

ABSTRACT

Title of Thesis: QUARRY FINES-AMENDED CHESAPEAKE BAY DREDGED
SEDIMENTS AS POTENTIAL HIGHWAY EMBANKMENT
MATERIALS

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Several hundred million cubic yards of sediment are dredged from various U.S. ports, harbors, and waterways annually to maintain and improve the nation's navigation system for commercial, national defense, and recreational purposes. Most of the dredged materials in these facilities typically classify as ML and MH soils. The current study aims to explore the use of sediments dredged from Chesapeake Bay as potential highway embankment materials by amending them with quarry by-products. Geotechnical analysis is coupled with environmental assessment to ensure satisfactory performance of the dredged materials as an embankment fill material. The compaction and shear properties of the dredged sediments improved upon