of silver, cadmium, mercury, or selenium (less than 0.17, 1.67, 6.67, and 16.67 mg/kg, respectively) in either the topsoil or DM. Table 9 and Figure 14 compare various dredged material concentrations of seven of the ten metals measured in this study to those of sediments from other locations reported in the literature. As compared to other dredged sediments, the Chesapeake Bay material had low concentrations of arsenic, lead and zinc, and mid-range concentrations of chromium and copper. Silver and cadmium are typically found in low to undetectable concentrations in agreement with the findings of this study.

Table 8: Metals concentrations as measured by EPA Method 3050B and EDTA extraction (mg/kg).

	Ag	As	Ba	Cd	Cr	Cu	Hg	Pb	Se	Zn
3050B										
TS	<0.17	<6.67	111.49±12.05	<1.67	14.25±0.11	116.27±7.64	<6.67	<2.0	<16.67	200.56±14.27
TS-C	<0.17	<6.67	137.16±1.70	<1.67	17.48±0.39	138.08±1.97	<6.67	9.27±0.45	<16.67	248.68±2.80
0DM	<0.17	7.61±0.20	35.09±0.28	<1.67	82.42±5.00	83.66±2.34	<6.67	54.56±40.05	<16.67	140.60±1.69
48DM	<0.17	7.13±0.10	45.19±1.33	<1.67	94.72±5.33	94.15±2.09	<6.67	37.52±2.44	<16.67	154.17±18.07
48DM-C	<0.17	6.84±0.10	41.85±1.32	<1.67	90.25±2.65	95.90±1.99	<6.67	33.27±1.18	<16.67	146.19±1.96
MDL	0.17	6.67	16.67	1.67	3.33	1.67	6.67	6.67	16.67	6.67
EDTA										
TS	<0.05	2.19±0.18	16.33±1.66	<0.5	<1.0	38.29±1.79	<2.0	10.17±1.31	<5.0	132.07±7.26
TS-C	<0.05	<2	18.83±3.12	<0.5	<1.0	44.50±1.47	<2.0	9.05±0.34	<5.0	125.18±3.33
0DM	<0.05	<2	16.00±0.91	<0.5	<1.0	30.16±0.43	<2.0	7.40±5.89	<5.0	54.71±1.02
48DM	<0.05	<2	16.09±0.98	<0.5	<1.0	42.11±9.46	<2.0	12.13±6.28	<5.0	42.78±3.33
48DM-C	<0.05	<2	26.42±9.87	<0.5	<1.0	35.05±1.28	<2.0	5.67±0.37	<5.0	46.31±5.58
MDL	0.05	2.0	5.0	0.5	1.0	0.5	2.0	2.0	5.0	2

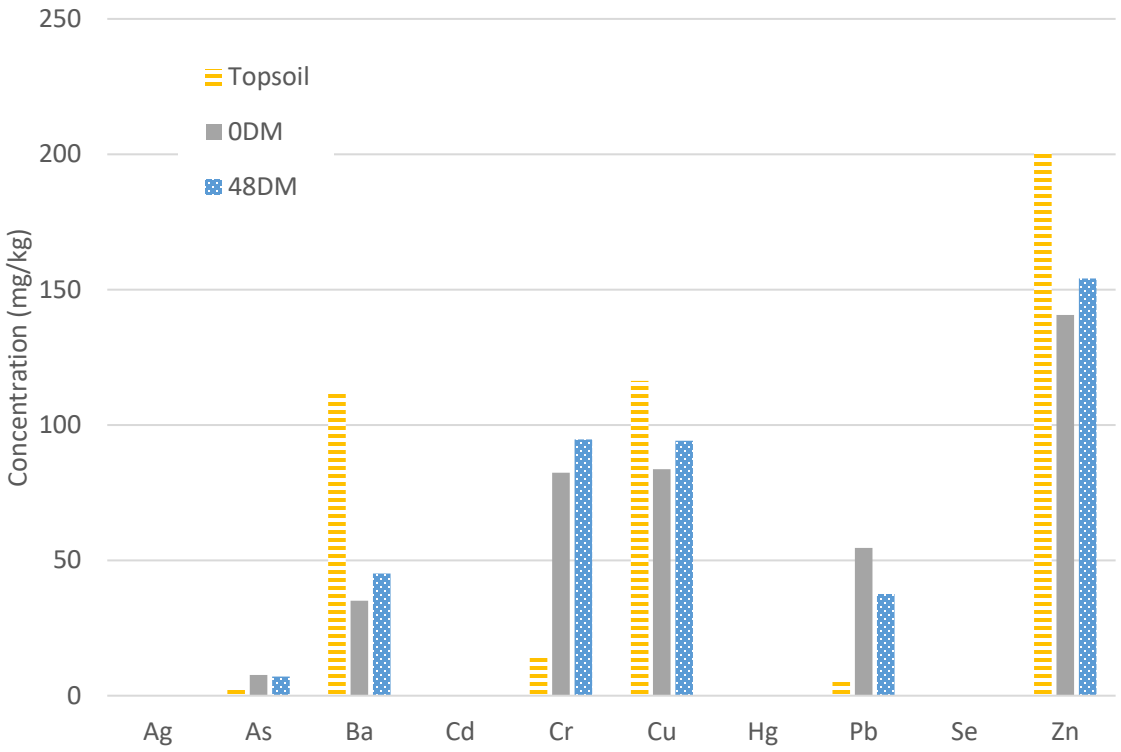

Figure 13: Comparison of total metals concentration in topsoil, unwashed DM and washed DM (48 hours of washing at 25 mm/hr) as measured by EPA Method 3050B.

Table 9: Comparison of total metal concentrations (mg/kg dry weight) of various dredged sediments (adapted from Ho et al. 2002).

Sediment	Ag	As	Cd	Cr	Cu	Pb	Zn
Long Island Sound	<DL*	13.2	<0.6	5.0	47.7	40.0	148
New Bedford Harbor (MA)	6.2	11.2	10.2	474	904	468	1230
Elizabeth River (VA)	<DL*	18.0	<0.6	72.9	93.8	72.1	267
New York Harbor	5.9	29.8	2.4	419	200	186	324
Chesapeake Bay (this study)	<0.17	7.61	<1.67	82.4	83.7	54.6	141

*Detection limit not specified.

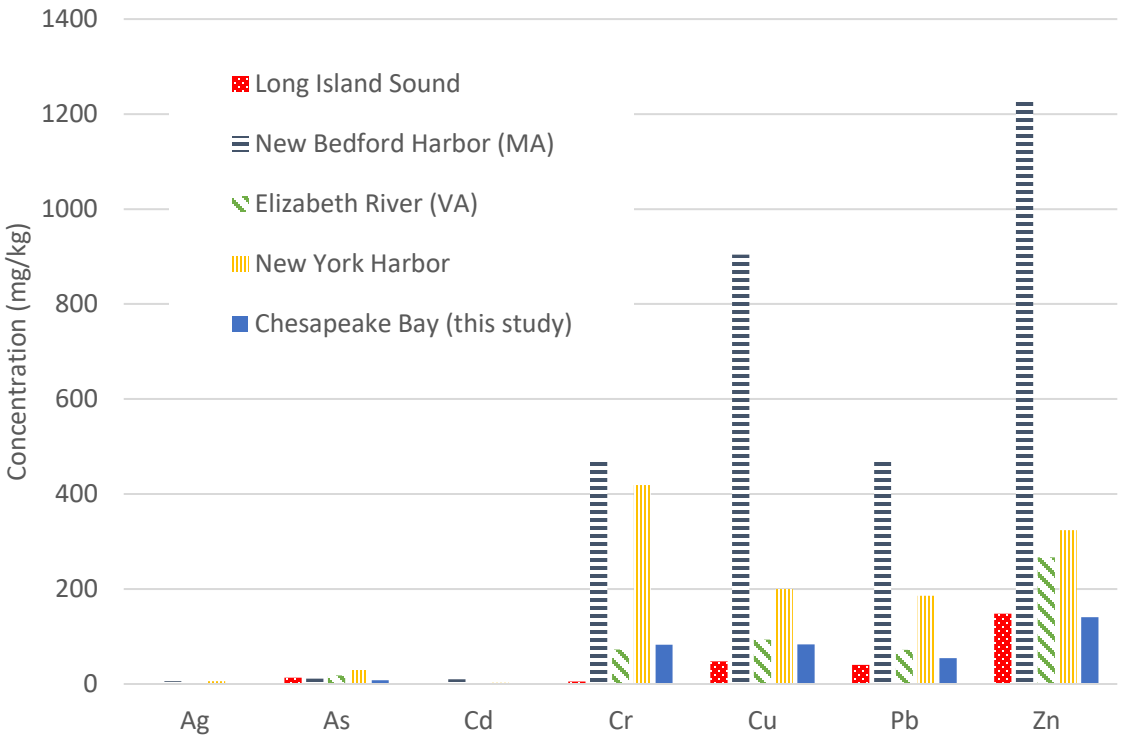

Figure 14: Comparison of total metal concentrations (mg/kg dry weight) of various dredged sediments (adapted from Ho et al. 2002).

3.4 EDTA Extraction

An EDTA extraction was performed to determine the concentrations of metals in the available and reducible fractions of the materials, i.e., those bound to the carbonates and oxide/hydroxides (Ding et al. 2013). These fractions become soluble in the presence of chelating agents such as EDTA and represent the fraction that is potentially mobile with changes in pH due to desorption from oxides and carbonates. As seen in Table 8 and Figure 15, the metals extracted using EDTA varied greatly from the total metal extraction using EPA Method 3050B. As expected, the metals that were below detection limits for the total digestion (silver, cadmium, mercury and selenium) were not detected in the EDTA extraction.

Chromium was also not detected in the EDTA extraction, although there were high total concentrations (up to 94.7 mg/kg) in the dredged material. This suggests that most of the chromium is present in the organic matter or residual fractions, which is consistent with previous work that had the same findings (Balasoiu et al. 2001; Stephens et al. 2001). Although the dredged material had higher total concentrations of arsenic and lead, the oxidizable and reducible fractions as determined by the EDTA extraction were lower than or comparable to concentrations in topsoil. Arsenic concentrations were below the detection limit of 2 mg/kg for all soil samples except for the topsoil, indicating that although there were higher total concentrations in DM, arsenic has the potential to be more mobile in the topsoil.

Lead extracted from topsoil using EDTA comprised 98-185% of the total lead concentrations as determined by EPA Method 3050B. While the higher

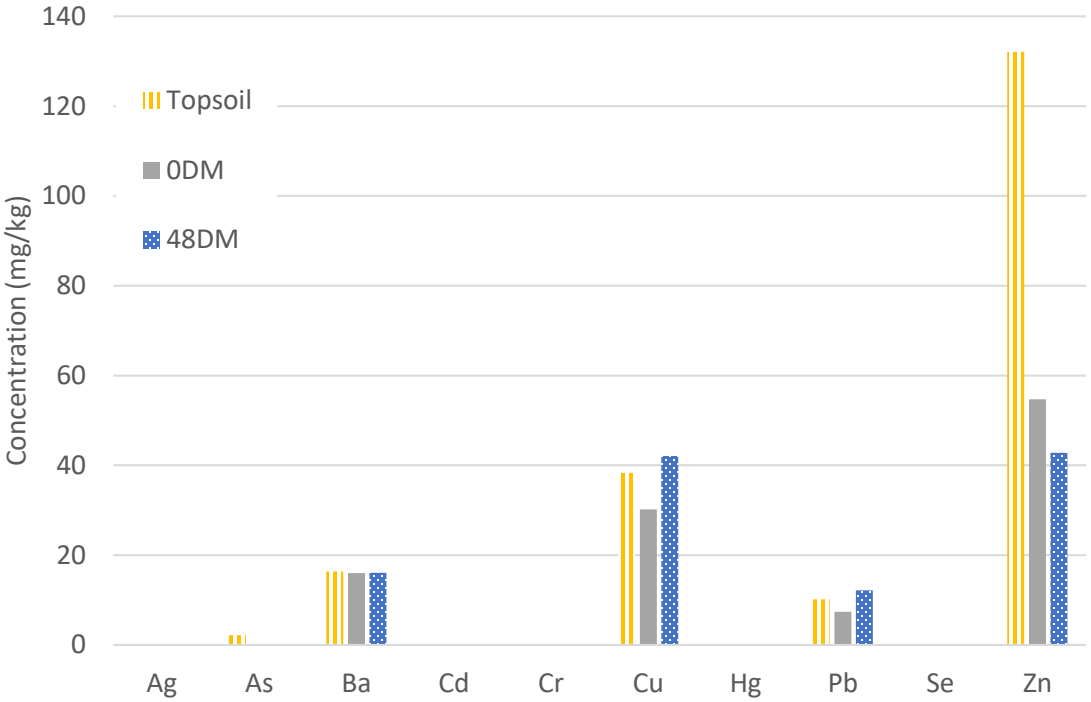

Figure 15: Comparison of metals extracted with EDTA in topsoil, unwashed DM and washed DM (48 hours of washing at 25 mm/hr).

concentrations could be explained by a hotspot of lead in the sample tested, it is clear that lead in topsoil is primarily in the potentially mobile form. Lead has a high affinity for organic matter and oxides, and forms lead carbonate at pH 6.9 (Fendorf et al. 2004). Topsoil has a lower pH than the DM, so it is not expected that the EDTA extracted metals are in the form of carbonates or oxides. The majority of the lead may be present in DM in the organic matter or residual fractions due to the low percentage extracted with EDTA.

Much higher concentrations of copper and zinc were extracted using EDTA than other metals analyzed for both dredged material and topsoil. Copper and zinc are both cations, and adsorption increases with pH. A slightly larger fraction of the copper was extracted with EDTA from the 48DM as compared to the topsoil, with the opposite trend for zinc. Zinc commonly has large fractions associated with iron and manganese oxides (Boulding 1996), so the high concentrations extracted from the DM are likely due to dissolution of oxides. At lower pH values, more zinc is exchangeable as evidenced by the high concentrations extracted from the topsoil. Copper forms strong complexes with organic matter (Sims 1986) so the material with a higher organic matter content as measured by loss on ignition had a smaller percent extracted with EDTA.

The three dredged material samples tested had varying fractions of barium extracted from the EDTA extraction (36-63%) as compared to total barium concentrations. The EDTA extraction for topsoil was similar to that of DM for barium, even though topsoil had much higher total concentrations. Barium sorbs onto metal oxides (Choudhury and Cary 2001), so the material with the higher pH exhibits

more sorption. The EDTA extraction causes metals in the oxide fraction to become soluble, so it is expected that since DM has a higher pH than topsoil, it has more barium sorbed to metal oxides than the topsoil, which is why the fraction extracted with EDTA is much higher for DM than topsoil.

The EDTA extraction shows that although there are high total metals concentrations in the dredged sediments, the metals are not in the exchangeable or reducible fractions and pose less of an environmental risk. The metals extracted with EDTA (barium, copper, lead and zinc) are comparable between topsoil and DM, with the exception of much higher zinc concentrations extracted from topsoil.

3.5 Toxicity Characteristic Leaching Procedure

The TCLP method was used to analyze metal leaching of the washed dredged material in triplicate for Ag, As, Ba, Cd, Cr, Hg, Pb, and Se. The pH of the TCLP extract was 4.88. The dredged material showed no detectable concentrations (below 0.005, 0.2, 0.5, 0.05, 0.1, 0.2, 0.2, and 0.5 mg/L, respectively) of the metals analyzed in the TCLP leachate as shown in Table 10. These results show that the dredged material cannot be classified as a hazardous waste due to toxicity of heavy metals. Dredged sediments, such as those from Bayou d'Inde, Louisiana and the Craney Island confined disposal facility in Hampton Roads, Virginia, have also passed TCLP criteria, confirming that sediments may not be hazardous due to binding of metals that prevent them from being leached using weak acids (Grubb et al. 2010; Hardaway et al. 1999).

3.6 Mehlich 3 Extraction

A Mehlich 3 extraction was performed to determine the concentration of phosphorus in the sediments, as shown in Table 11. A value of 45-50 mg/kg is optimal for plant growth when using the Mehlich 3 extraction; however, less phosphorus may be required for fine-textured soils (Pierzynski 2000). The dredged material has much less phosphorus than the topsoil (18.2 mg/kg as compared to 631 mg/kg), which may inhibit plant growth. However, a conclusion cannot be made without a detailed plant growth study under controlled conditions.

3.7 Column Leach Tests

The column samples were labeled considering the amount of water used for washing and the replicate type. For instance, the unwashed dredged material (e.g., washed with synthetic rainwater for 0 hours at 25 mm/hr) was labeled as 0DM, with the first replicate referred to as column "A" and the second and third as "B" and "C", respectively. Similar labeling was used for all other dredged material (DM) or topsoil (TS) columns with different amounts of washing duration (i.e., 12, 24, and 48 hours) and used throughout the discussion below.

3.7.1 General Observations

Column leach testing occurred in two phases: the first phase included columns with the DM that met SHA requirements (48DM) and an SHA-approved topsoil as a control (TS). The second phase investigated the effects of the initial dredged material washing, and included columns in 0, 12, and 24 hours of washing (0DM, 12DM, and

Table 10: TCLP effluent metal concentrations for washed dredged material.

Metal	**Ag**	**As**	**Ba**	**Cd**	**Cr**	**Hg**	**Pb**	**Se**
Concentration (mg/L)	<0.005	<0.2	<0.5	<0.05	<0.1	<0.2	<0.2	<0.5
EPA Allowable Limit (mg/L)	5	5	100	1	5	0.2	5	1
MDL (mg/L)	0.005	0.2	0.5	0.05	0.1	0.2	0.2	0.5

Table 11: Concentrations of Mehlich 3 extractable phosphorus (mg/kg).

Material	**Mehlich 3-Extractable P (mg/kg)**
TS	631 ± 34.3
TS-C	470 ± 4.36
0DM	11.2 ± 0.64
48DM	18.2 ± 0.53
48DM-C	17.2 ± 0.23

24DM). At the end of the 252 hours of the first phase of column leach testing (48DM and TS columns), there was a disruption in flow which is referred to in this study as "clogging." Clogging occurred when the sediments in the column appeared to be pushed up, resulting in separation of sediments within the column and prevention of water moving through the sediments. In the first phase of testing, this occurred for column 48DM-B for the duration of two rain events (hours 150-162), after which the sediment was removed from the column, mixed up and placed in a new column. No other clogging occurred during the first phase of testing; however, clogging was a persistent issue during the second phase.

During the second phase of testing, column 12DM-B clogged during hours 90-96 and was transferred to a new column and had no subsequent problems. Starting at hour 192, columns 24DM-A and 0DM-C started clogging and were transferred to new columns. 24DM-A continued to clog, even after transfer, through hour 222. Transfer of column 0DM-C initially resolved the clogging until hour 216 when the issue arose again. 0DM-B also demonstrated clogging at hours 204 and 222. The clogging issue resulted in more particulates in the effluent, because the water was not flowing through the sediments, instead pushing it up. This also prevented drainage of water that had already passed through the soil, resulting in pooling of water at the top, which was pushed out as the sediment moved upwards through the column. The causes and implications of clogging are discussed later in this section.

3.7.2 pH and Electrical Conductivity

The effluent pH of DM columns was higher than that of topsoil, due to the large difference in the pH of the topsoil as compared to DM. The topsoil effluent started

around pH 5.2 and increased to between 7-7.5 at around 20 pore volumes (Figure 16). Dredged material blends ranged from 7-8.5 throughout the column leach testing. The unwashed DM (0DM) had the highest pH throughout the testing, with an average of 7.86 ± 0.02 throughout the 15 weeks, compared to averages of 7.59 ± 0.02 (12DM), 7.72 ± 0.01 (24DM), 7.76 ± 0.06 (48DM) and 7.03 ± 0.09 (TS). The 48DM was statistically higher than the 0DM, 12DM and the TS, but not statistically different from the 24DM when using a t-test with α=0.05. The electrical conductivity of leachates from the topsoil showed a washout trend, which decreased to below 2 mS/cm after 10 pore volumes. The washed dredged material EC started off at a lower value (approximately 4 mS/cm) and decreased to around the influent value of 1.3 mS/cm within 100 hours (Figure 17).

3.7.3 Metals

Silver

No detectable concentrations (below 2.5 µg/L) of silver were present in leachate analyzed for any of the columns throughout the testing period. Silver is known to be highly immobile due to strong adsorption by clay and complexation with organic matter, as well as forming highly insoluble precipitates such as AgCl, Ag_2SO_4, and $AgCO_3$ (Boulding 1996).

Cadmium

Cadmium was detected above the 1 µg/L detection limit in effluent from topsoil columns at the beginning of the testing period (hours 0-100) as shown in Figure 18; however, all detected concentrations were below the 0.005 mg/L MCL. Cadmium concentrations above the detection limit of 1 µg/L were not detected in dredged

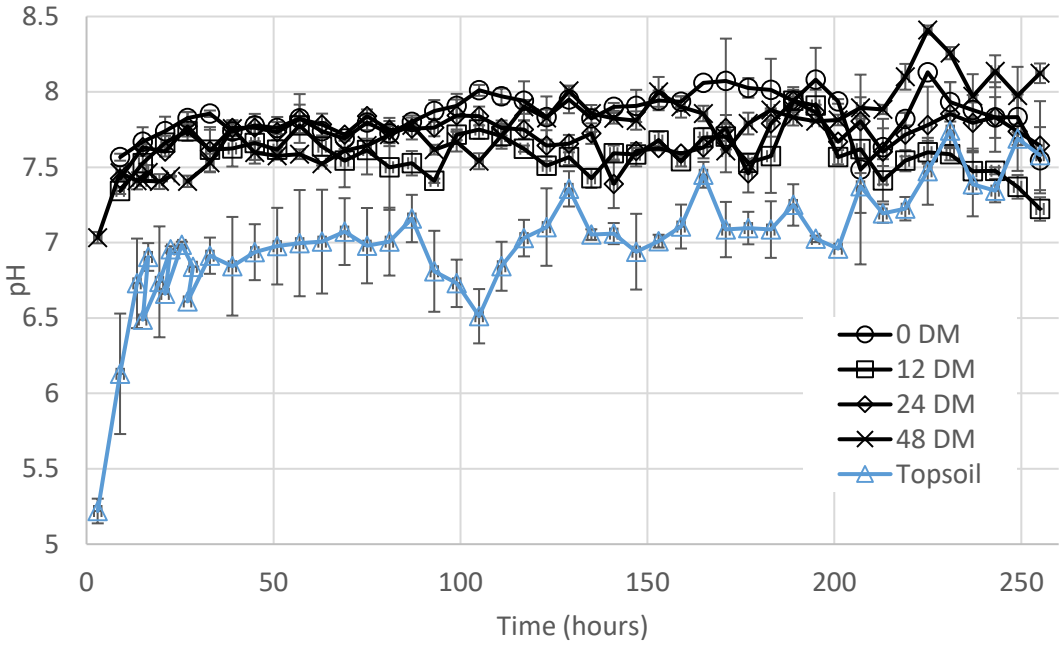

Figure 16: Average effluent pH of triplicate columns as a function of washing time with 0.01 M NaCl at 25 mm/hr for column leach testing.

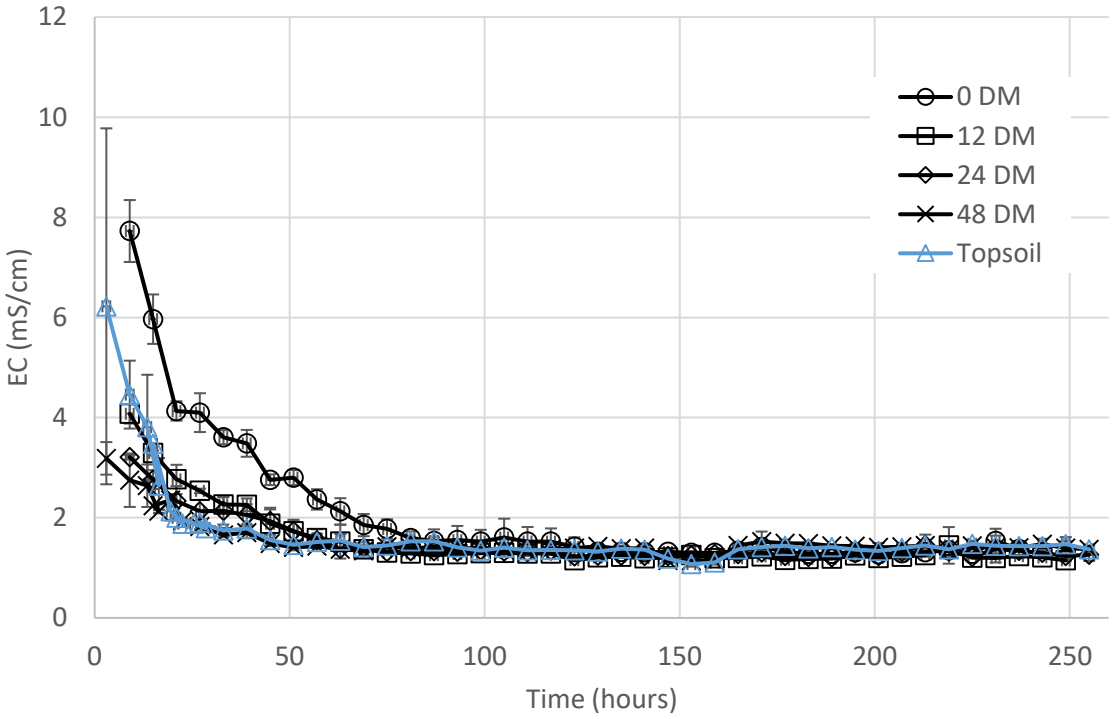

Figure 17: Average effluent EC of triplicate columns as a function of washing time with 0.01 M NaCl at 25 mm/hr for column leach testing.

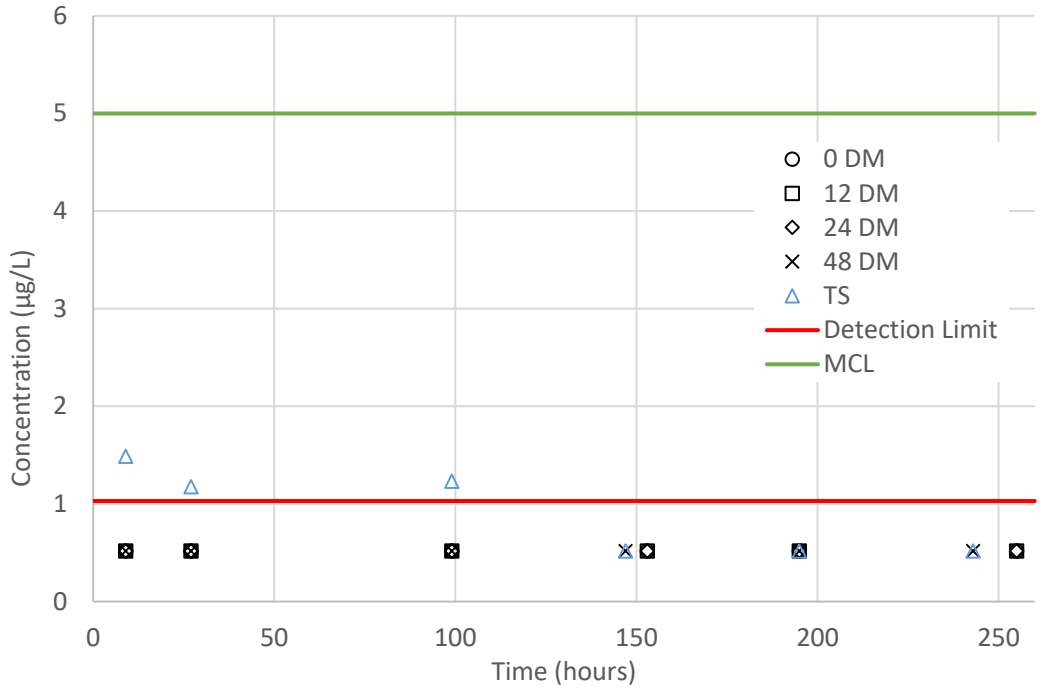

Figure 18: Cadmium column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

material effluent throughout the entirety of testing. Cadmium likely leached from topsoil due to the lower pH of the material, since cadmium is adsorbed by clay minerals, carbonates and hydrous oxides. In neutral and alkaline soils, concentrations are typically limited by precipitation as cadmium carbonate ($CdCO_3$), which is likely at the dredged material's neutral pH of 6.80 but not at topsoil's pH of 5.21 (Boulding 1996).

Selenium

Selenium was detected in all column effluents at the beginning of testing, as shown in Figure 19. Concentrations of selenium dropped below the detection limit of 5.2 µg/L for topsoil columns after the first data point measured; however, the DM columns leached low levels of selenium from hours 150 through the end of testing. All concentrations were below the 0.05 mg/L MCL.

Selenium is predominantly present in soils either as selenite, Se(IV) or selenate, Se(VI) but can also be present as elemental Se, selenides (-II), and organic Se compounds (Elrashidi et al. 1989). Selenium is generally thought to be controlled by adsorption mechanisms instead of precipitation/dissolution mechanisms, and sorption can be related to iron oxides (Elrashidi et al. 1989). Selenium is more mobile at higher pHs, which may explain the higher concentrations eluted from DM (pH 6.80) as compared to topsoil (pH 5.21).

Barium

Topsoil columns showed an initial leaching of barium, while none of the dredged material leached measurable concentrations (above 10 µg/L), as shown in Figure 20.

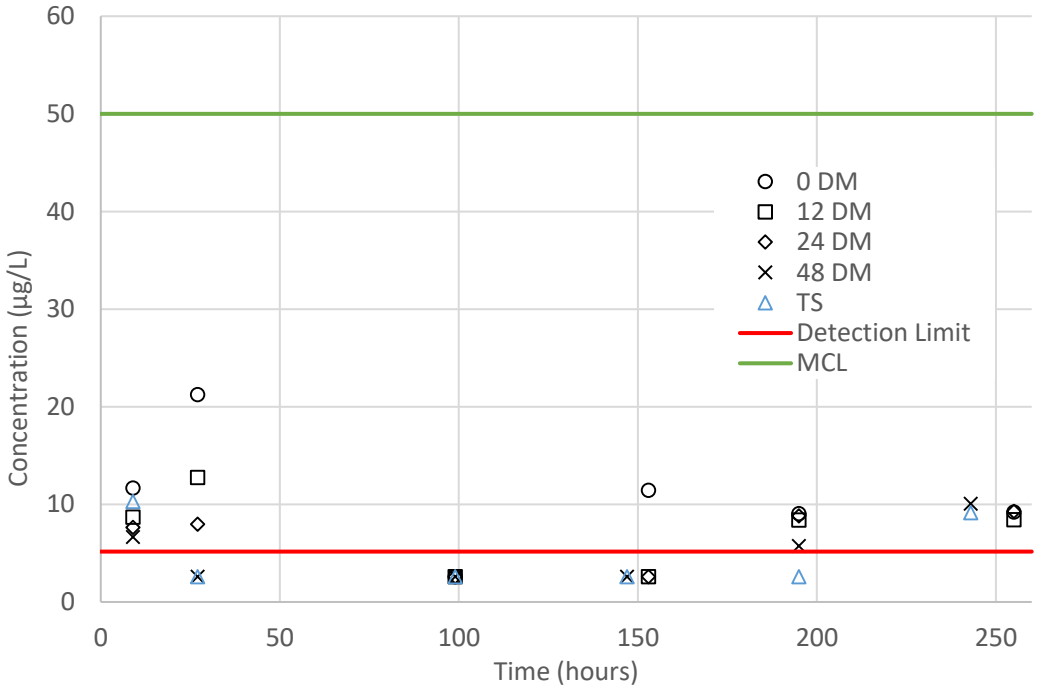

Figure 19: Selenium column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

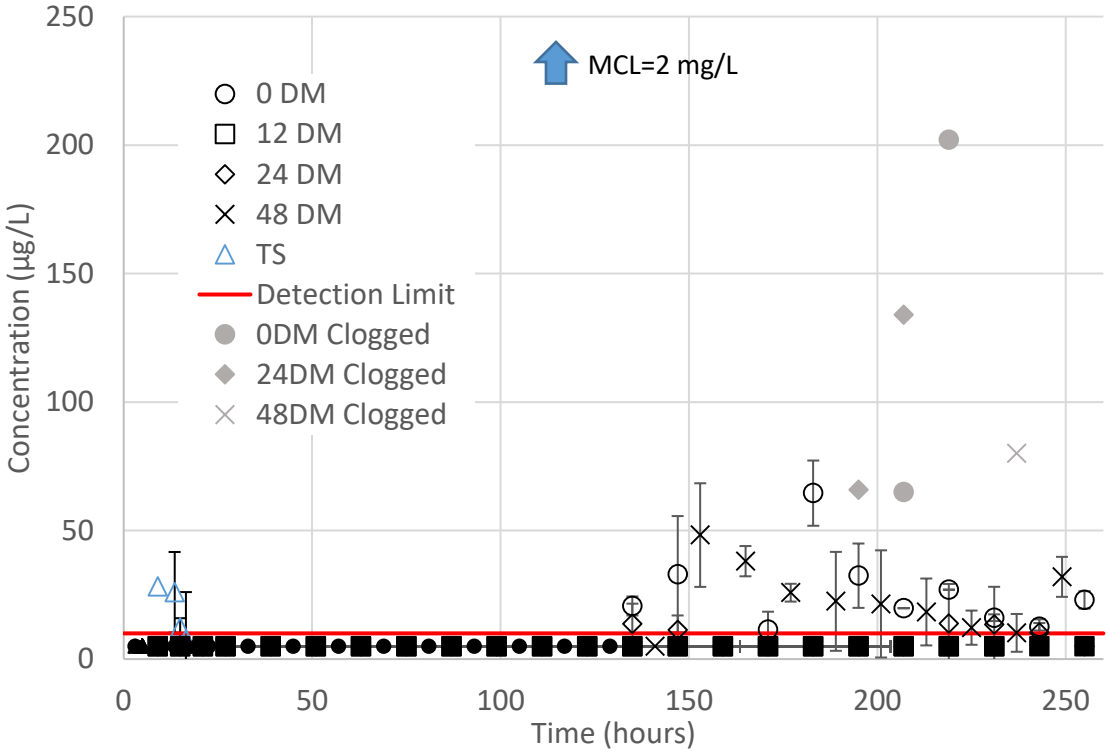

Figure 20: Barium column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

The 48DM columns leached barium starting at an average of 48 µg/L at hour 153 and decreased throughout the remainder of testing, with slightly elevated concentrations (33 µg/L) being measured for the last two samples (i.e., at hours 237 and 249). The 0DM and 24DM columns leached measurable barium concentrations starting at hour 135, with the columns having average concentrations at 20.7 µg/L and 13.7 µg/L, respectively. The 0DM columns had a peak average barium concentration of 115 µg/L at hour 219, but had a large standard deviation of 124 µg/L. The 24DM columns had a peak average barium concentration of 69.5 µg/L at hour 207, also with a large standard deviation of 91.2 µg/L. Average concentrations of both 0DM and 24DM columns decreased from peak concentrations to close to or below the detection limit of 10 µg/L at the end of testing. Elevated concentrations coincided with storm events where individual columns experienced clogging, as discussed in Section 3.3.2 and shown in Figure 20 as gray data points. The clogging caused water to pool up on top of the DM since it could not drain through it, which increased the contact time of water with the sediments and resulted in larger effluent concentrations.

Barium is a divalent cation that sorbs to soils through specific sorption onto metal oxides and non-specific sorption caused by electrostatic forces. Barium sulfate is naturally present in soils; however, is not typically mobile because it forms salts that are not water soluble. These compounds can become soluble under acidic conditions and leach into nearby waters. Barium can replace other metals from manganese, silicon, or titanium dioxides through ion exchange, and has limited complexation by organic matter in soils (Choudhury and Cary 2001). Under the acidic conditions of the topsoil, barium compounds could be water soluble, which

could be the reason higher initial concentrations of barium leached from the topsoil as compared to the DM.

Chromium

The 48DM column leached low concentrations (<40 µg/L) of chromium in the first 35 hours of rainwater application (hours 3 and 33), as shown in Figure 21. After this initial leaching, none of the columns leached detectable concentrations (above 10 µg/L) of chromium until hour 135. From hour 135 through the end of testing, the 0DM and 48 DM columns leached average concentrations of chromium up to 125 µg/L and 60 µg/L, respectively. These concentrations were variable between the column triplicates, with concentrations due to clogging shown in gray, and up to 227 µg/L for the 0DM-C column and 111 µg/L for the 24DM-A column. The 24DM-A column eluted measurable chromium from hours 192 through the end of testing, with a higher elution at hour 219 that decreased through hour 255.

Chromium is a transition metal, with Cr(III) and Cr(IV) dominating in the Eh-pH conditions typical of natural environmental systems. Cr(III) is present in low Eh environments and adsorbs easily to iron and manganese oxides as well as clay minerals; as typical of cationic metals, adsorption increases with pH (Richard and Bourg 1991). Cr(IV) is an anion present under oxidizing conditions, and adsorption is influenced by competition of other anions such as Cl^-, NO_3^-, SO_4^{-2}, and HCO_3^- that are typically present in soil or groundwater conditions. As a result, Cr(IV) is typically very mobile and is controlled mainly by reduction to Cr(III) in soil systems. In the oxidizing environment of this study, chromium could be in the anionic Cr(IV) form,

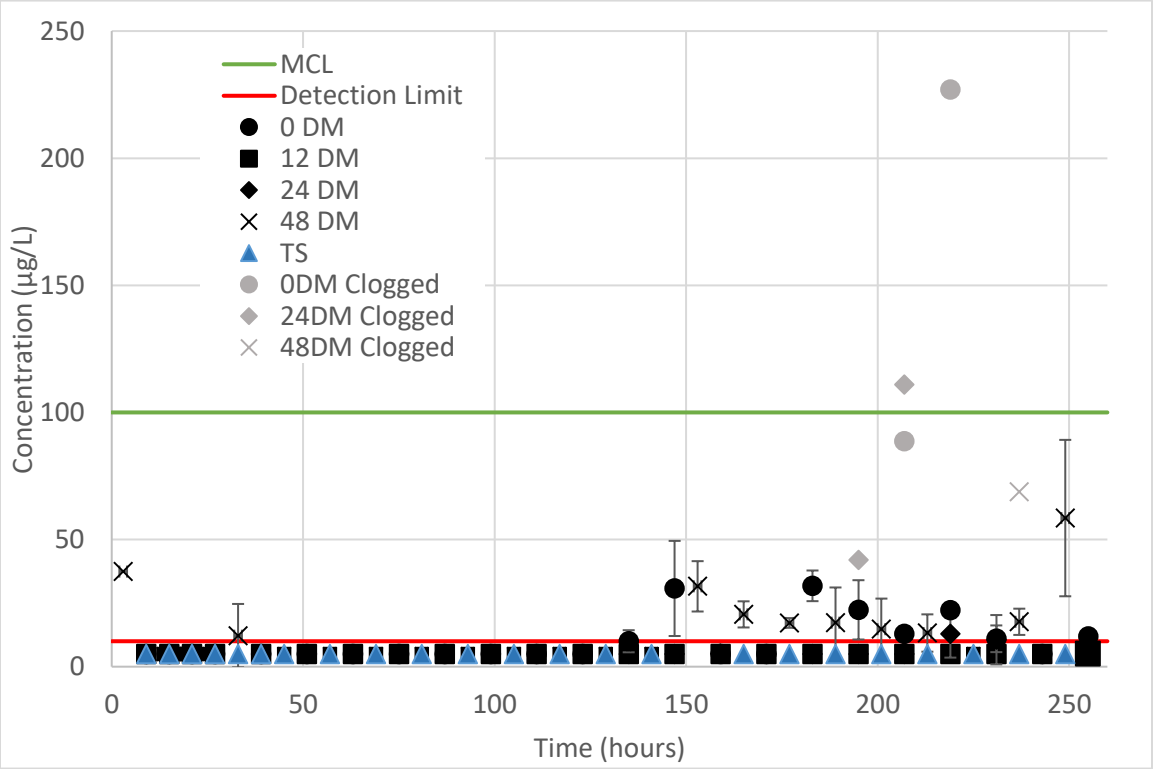

Figure 21: Chromium column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

for which adsorption decreases with increasing pH. The DM, with a higher pH than topsoil, leached chromium both at the beginning and middle to end of testing, while topsoil did not leach concentrations above the detection limit of 10 µg/L throughout testing. Chromium IV would be adsorbed more in the topsoil because of the lower pH, so it was not mobile whereas less was adsorbed in the DM, causing mobility. The total acid digestion showed that there was more chromium in the DM as compared to topsoil, while the results from the EDTA extraction predict that chromium would not be mobile in either sediment. Although there were higher concentrations of chromium eluted from the DM, with some concentrations above the MCL, these spikes are thought to be primarily due to clogging. However, it is evident that the higher total concentration of chromium in the DM resulted in more elution during column leach testing.

Copper

The copper elution curves for topsoil and 48DM showed a first flush pattern (Figure 22). The effluent from the washed and unwashed dredged material had consistently lower copper concentrations than that from the topsoil, with a maximum concentration of 150 µg/L compared to 938 µg/L. The dredged material stabilized close to the detection limit of 10 µg/L within the first 50 hours of storms, whereas the topsoil showed a decrease until about 150 hours, stabilizing at approximately 50 µg/L. All effluent concentrations for both topsoil and dredged material were below the drinking water MCL of 1 mg/L. 0DM, 12DM, and 24DM yielded lower initial effluent concentrations of copper than the 48DM columns, averaging at 19.9, <10,

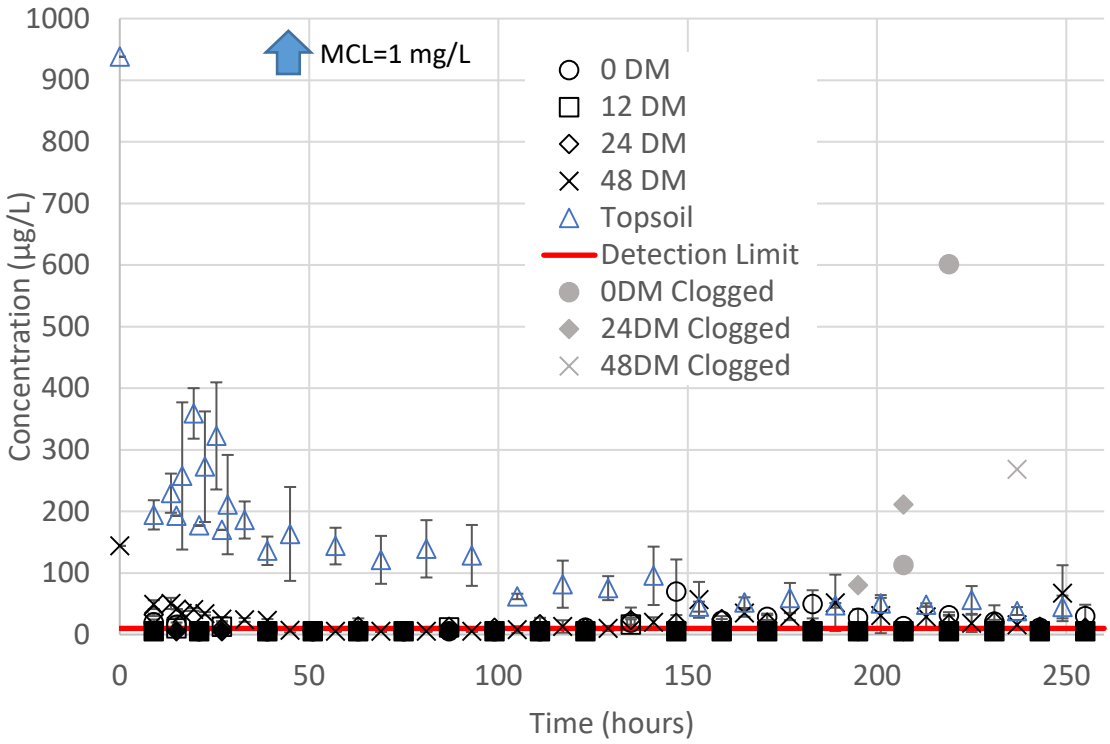

Figure 22: Copper column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

and 32.0 µg/L, respectively, versus 144 µg/L (48DM) for the samples collected within the first 9 hours. The concentrations stabilized around or below the detection limit of 10 µg/L within the first 20 hours of water application, with elevated levels (above 20 µg/L) starting at hour 135 for 0DM and 24DM columns. Higher concentrations persisted throughout the remainder of the testing period for 0DM, with a maximum average concentration of 316 µg/L at hour 219 due to a high concentration in column 0DM-C, shown in gray, and lowered to 10-20 µg/L for the remainder of testing. The 24DM columns showed a similar trend due to elevated concentrations leaching out of column 24DM-A and decreased below detection limits for the last two data points measured (hours 243 and 255). The 12DM columns did not leach detectable concentrations of copper after hour 135, as found with chromium and barium. The increased concentration of copper in topsoil effluent compared to DM effluent is likely due to the pH difference in the topsoil itself (5.21 as compared to 6.80 for DM). At higher pH, sorption of copper increases as it associates with oxides (Sims 1986). This typically occurs above pH 6.9, so less of the copper in the topsoil was adsorbed than in the DM. Complexation with organic matter is an important mechanism for copper, so the topsoil (15.48% OM) likely had more complexation than the DM (5.24% OM). Complexation could increase mobility if the organic matter is easily dissolved, which could account for the more elution of copper from the topsoil than the DM.

Zinc

The zinc elution curve, similar to copper, shows an initial flushing for both the dredged material and the topsoil, as shown in Figure 23. Concentrations in topsoil

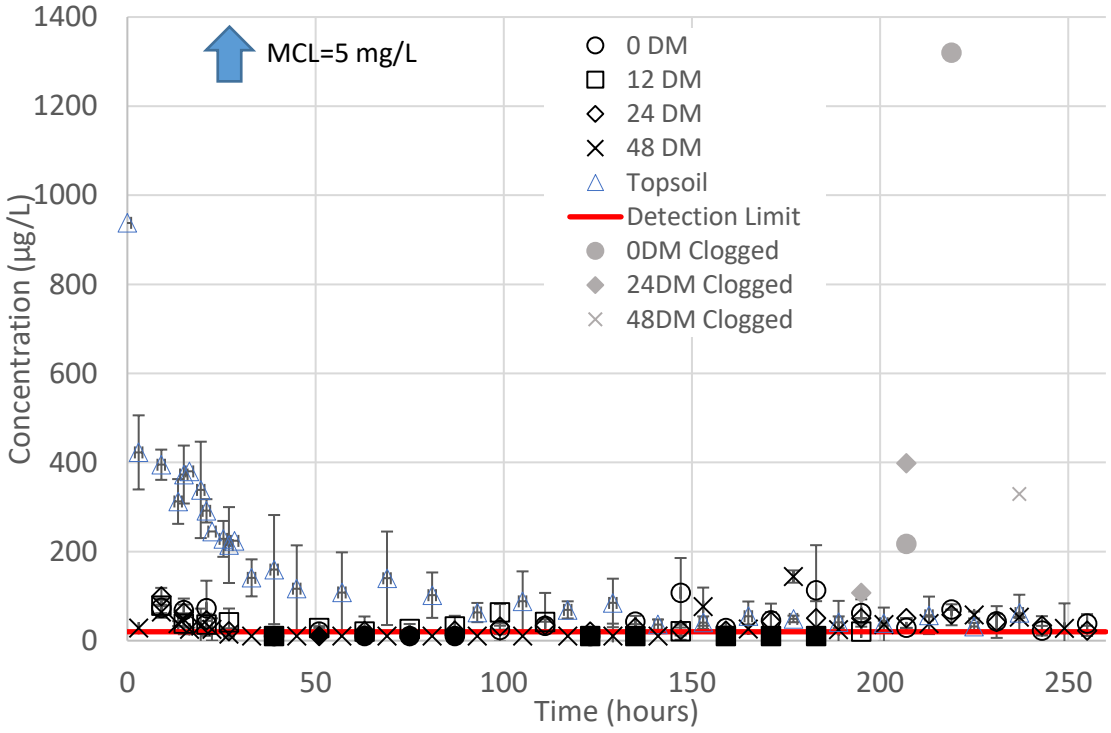

Figure 23: Zinc column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

were consistently higher than in DM and took longer to be reduced below 100 µg/L. Zinc concentrations were reduced to below the detection limit of 20 µg/L for some of the dredged material columns, and all stayed below 100 µg/L after the first flush. Zinc concentrations in the topsoil effluent dropped to under 100 µg/L at about 75 hours of water application. Similar to copper, zinc is adsorbed by clay minerals, carbonates and oxides, with hydrolysis occurring at pH>7.7. Zinc typically has a high percentage associated with iron and manganese oxides (Boulding 1996). As pH increases, zinc adsorption increases and exchangeable fractions are transformed to organic or oxide fractions (Sims 1986). As discussed for copper, the higher zinc concentrations in the topsoil effluent as compared to the DM effluent could be due to the lower pH of the topsoil, because zinc cannot associate with oxides at pH less than 7.7. Dredged material shows typically lower concentrations of zinc than topsoil, especially in the first flush, which is believed to be due to presence of oxides that bind the metal and aligns with the lower concentrations of zinc extracted from the DM than topsoil with EDTA and EPA Method 3050B.

Mercury

Six data points for the 250 hour testing period were measured for mercury concentrations (hours 9, 27, 99, 147/153, 195, and 243/255) as shown in Figure 24. These data points were chosen due to difficulty in measuring mercury at low concentrations. Effluents from the 48DM columns were the only ones to show concentrations above the 2 µg/L detection limit, at 2.96 µg/L average at hour 147. As mentioned above, most samples were kept for longer than the EPA recommended

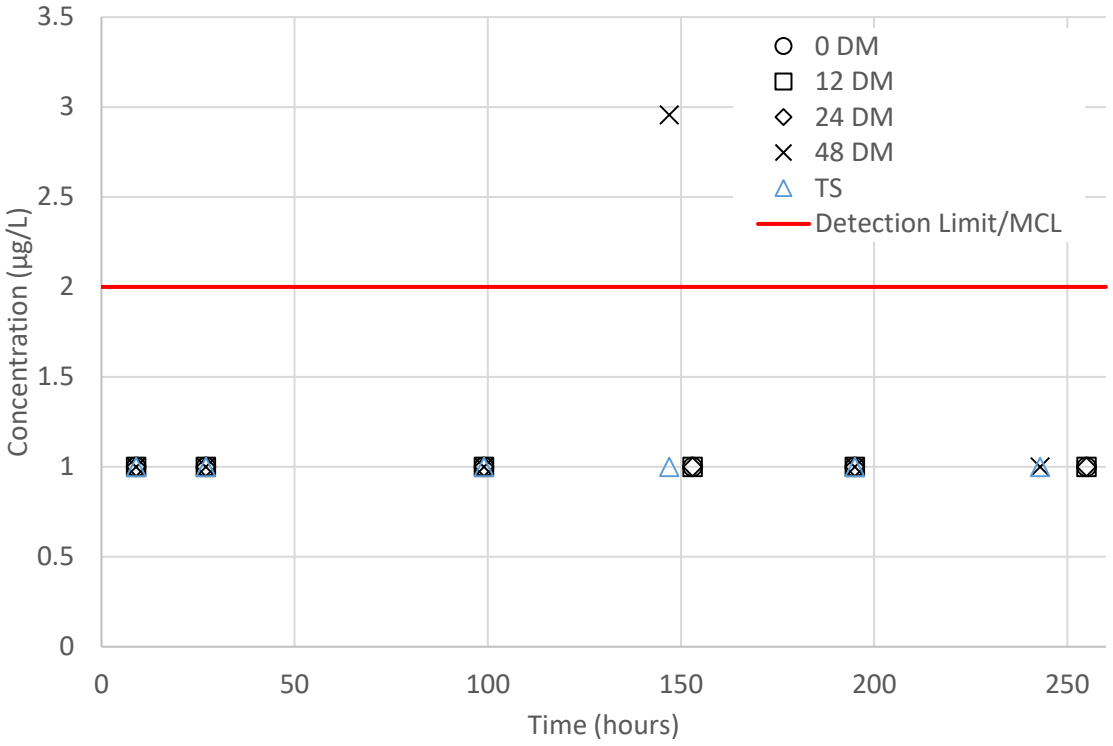

Figure 24: Mercury column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

holding time of 28 days, which could have produced inaccurate results due to volatilization of mercury. Samples tested within the 28-day holding time were below detection limits of 2 µg/L, suggesting that the holding time did not influence results.

In soils, mercury can be present as elemental mercury (Hg), mercurous ions (Hg_2^{2+}) or mercuric ions (Hg^{2+}), with the ions adsorbing onto clay minerals, oxides and organic matter. As typical of cations, adsorption increases with pH. Mercurous mercury can also form stable phosphate precipitates, and mercuric mercury can precipitate with carbonate and hydroxide. Under reducing conditions, elemental mercury can be formed and converted to methyl or ethyl mercury, which are toxic and volatile (Boulding 1996).

Arsenic

The same six samples measured for mercury were also measured for arsenic concentrations, as shown in Figure 25. Effluent concentrations from topsoil columns exceeded the drinking water MCL of 0.01 mg/L for three of the six measured data points. Concentrations were lower after the first half of testing and appeared to stabilize around 3 µg/L towards the end of testing. The dredged material showed less leaching of arsenic than topsoil, with no detectable concentrations above the MCL of 0.01 mg/L. The average concentrations of all DM columns were below the detection limit of 2.3 µg/L, except for the last data point for the 48DM.

Arsenic is an oxyanion typically present as arsenate, As(V) or arsenite, As(III) in natural environmental systems. At high redox levels As(V) predominates, with corresponding low mobility due to the formation of insoluble iron, aluminum and calcium precipitates. As an oxyanion, adsorption of arsenate decreases with pH, with

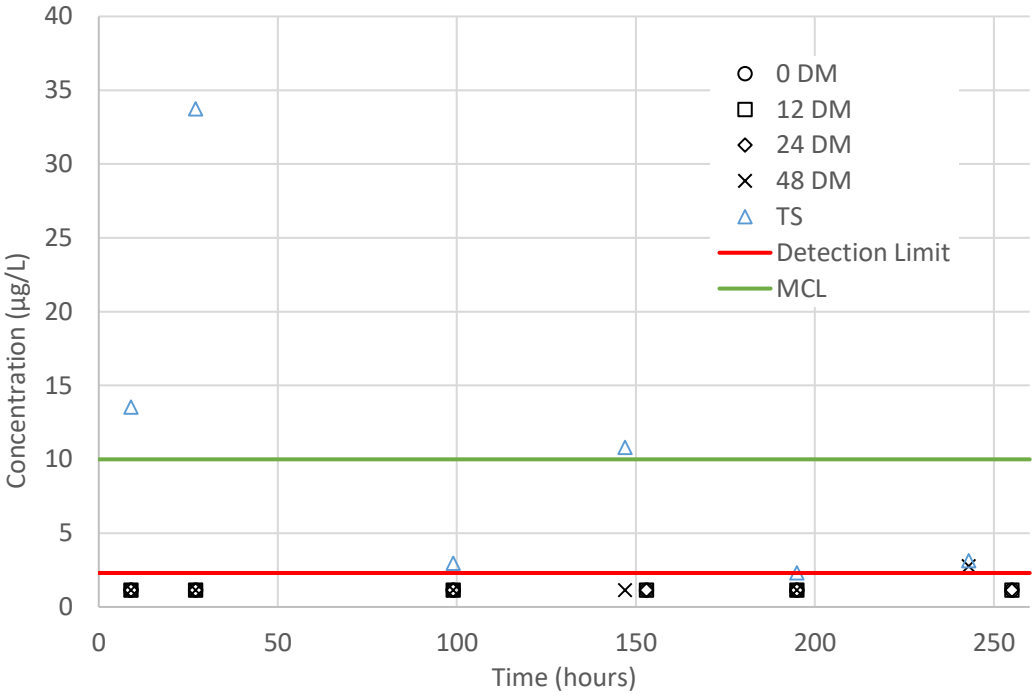

Figure 25: Arsenic column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

maximum adsorption at pH 3-4 (Boulding 1996). At low redox potentials or high pH, the more toxic As(III) predominates, and is more susceptible to leaching due to high solubility. Arsenite adsorbs to iron oxides and minerals such as kaolinite and montmorillonite, with adsorption increasing with pH. Manganese oxides can be electron acceptors in the oxidation of As(III) to As(V) (Boulding 1996). Topsoil, with a lower pH and high redox levels, should therefore have more arsenic adsorbed to oxides and be less mobile; however, that is not the trend seen in this study. Arsenate can be reduced to arsenite in organic soils, as organic matter provides conditions for reduction to As(III) (Balasoiu et al. 2001). Organic matter can mediate conditions for microbes to reduce iron oxyhydroxides that arsenic can be sorbed to, resulting in their release into a water phase (Anawar et al. 2013). Due to much higher organic matter content of the topsoil (15% as compared to 5% in the DM), it is possible that the reduction of arsenate to arsenite occurred, and the more mobile arsenite was leached from the topsoil in column leach tests. The higher concentrations of arsenic eluted from topsoil aligns with the EDTA extraction (2.2 mg/kg), which extracted arsenic in topsoil but not dredged material, which predicts a higher mobility of arsenic from topsoil.

Lead

The same six samples measured for mercury and arsenic were also measured for lead concentrations; however, the detection limit of 0.042 mg/L was higher than the MCL of 0.015 mg/L. Nine of the 58 samples measured, with column averages shown in Figure 26, had concentrations above the detection limit. All columns eluted

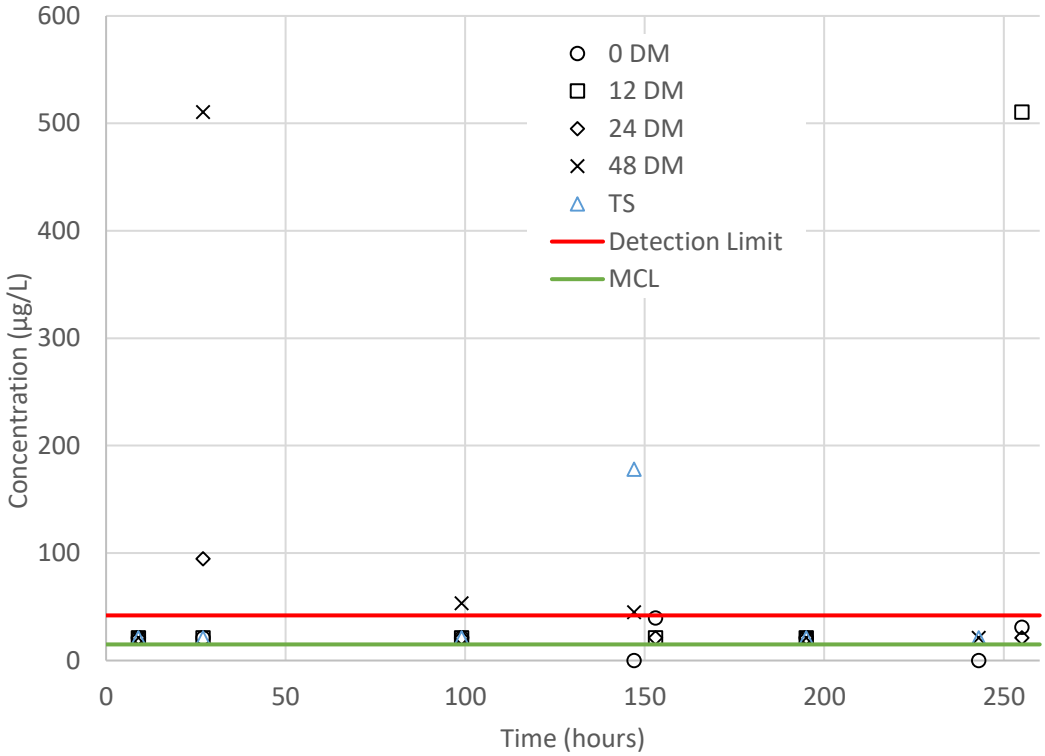

Figure 26: Lead column leach elution curve for topsoil and DM for 258 hours of column leach testing (25 mm/hr). Concentrations below the detection limit are plotted as half of the detection limit.

measurable concentrations during the testing; however, there are not enough data to discern a trend. 12DM and 48DM columns eluted higher average concentrations of lead than topsoil (>510 µg/L as compared to 178 µg/L); however, 0DM and 24DM columns eluted <100 µg/L maximum average concentrations throughout testing.

Lead is a divalent cation that has limited solubility in soil due to reactions with clays, phosphates, sulfates, carbonates, hydroxides and complexation with organic matter (Boulding 1996). Adsorption of lead is strongly pH dependent, and organic matter content has been shown to be the controlling factor of complexation in soils (Lee et al. 1998). Hence, it would be expected that adsorption in topsoil, with a low pH (5.21) and high organic matter content (15%), would be controlled by organic matter, and adsorption in DM, with higher pH (6.80) and lower organic matter content (5%), would be controlled by pH.

Table 12 shows the maximum average concentration of each metal eluted from each set of columns With the exception of singular data points for chromium and mercury, and an unknown number of data points for lead, metals leaching of washed and unwashed DM was shown to be below the EPA's maximum contaminant levels, indicating that the material does not pose a threat of metals contamination to nearby ground waters if used in highway slope applications. DM leached lower concentrations of arsenic, cadmium, copper and zinc than the SHA-approved topsoil throughout testing, showing that it would be a comparable, if not more suitable replacement.

Table 13 shows the flow weighted average metals concentration in mg/kg

Table 12: Maximum concentrations (µg/L) of metals eluted during 258 hours of column leach testing, measured as the average of triplicate columns.

Column	**Ag**	**As**	**Ba**	**Cd**	**Cr**	**Cu**	**Hg**	**Pb**	**Se**	**Zn**
0DM	9.83	<2.27	114.5	<10	*124.6*	316.1	<2	*39.5*	<10	694.8
12DM	65.5	<2.27	<10	<10	<10	16	<2	*>511*	<10	78.3
24DM	32.1	<2.27	69.5	<10	58.0	108	<2	*94.7*	<10	224.2
48DM	<2.5	2.77	48.3	<10	80.2	99.9	*2.96*	*>511*	<10	144
TS	<2.5	*33.74*	28.3	<10	<10	359	<2	*178*	<10	422.7
MCL	**100**	**10**	**2000**	**5**	**100**	**1000**	**2**	**15**	**50**	**5000**

Table 13: Metals concentration (mg/kg) eluted from columns during 258 hours of column leach testing, measured as the average of triplicate columns.

Column	**As**	**Ba**	**Cd**	**Cr**	**Cu**	**Se**	**Pb**	**Zn**
0DM	<0.0726	0.630	<0.0325	0.535	1.07	0.318	<1.33	2.37
12DM	<0.0726	<0.316	<0.0325	<0.316	<0.316	0.207	2.54	0.683
24DM	<0.0726	0.366	<0.0325	<0.316	0.602	0.187	<1.33	1.36
48DM	<0.0726	0.422	<0.0325	0.364	0.886	<0.163	3.57	0.889
TS	0.355	<0.316	<0.0325	<0.316	4.11	<0.163	1.75	4.05
Detection Limit	0.0726	0.316	0.0325	0.316	0.316	0.163	1.33	0.632

eluted from each of the columns during the 258 hours of testing for the metals tested in this study, with the exception of silver and mercury due to undetectable concentrations. Copper and zinc had the highest concentrations eluted from topsoil columns at 4.11 and 4.05 mg/kg, respectively. DM columns eluted varying concentrations for copper and zinc (<0.316 to 1.07 mg/kg and 0.683 to 2.37 mg/kg, respectively) at lower masses than the topsoil columns. Chromium and barium concentrations were higher for DM columns than topsoil columns (<0.316 to 0.630 mg/kg compared to <0.316 mg/kg for barium and <0.316 to 0.535 mg/kg compared to <0.316 mg/kg for chromium). The arsenic load was higher for topsoil than DM (0.355 mg/kg compared to <0.0726 mg/kg).

3.7.4 Partial Clogging of the Columns

As shown by the large standard deviations in triplicate columns, individual columns experienced decreased flow that increased metal leaching throughout testing, primarily those in the 0DM and 24DM columns. Clogging of columns, as discussed previously, coincided with higher metal concentrations in the effluent that was pooled at the top with higher particulates. Initially, it was hypothesized that the metals were bound to the particulate matter instead of dissolved in the effluent, resulting in higher concentrations. This theory was tested by filtering a portion of the effluent through a 0.22-µm filter to remove the particulates and measuring the unfiltered and filtered samples on the ICP-OES for comparison. However, the filtered samples were similar to unfiltered samples, showing an average difference of 20% as discussed in the Materials and Methods section, indicating that the metals were dissolved in the effluent. This is likely due to the increased contact time with the sediments as the

pooled water was not drained as in the other columns, instead being pooled on top of the sediments in between storms for 40-54 hours. This could potentially cause problems in a field application if there is slow drainage and water is exposed to the DM for longer than the 6 hours at a time tested in this study.

The clogging of the columns became a major concern in the second phase of testing (i.e., sediments washed for 0-24 hours). An initial hypothesis was formed based on the salt content of the materials. The first phase tested dredged material washed with 48 inches of rainwater to leach soluble salts from the material in order to meet SHA requirements. The second phase tested material with higher salt contents, because the DM was only washed with 0, 305, and 610 mm of rainwater. Increased salt content may have caused a decrease in hydraulic conductivity as the salts move up through the sediments and accumulate, thus making the upper layer of the sediments impermeable. This hypothesis was tested by removing material from the columns and separating them into two halves: top and bottom. Each half was tested for soluble salts, with the prediction that the top half would have significantly more salts which caused the clogging. This hypothesis was disproved when only five of the nine columns had higher soluble salts in the top layer, shown in Table 14.

Another hypothesis to determine the cause of clogging was that the washing process changed the particle size distribution of the materials by removing the fines, and the unwashed dredged material caused clogging due to migration of the fines. This was determined by measuring the particle size distribution of the materials that went into the columns, i.e., the washed material that passed through a No. 10 sieve. Sediments were measured in triplicate, with results shown in Figure 27. As shown,

Table 14: Comparison of soluble salts measurements of dredged material extracted from columns after column leach testing, separated by top and bottom.

Column	EC Top (µs/cm)	EC Bottom (µs/cm)
0DM-A	449	335
0DM-B	402	441
0DM-C	437	396
12DM-A	400	367
12DM-B	402	458
12DM-C	350	343
24DM-A	333	451
24DM-B	376	389
24DM-C	350	339

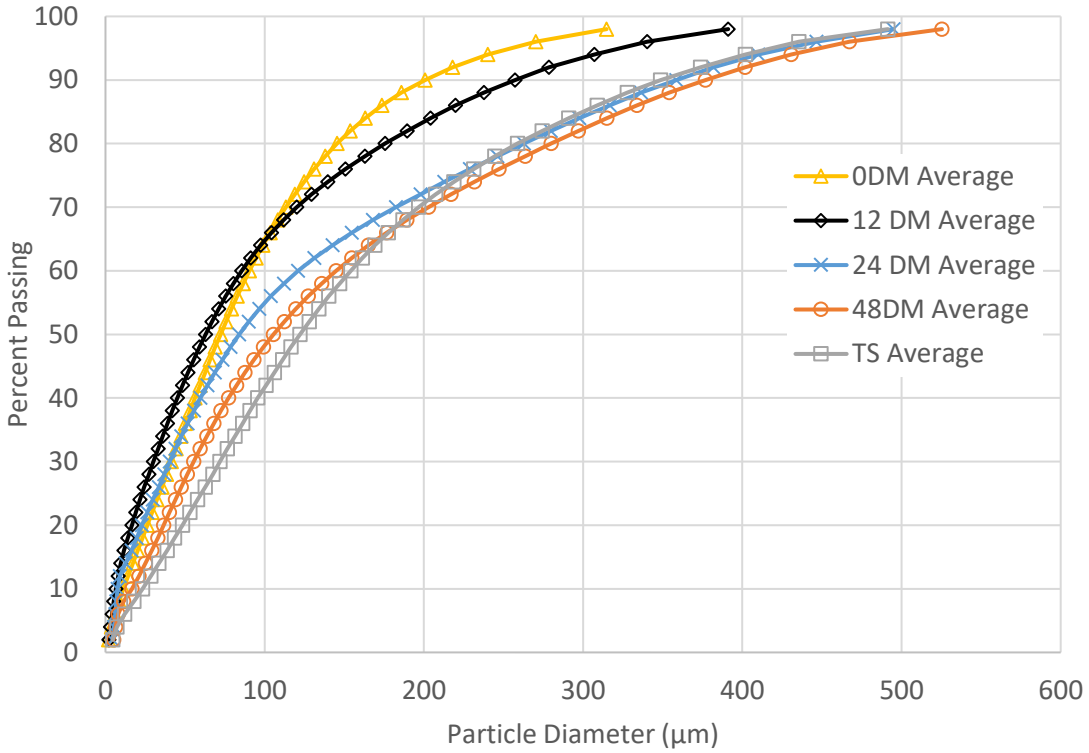

Figure 27: Comparison of particle size distribution for 0DM, 12DM, 24DM, 48DM, and topsoil using SALD-2300 particle size analyzer.

the more the dredged sediment is washed, the fewer fines are present. These data is also presented with D_{10}, D_{50}, and D_{90} values in Table 15, which are the particle diameters representing the 10, 50, and 90 percent cumulative value, respectively. Therefore, the cause of the clogging is most likely buildup of fines in the sediment column that decreased hydraulic conductivity and prevented water flow.

The hydraulic conductivity of soils and sediments is heavily influenced by their exchangeable sodium percentage and the composition of the solution moving through them. At low ESP values, clay dispersion is the primary mechanism for decrease in hydraulic conductivity due to blockage of conducting pores by accumulated clay platelets, while swelling is responsible in sediments with high ESP values. Sediments with low silt content, such as the DM studied herein, exhibit clay dispersion which can block conducting pores of the sediments when the salinity decreases below the concentration at which clay particles flocculate, decreasing hydraulic conductivity (Pupisky and Shainberg 1979). These mechanisms are highly dependent on sediment properties not measured in this study, such as ESP, SAR, and mineralogy, but the clogging exhibited in the DM demonstrates the variability of hydraulic conductivity in sediments with different textures and salt contents.

3.7.5 Comparison of Metals Extractions and Column Leach Results

The metals extraction data give context to the findings from the column leach testing. Zinc and copper were eluted from both topsoil and dredged material at concentrations much higher than other metals measured, and topsoil columns consistently leached both of these metals throughout the testing and had a higher mass load than DM. Chromium was not detected in leachate from topsoil columns,

Table 15: Comparison of particle size distribution of materials used in column leach testing.

Material	**D_{10}**	**D_{50}**	**D_{90}**
0DM	11.26	72.23	200.73
12DM	6.48	62.83	257.25
24DM	7.66	84.04	358.48
48DM	16.72	105.53	376.76
Topsoil	23.17	122.16	348.716

but was eluted from three of the four sets of DM columns, due to the large difference in total chromium content in the sediments. Interestingly, topsoil had much larger total concentrations of barium than dredged material, but the dredged material columns eluted higher concentrations of barium in testing. Although higher concentrations of barium were leached from the dredged material, they seem to be correlated to clogging as discussed in Section 3.7.4, instead of a typical first flush pattern that was seen with topsoil.

The results of the total metals and EDTA extractions generally align with the metals concentrations eluted from each material during column leach testing. The metals eluted at the highest concentrations during column leach testing were copper, lead and zinc, while copper and zinc had the largest concentrations extracted with EDTA for both DM and topsoil. Lead concentrations eluted during column leach testing showed large variation among columns, with error introduced due to the larger time increments, which could put disproportionate weight on larger or smaller intermediate values of the flow weighted average concentrations. Although the concentrations of copper extracted with EDTA were similar between DM and topsoil, the topsoil eluted more copper than DM throughout the column leach testing, indicating that the EDTA extraction underestimated the mobile copper in the topsoil. The EDTA extraction also underestimated the amount of barium that would leach from the DM relative to topsoil, as the extraction predicted similar concentrations for topsoil, unwashed DM, and washed DM, while DM eluted larger amounts of barium throughout column leach testing. Barium concentrations seemed to be heavily influenced by the clogging of

columns, so it is unclear if the discrepancy is due to the clogging or mobility of barium in the DM.

Figure 28 compares the metals concentrations (mg/kg) in topsoil, 0DM, and 48DM as measured by total metals extraction, EDTA extraction, and column leach testing. While the distribution of metals varies between topsoil and DM, similar total metals concentrations are similar, with a small percentage of total metals eluted during column leach testing. Both dredged material and topsoil eluted metals concentrations above the MCL during column leach testing; arsenic for topsoil, and singular data points of chromium and mercury for DM. Extraction data, along with the column leach test results, shows that the higher total metals content in the DM will likely not have an adverse effect in typical environmental conditions due to limited mobility. Physical properties of the dredged material indicate that metals should be more adsorbed due to the higher pH and higher clay content, and less likely to be reduced by organic matter, which can facilitate leaching of metals sorbed to oxides. The metals testing done in the current study indicates that dredged material would not pose more of a threat of drinking water contamination as compared to a conventional topsoil.

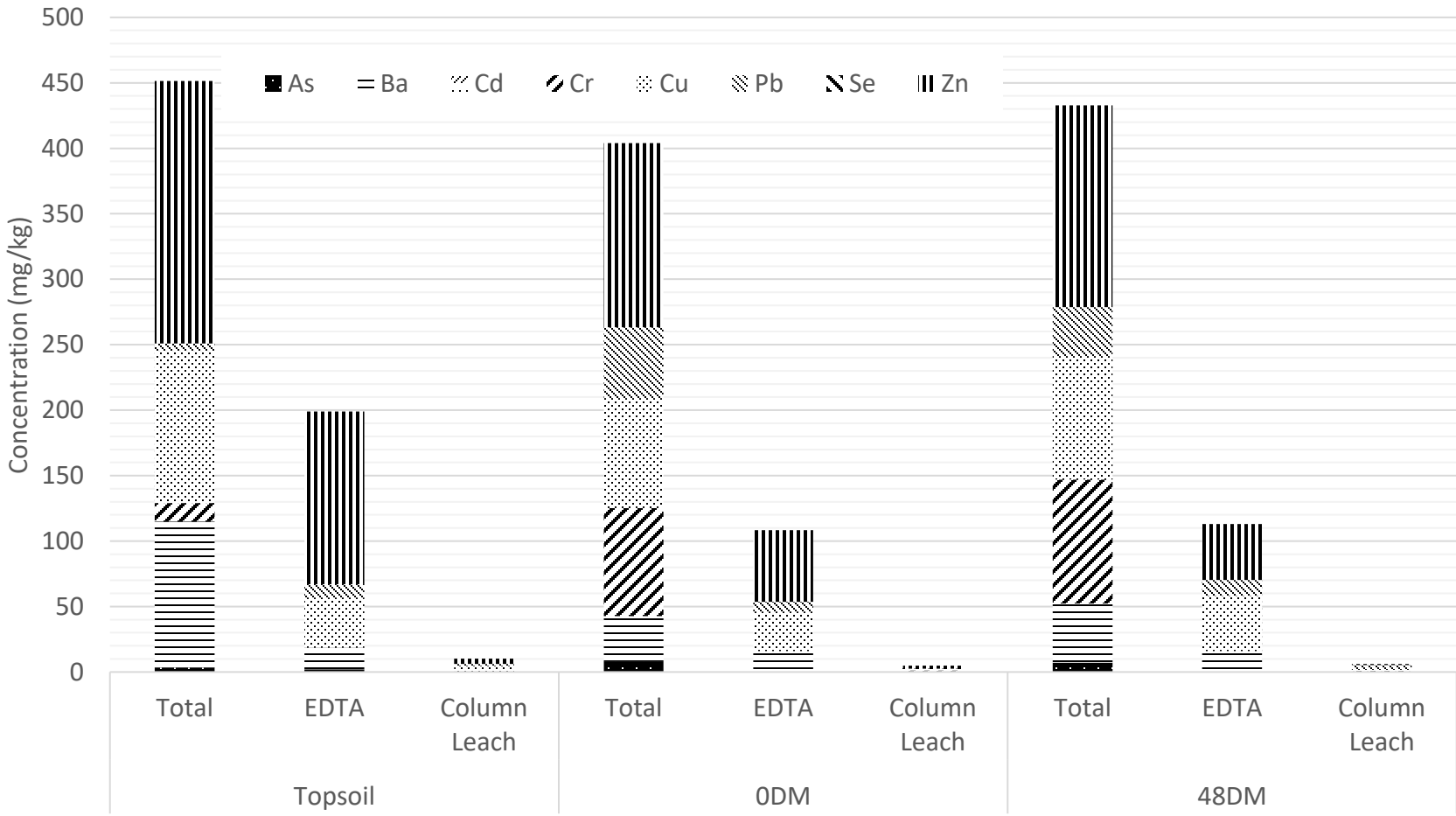

Figure 28: Comparison of metals concentration (mg/kg) extracted with total metals extraction (EPA Method 3050B), EDTA extraction, and column leach testing for topsoil, unwashed DM (0DM) and washed DM (48DM).

Chapter 4

Conclusions and Recommendations

4.1 Summary and Conclusions

A research study was conducted to evaluate suitability of Chesapeake Bay dredged material samples for their use as a topsoil alternative according to MDOT SHA's topsoil specifications. The dredged material (DM) properties were within specifications for pH, organic matter and particle size distribution, and acid volatile sulfides were shown to be below detection limits, indicating that the pH of the material should not significantly change with time. Elevated levels of soluble salts (>500 ppm) prevented the material from being classified as a furnished topsoil. Gypsum treatment of DM proved unsuccessful in lowering soluble salts, but synthetic rainwater passing through the DM reduced salt concentrations. Sediment washing experiments were performed to determine the amount of water needed to reduce the salt content of the material to the suitable level of 500 ppm. Small-scale (25-mm diameter columns) and larger-scale (262-mm diameter buckets) systems, each with a 152 mm thick layer of DM, showed that 813 and 1219 mm, respectively, of rainwater was required to meet the limit.

A total metals extraction and EDTA extraction were performed on the dredged material and topsoil to determine the environmental risk of the materials. Although there were higher total concentrations of arsenic, chromium and lead in the dredged material as compared to the topsoil, the EDTA extraction demonstrates that the concentrations of metals in the oxidizable/reducible fractions, i.e., those potentially mobile with changes in pH, are comparable for topsoil and DM. Barium, copper, lead and zinc were extracted using EDTA for both topsoil and DM with the

concentrations decreasing in the order: Zn > Cu > Ba > Pb. A TCLP was performed and confirmed that the dredged material is characterized as non-hazardous. A Mehlich 3 extraction was performed to measure phosphorus concentrations in topsoil and DM. Washed dredged material (48DM) contains much less phosphorus than topsoil (18.2 mg/kg versus 641 mg/kg), which could cause a nutrient deficiency affecting plant growth therefore impacting slope stability and erosion.

Column leach testing was performed on dredged material and an SHA-approved topsoil to evaluate metal leaching behavior, and compared to the EPA's drinking water maximum contaminant levels. Dredged material met drinking water MCL's for 100% of the data points tested for silver, arsenic, barium, cadmium, copper, selenium and zinc, 98.9% of the data points tested for chromium, and 96% of the data points tested for mercury. The DM performed better than topsoil in respect to arsenic, which only met drinking water MCL's for 50% of the data points tested. Topsoil effluent was lower than MCLs for 100% of the data points tested for silver, barium, cadmium, chromium, copper, mercury, selenium and zinc. Although select data points did not meet drinking water MCLs, the DM did not leach metals above the EPA limits for the majority of the testing period.

4.2 Recommendations for Future Research

As demonstrated by this study, beneficial reuses such as topsoil show promise for reducing the required storage of dredged material. The major physical property that prevents reuse in such applications is the high levels of soluble salts in the DM. In this study, large volumes of synthetic rainwater was applied to DM in order to reduce

the salts to acceptable levels, however the application was done in small-scale systems and was not optimized for use in the field. Although the small scale was suitable for the testing done in this study, this could be challenging if large amounts of material needed to be washed for reuse. Optimization of the washing process for a field-scale application is a challenge that needs to be investigated for reuses such as topsoil to be economically feasible.

A rational next step would be to test the suitability of the dredged material for plant growth. Although this study has showed that the DM is environmentally and geotechnically comparable to a natural topsoil, a greenhouse-scale study to ensure that it can support plant growth would further support the use of DM in field applications.

This study measured environmental risk through metals leaching behavior, however other contaminants of concern are relevant when reusing dredged material. Other studies have shown that DM has potentially hazardous levels of organic pollutants such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls (Ho et al. 2002; Hue et al. 2002). The extent of organic pollutant contamination of Chesapeake Bay DM should be investigated to fully evaluate its environmental risk as a topsoil alternative.

Appendix: Column Leach Metals Data

Arsenic column leach concentrations for columns 48DM and TS.

	Hour	**DM1**	**DM2**	**DM3**	**48 AVG**	**T1**	**T2**	**T3**	**TS AVG**
E1/E2	9	1.14	1.14		1.14	13.20779	13.87		13.54
E4/E7	27	1.14		1.14	1.14		53.70	13.768	33.735
E16/20	99		1.14	1.14	1.14	1.14		4.761	2.951
E28	147		1.14	1.14	1.14		11.87	9.760	10.813
E25	153								
E32/36	195	1.14	1.14		1.14	1.14		3.462	2.301
E44	243		2.917	2.616	2.767	2.767	3.513		3.140
E42	255								

Arsenic column leach concentrations for columns 0DM, 12DM, and 24DM.

	Hour	**0A**	**0B**	**0C**	**0 AVG**	**12A**	**12B**	**12C**	**12 AVG**	**24A**	**24B**	**24C**	**24 AVG**
E1/E2	9			1.14	1.14		1.14	1.14	1.14		1.14		1.14
E4/E7	27	1.14		1.14	1.14	1.14	1.14		1.14		1.14	1.14	1.14
E16/20	99	1.14	1.14		1.14		1.14	1.14	1.14		1.14	1.14	1.14
E28	147												
E25	153		1.14	1.14	1.14		1.14	1.14	1.14	1.14		2.439	1.14
E32/36	195	1.14	1.14		1.14	1.14		1.14	1.14	2.468	1.14		1.14
E44	243												
E42	255	1.14	1.14		1.14	1.14		1.14	1.14	1.14	1.14		1.14

Barium column leach concentrations for columns 0DM, 12DM, and 24DM.

	Time	0A	0B	0C	0 AVG	0STDEV	12A	12B	12C	12AVG	12STDEV	24A	24B	24C	24 AVG	24 STDEV
E1	9	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E2	15	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E3	21	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E4	27	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E6	39	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E8	51	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E10	63	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E12	75	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E14	87	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E16	99	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E18	111	5	5	5	5	0	5	5	5	5	0	5	5	12.8	5	
E20	123	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E22	135	16.5	23.6	21.9	20.66667	3.7072	5	5	5	5	0	20.3	5	15.8	13.7	7.863205
E24	147	26.1	14.7	58.3	33.03333	22.6118	5	5	5	5	0	15.6	5	13.5	11.36667	5.612783
E26	159	11.8	5		5	0	5	5	5	5	0	5			5	
E28	171	10.4	18.9	5	11.43333	7.007377	5	5	5	5	0	5	5	5	5	0
E30	183	79.1	58.9	55.7	64.56667	12.68753	5	5	5	5	0		5	14.8	5	0
E32	195	23.6	41.3		32.45	12.51579	5	5	5	5	0	65.9	5		35.45	43.0628
E34	207		65	19.8	42.4	31.96123	5	5	5	5	0	134	5		69.5	91.21677
E36	219		27	202	114.5	123.7437	5	5	5	5	0	31.6	5	5	13.86667	15.35752
E38	231	15.5	15.2	17.6	16.1	1.30767		5	5	5	0	30.4	5	5	13.46667	
E40	243	13.9	11	12.8	12.56667	1.464013	5	5	5	5	0	15.2	5	10.9	10.36667	
E42	255	26.9	21.7	20.5	23.03333	3.40196	5	5	5	5	0	18.4	5	5	5	

Barium column leach concentrations for columns 48DM and TS.

	Hour	DM1	DM2	DM3	48DM AVG	48 STDEV	T1	T2	T3	TS Avg	TS STDEV
	0										
E1	3		5		5		5			5	
E2	9	5	5	5	5	0	15.3	23.9	45.7	28.3	15.67035
E3	13.5		5	5	5	0	12.9	39.1		26	18.5262
E4	16.5		5	5	5	0	5	10.1		7.55	3.606245
E3/4	15	5			5				12.3	12.3	
E5	19.5	5	5		5	0	5	5		5	0
E6	22.5	5	5		5	0	5	5		5	0
E5/E6	21								5	5	
E7	25.5						5	5		5	0
E8	28.5						5	5		5	0
E7/E8	27	5	5	5	5	0			5	5	
E9	33	5	5	5	5	0	5	5	5	5	0
E10	39	5	5	5	5	0	5	5	5	5	0
E11	45	5	5	5	5	0	5	5	5	5	0
E13	57	5	5	5	5	0	5	5	5	5	0
E15	69	5	5	5	5	0	5	5	5	5	0
E17	81	5	5	5	5	0	5	5	5	5	0
E19	93	5	5	5	5	0	5	5	5	5	0
E21	105	5	5	5	5	0	5	5	5	5	0
E23	117	5	5	5	5	0	5	5	5	5	0
E25	129	5	5	5	5	0	5	5	5	5	0
E27	141		11.9	5	5	0	5	5	5	5	0
E29	153	62.5		34	48.25	20.15254	5	5		5	0
E31	165	33.8	35.7	44.8	38.1	5.879626	5	5	5	5	0
E33	177	26.2	22.2	29.1	25.83333	3.464583	5	5	5	5	0
E35	189	43.1	19.3	5	22.46667	19.24638	5	5	5	5	0
E37	201	44.9	14.5	5	21.46667	20.84234	5	5	5	5	0
E39	213	31	19	5	18.33333	13.01281	5	5	5	5	0
E41	225	18.1	13.6	5	12.23333	6.656075	5	5	5	5	0
E43	237	80	15.4	5	33.46667	40.63316	5	5	5	5	0
E45	249		26.5	37.5	32	7.778175	5		5	5	0

Cadmium column leach concentrations for columns 48DM and TS.

	Hour	**DM1**	**DM2**	**DM3**	**48 AVG**	**T1**	**T2**	**T3**	**TS AVG**
E1/E2	9	0.52	0.52		0.52	0.52	2.462		1.491
E4/E7	27	1.111		0.52	0.52		1.147	1.207	1.177
E16/20	99		0.52	0.52	0.52	1.947		0.52	1.233
E28	147		0.52	0.52	0.52		0.52	0.52	0.52
E25	153								
E32/36	195	0.52	0.52		0.52	0.52		0.52	0.52
E44	243		1.148	0.52	0.52	0.52	0.52		0.52
E42	255								

Cadmium column leach concentrations for columns 0DM, 12DM, and 24DM.

	Hour	**0A**	**0B**	**0C**	**0 AVG**	**12A**	**12B**	**12C**	**12 AVG**	**24A**	**24B**	**24C**	**24 AVG**
E1/E2	9			0.52	0.52		0.52	0.52	0.52		0.52		0.52
E4/E7	27	1.133		0.52	0.52	0.52	0.52		0.52		0.52	0.52	0.52
E16/20	99	0.52	0.52		0.52		1.066	0.52	0.52		0.52	0.52	0.52
E28	147												
E25	153		0.52	0.52	0.52		0.52	0.52	0.52	0.52		0.52	0.52
E32/36	195	0.52	0.52		0.52	0.52		0.52	0.52	0.52	0.52		0.52
E44	243												
E42	255	0.52	0.52		0.52	0.52		0.52	0.52	0.52	0.52		0.52

Chromium column leach concentrations for columns 0DM, 12DM, and 24DM.

	Time	0A	0B	0C	0 AVG	0 STDEV	12A	12B	12C	12 AVG	12 STDEV	24A	24B	24C	24 AVG	24 STDEV
E1	9	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E2	15	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E3	21	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E4	27	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E6	39	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E8	51	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E10	63	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E12	75	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E14	87	5	5	5	5	0	5	11.3	5	5	0	5	5	5	5	0
E16	99	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E18	111	5	5	5	5	0	5	5	5	5	0	5	5	10	5	0
E20	123	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E22	135	5	12.9	12.1	10	4.348563	5	5	5	5	0	5	5	5	5	0
E24	147	26	14.9	51.4	30.76667	18.71105	5	5	5	5	0	10.1	5	5	5	0
E26	159	10.6	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E28	171	5	14.3	5	5	0	5	5	5	5	0	5	5	5	5	0
E30	183	38.7	29.2	27.5	31.8	6.035727	5	5	5	5	0	5	5	5	5	0
E32	195	14.1	30.6		22.35	11.66726	5	5	5	5	0	42	5		23.5	26.16295
E34	207		88.7	12.9	50.8	53.59869	5	5	5	5	0	111	5		58	74.95332
E36	219		22.2	227	124.6	144.8155	5	5	5	5	0	23.2	5	10.5	12.9	9.334345
E38	231	13	5	14.9	10.96667	5.253887	5	5	5	5	0	21.8	5	5	10.6	9.699485
E40	243	5	5	5	5	0	5	5	5	5	0	12.7	5	5	5	4.445597
E42	255	13.1	10.3	12.3	11.9	1.442221	5	5	5	5	0	15.8	5	5	5	6.235383

Chromium column leach concentrations for columns 48DM and TS.

	Hour (midpoint)	DM1	DM2	DM3	48DM AVG	48 STDEV	T1	T2	T3	TS Avg	TS STDEV
E1	3		37.4		37.4						
E2	9	5	5	5	5	0	5	5	5	5	0
E3	13.5		5	5	5	0	5	5		5	0
E4	16.5		5	5	5	0	5	5		5	0
E3/4	15	5			5				5	5	
E5	19.5	5	5		5	0	5	5		5	0
E6	22.5	5	5		5	0	5	5		5	0
E5/E6	21								5	5	
E7	25.5						5	5		5	0
E8	28.5						5	5		5	0
E7/E8	27	5	5	5	5	0			5	5	
E9	33	5	5	26.6	12.2	12.47077	5	5	5	5	0
E10	39	5	5	5	5	0	5	5	5	5	0
E11	45	5	5	5	5	0	5	5	5	5	0
E13	57	5	5	5	5	0	5	5	5	5	0
E15	69	5	5	5	5	0	5	5	5	5	0
E17	81	5	5	5	5	0	5	5	5	5	0
E19	93	5	5	5	5	0	5	5	5	5	0
E21	105	5	5	5	5	0	5	5	5	5	0
E23	117	5	5	5	5	0	5	5	5	5	0
E25	129	5	5	5	5	0	5	5	5	5	0
E27	141		5	11.8	5	0	5	5	5	5	0
E29	153	38.6		24.6	31.6	9.899495	5	5		5	0
E31	165	17.4	17.8	26.5	20.56667	5.142308	5	5	5	5	0
E33	177	15.4	17	19.2	17.2	1.907878	5	5	5	5	0
E35	189	32.3	14.6	5	17.3	13.84883	5	5	5	5	0
E37	201	28.2	11	5	14.73333	12.04215	5	5	5	5	0
E39	213	19.1	15.6	5	13.23333	7.341889	5	5	5	5	0
E41	225	12.1	<10	5	5	0	5	5	5	5	0
E43	237	68.8	21.3	14	34.7	29.75618	5	5	5	5	0
E45	249		36.7	80.2	58.45	30.75914	5		5	5	0

Copper column leach concentrations for columns 0DM, 12DM, and 24DM.

	Time	0A	0B	0C	0 AVG	0STDEV	12A	12B	12C	12AVG	12STDEV	24A	24B	24C	24 AVG	24 STDEV
E1	9	14.8	23.6	21.4	19.93333	4.579665	5	5	5	5	0		30.6	33.4	32	1.979899
E2	15	19.2	11.6	16.5	15.76667	3.852705	5	38	5	16	19.05256	5	5	5	5	0
E3	21	5	5	5	5	0	5	5	5	5	0	5	5	11.3	5	0
E4	27							17.4	5	11.2	8.768124	5	5	5	5	0
E6	39	5	5	5	5	0	5	5	5	5	0	5	5	5	5	0
E8	51	5	5	5	5	0	5	5	5	5	0	10.6	12.4	5	5	0
E10	63	5	5	5	5	0	16.2	5	5	5	0	5	5	28.4	12.8	13.51
E12	75	5	5	5	5	0	5	11.1	5	5	0	13.6	5	5	5	0
E14	87	5	5	11.2	5	0	5	14.9	16.9	12.26667	6.372074	15.8	10.2	11.7	12.56667	2.89885
E16	99	5	5	10.9	5	0	5	5	5	5	0	16.5	5	10.8	10.76667	5.750072
E18	111	5	5	16.1	5	0	5	5	5	5	0	21.1	5	24.4	16.83333	10.37995
E20	123	12.7	5	14.4	10.7	5.008992	5	5	5	5	0	22.5	5	5	10.83333	10.10363
E22	135	11	18.1	28.1	19.06667	8.590887	5	5	20.2	10.06667	8.775724	45.4	5	19.9	23.43333	20.43045
E24	147	49.6	30.3	129	69.63333	52.31083	5	5	5	5	0	31.1	5	19.5	18.53333	13.07682
E26	159	27.7	16.9		22.3	7.636753	5	5	5	5	0	25.1			25.1	
E28	171	25.2	34.7	26.6	28.83333	5.128678	5	5	5	5	0	24.4	5	28	19.13333	12.37147
E30	183	75.3	33.3	38.8	49.13333	22.82725	5	5	5	5	0		5	15	10	7.071068
E32	195	16.8	37.2		27	14.42498	5	5	5	5	0	79.8	5		42.4	52.89159
E34	207		113	13.3	63.15	70.49855	5	5	5	5	0	211	5		108	145.664
E36	219		31.2	601	316.1	402.9094	5	5	5	5	0	39.4	5	5	16.46667	19.86085
E38	231	17.9	21.1	23.8	20.93333	2.953529	5	5	5	5	0	51.7	5	5	20.56667	26.96226
E40	243	5	13.1	14.9	11	5.273519	5	5	5	5	0	18.8	5	5	5	7.967434
E42	255	28.6	49	11.6	29.73333	18.72574	5	5	5	5	0	16.7	5	5	5	6.754998

Copper column leach concentrations for columns 48DM and TS.

	Hour	DM1	DM2	DM3	48DM AVG	48 STDEV	T1	T2	T3	TS Avg	TS STDEV
	0		144		144		938			938	
E1	3										
E2	9	56.9	44.8	44.1	48.6	7.196527	167	210	206	194.3333	23.7557
E3	13.5		57	44.2	50.6	9.050967	207	252		229.5	31.81981
E4	16.5		37.1	31.9	34.5	3.676955	173	342		257.5	119.501
E3/4	15	41.2			41.2				193	193	
E5	19.5	39	42.1		40.55	2.192031	330	388		359	41.01219
E6	22.5	32	35.7		33.85	2.616295	209	336		272.5	89.80256
E5/E6	21								177	177	
E7	25.5						261	384		322.5	86.97413
E8	28.5						154	268		211	80.61017
E7/E8	27	29	24	22.2	25.06667	3.523256			170	170	
E9	33	20.4	26.6	24.2	23.73333	3.126233	153	212	193	186	30.11644
E10	39	22.5	25.3	20.4	22.73333	2.458319	110	144	154	136	23.06513
E11	45	5	10.6	5	6.866667	3.233162	156	91.1	243	163.3667	76.21747
E13	57	5	5	5	5	0	112	148	171	143.6667	29.73774
E15	69	5	5	5	5	0	87.9	112	164	121.3	38.89306
E17	81	5	5	5	5	0	87.6	152	178	139.2	46.53945
E19	93	5	5	5	5	0	116	86.5	183	128.5	49.44947
E21	105	14.2	5	5	8.066667	5.311622	57.6	61.6	66.5	61.9	4.457578
E23	117	10	24.4	5	13.13333	10.0724	49.4	72	124	81.8	38.25337
E25	129	11.8	12.8	5	9.866667	4.244212	59.3	97	69.8	75.36667	19.4567
E27	141		25.6	13.9	19.75	8.273149	56.1	82	148	95.36667	47.38569
E29	153	77		35.8	56.4	29.1328	51.1	39.6		45.35	8.131728
E31	165	31.8	31.2	42.1	35.03333	6.127261	48.7	45.1	61.6	51.8	8.675828
E33	177	23.2	29.4	34.5	29.03333	5.658916	86.3	38.9	53.3	59.5	24.30062
E35	189	101	42.9	10.5	51.46667	45.85415	43.9	46.8	51.4	47.36667	3.781975
E37	201	63.9	15.8	13	30.9	28.61311	42.1	42.9	66.2	50.4	13.68905
E39	213	43.4	31.7	10.8	28.63333	16.51494	45.6	50.7	48.3	48.2	2.55147
E41	225	31.7	19.5	3.51	18.23667	14.1374	53.7	34.9	79.9	56.16667	22.60118
E43	237	268	21.4	10.2	99.86667	145.7154	34.5	34.5	45.6	38.2	6.408588
E45	249		35.1	99.3	67.2	45.39626	31.7		57.8	44.75	18.45549

Mercury column leach concentrations for columns 48DM and TS.

	Hour	**DM1**	**DM2**	**DM3**	**48 AVG**	**T1**	**T2**	**T3**	**TS AVG**
E1/E2	9		1.1584	1.3958	1		1.8464		1.2536
E4/E7	27	1.3899		1.0733	1		1.2732		1.1528
E16/20	99	1.1146	1.0821	1.1375	1		1.043	1.1578	1.076
E28	147	3.6023	2.3115		2.9569	0.912733	1.5762	1.9701	
E25	153								
E32/36	195	1.546	1.2104	1.104	1		1.0321		1.0361
E44	243		1.2366	1.8684	1		1.2224	1.1083	
E1/E2	9		1.1584	1.3958	1		1.8464		1.2536

Mercury column leach concentrations for columns 0DM, 12DM, and 24DM.

	Hour	**0A**	**0B**	**0C**	**0 AVG**	**12A**	**12B**	**12C**	**12 AVG**	**24A**	**24B**	**24C**	**24 AVG**
E1/E2	9	1.9883	1.4437		1		1.3269		1.7625	1			1.2893
E4/E7	27	0.5		1.0724	1		1.1588		1.1506	1		1.177	1.1098
E16/20	99	1.1948	1.1414	1.1083	1		1.2009	1.1437	1.8409	1		1.1072	1.1541
E28	147												
E25	153	1.3234	1.4006		1			1.1681	1.237	1		1.1739	1.8061
E32/36	195	1.1373	1.1253		1		1.0689	1.0843	1.0823	1		1.2455	1.1497
E44	243												
E42	255	1.3207	1.1246	1.1245	1	0	1.0807	1.0624	1.067	1		1.0952	1.1376

Lead column leach concentrations for columns 48DM and TS.

	Hour	**DM1**	**DM2**	**DM3**	**48 AVG**	**T1**	**T2**	**T3**	**TS AVG**
E1/E2	9	21	21		21	21	21		21
E4/E7	27	1000		21	510.5		21	21	21
E16/20	99		21	85.6	53.283	21		21	21
E28	147		68.6	21	44.82		21	335	178.178
E25	153								
E32/36	195	21	21		21	21		21	21
E44	243		21	21	21	21	21		21
E42	255								

Lead column leach concentrations for columns 0DM, 12DM, and 24DM.

	Hour	**0A**	**0B**	**0C**	**0 AVG**	**12A**	**12B**	**12C**	**12 AVG**	**24A**	**24B**	**24C**	**24 AVG**
E1/E2	9			21		21	21		21				21
E4/E7	27	21		21	21	21			168.445	21	21		21
E16/20	99	21	21			21	21		21	21	21	21	
E28	147												
E25	153		21	57.985		21	21	21		41.129		21	57.985
E32/36	195	21	21		21		21	21	21		21	21	
E44	243												
E42	255	21	40.744		21		>1000	21	21		21	40.744	

Selenium column leach concentrations for columns 48DM and TS.

	Hour	**DM1**	**DM2**	**DM3**	**48 AVG**	**T1**	**T2**	**T3**	**TS AVG**
E1/E2	9	6.507	6.813		6.660	12.751	7.851		10.301
E4/E7	27	2.58		2.58	2.58		6.708	2.58	2.58
E16/20	99		2.58	2.58	2.58	2.58		2.58	2.58
E28	147		2.58	2.58	2.58		2.58	2.58	2.58
E25	153								
E32/36	195	8.905	2.58		5.742	2.58		2.58	2.58
E44	243		9.959	10.19045	10.075	9.206	9.087		9.146
E42	255	6.507	6.813		6.660	12.751	7.85		10.301

Selenium column leach concentrations for columns 0DM, 12DM, and 24DM.

	Hour	**0A**	**0B**	**0C**	**0 AVG**	**12A**	**12B**	**12C**	**12 AVG**	**24A**	**24B**	**24C**	**24 AVG**
E1/E2	9			11.650	11.650		8.310	9.055	8.682		7.626		7.626
E4/E7	27	22.335		20.141	21.238	10.61787	14.879		12.748		8.664	7.2606	7.962
E16/20	99	6.080	2.58		2.58		2.58	2.58	2.58		2.58	2.58	2.58
E28	147												
E25	153		11.336	11.524	11.430		6.067	2.58	2.58	6.612		2.58	2.58
E32/36	195	9.237	8.857		9.047	8.404165		8.356	8.380	9.166	8.450		8.808
E44	243												
E42	255	9.225	9.166		9.195	8.428697		8.438	8.433	10.095	8.477		9.286

Zinc column leach concentrations for columns 0DM, 12DM, and 24DM.

	Time	0A	0B	0C	0 AVG	0STDEV	12A	12B	12C	12AVG	12STDEV	24A	24B	24C	24 AVG	24 STDEV
E1	9	91.2	72.9	56	73.36667	17.60464	84.6	90.6	59.6	78.26667	16.44182		113	86.2	99.6	18.95046
E2	15	74.9	76.4	53.9	68.4	12.57975	26.9	65	22.1	38	23.50553	75.8	27.3	86.2	63.1	31.43676
E3	21	41.6	144	32.6	72.73333	61.88258	35.6	44.6	27.9	36.03333	8.358429	61.4	31.1	43.1	45.2	15.25877
E4	27							63.1	19	41.05	31.18341	22.5	27.1	13.9	21.16667	6.700249
E6	39	27	20.3	10	10	0	10	11.3	11.1	10	0.7	12.2	10.9	20.2	10	5.036202
E8	51	12.1	34.3	15.5	20.63333	11.95715	6.55	66.7	10.4	27.88333	33.67129	14.1	24.5	12.1	10	6.657327
E10	63	13.1	5.01	7.22	10	0	23	30.4	8.56	20.65333	11.1075	14	18.3	32.9	21.73333	9.906732
E12	75	22.3	12.3	10.4	10	0	9.24	43.3		26.27	24.08406	14.3	24.4	11.8	10	6.671082
E14	87	16.4	10.8	21.1	10	0	13.2	50.8	31.3	31.76667	18.80434	16.5	28.3	23.4	22.73333	5.928181
E16	99	35	17.7	19.4	24.03333	9.535373	28.6	139	22.7	63.43333	65.50911	24.5	31.8	39	31.76667	7.250057
E18	111	42.2	33.7	23.3	33.06667	9.465904	24.8	61.5	38.9	41.73333	18.51333	38.2	19.8	46.5	34.83333	13.66467
E20	123	20.7	13.6	14.7	10	0	16.3	28.1	8.06	10	10.07256	23.9	26.3	10.8	20.33333	8.342861
E22	135	34.8	57.7	35.3	42.6	13.07937	10	31.7	10	10	12.5285	38.2	26.6	24.8	29.86667	7.27278
E24	147	82.7	44.9	195	107.5333	78.07063	10	42.7	10	20.9	18.87935	29.3	10	32.4	23.9	12.13713
E26	159	31	25.5		28.25	3.889087	10	21.1	10	10	6.408588	22.5			22.5	
E28	171	25.3	61.3	50.6	45.73333	18.48684	10	10	10	10	0	10	32	87.6	43.2	39.994
E30	183	230	58.2	49.8	112.6667	101.7004	10	10	10	10	0		22.9	77.4	50.15	38.53732
E32	195	40.4	83.8		62.1	30.68843	22.1	28.4	10	20.16667	9.351114	107	50.2		78.6	40.16367
E34	207		217	28.7	122.85	133.1482	10	36.1	10	10	0	398	50.4		224.2	245.7903
E36	219		69.6	1320	694.8	884.1663	10	31	10	10	0	73	31	70.4	58.13333	23.53409
E38	231	43.4	26.1	60.2	43.23333	17.05061	10	26.1	10	10	0	80.4	10	35.3	41.9	35.66104
E40	243	28	10	29.3	22.43333	10.78718	10	23.9	10	10	0	43.2	10	48.9	34.03333	21.0077
E42	255	62.9	27.2	25.7	38.6	21.05778	10	10	10	10	0	32.6	10	23.8	22.13333	11.39181

Zinc column leach concentrations for columns 48DM and TS.

	Hour (midpoint)	DM1	DM2	DM3	48DM AVG	48 STDEV	T1	T2	T3	TS Avg	TS STDEV
E1	3		144		144		938			938	
E2	9	29	10	35	24.66667	13.05118	334	435	499	422.6667	83.18854
E3	13.5		32	39.8	35.9	5.515433	371	419		395	33.94113
E4	16.5		35.3	40.7	38	3.818377	277	348		312.5	50.20458
E3/4	15	57.7			57.7				380	380	
E5	19.5	24.1	80.5		52.3	39.88082	327	419		373	65.05382
E6	22.5	45.4	10		27.7	25.03158	262	415		338.5	108.1873
E5/E6	21								245	245	
E7	25.5						273	310		291.5	26.16295
E8	28.5						200	257		228.5	40.30509
E7/E8	27	21.9	31.4	30.8	28.03333	5.320088			224	224	
E9	33	10	10	10	10	0	164	313	167	214.6667	85.17237
E10	39	10	10	10	10	0	109	126	188	141	41.58125
E11	45	10	19.3	10	10	5.369358	87.8	90	301	159.6	122.4609
E13	57	10	10	10	10	0	63.4	58	229	116.8	97.20556
E15	69	10	10	10	10	0	61.9	50.9	212	108.2667	90.00391
E17	81	10	10	10	10	0	65.4	94.8	260	140.0667	104.9004
E19	93	10	10	10	10	0	108	48.5	150	102.1667	51.00082
E21	105	19.2	10	10	10	5.311622	60.5	43.1	85.9	63.16667	21.52425
E23	117	10	27.3	10	10	9.98816	51.8	46.9	166	88.23333	67.39246
E25	129	59	10	10	26.33333	28.29016	51.2	66.7	89.5	69.13333	19.2656
E27	141		10	10	10	0	46.1	61	147	84.7	54.46531
E29	153	94.7		34.1	64.4	42.85067	44.3	28		36.15	11.52584
E31	165	35.2	30.2	49.5	38.3	10.01649	40.7	26.6	54.5	40.6	13.95027
E33	177	10	36.1	30.6	25.56667	13.75875	90.6	25.4	48.8	54.93333	33.02989
E35	189	122	10	10	47.33333	64.66323	40.4	54.3	51.8	48.83333	7.409678
E37	201	76.5	10	10	32.16667	38.39379	31.6	35.8	56.4	41.26667	13.27303
E39	213	41.7	23.7	10	25.13333	15.89853	44.3	33.6	40	39.3	5.384236
E41	225	23.4	10	10	14.46667	7.736494	38.9	26.8	105	56.9	42.09287
E43	237	329	10	10	116.3333	184.1747	33.1	22.8	39.1	31.66667	8.243988
E45	249		36.7	116	76.35	56.07357	32.9		91.1	62	41.15361

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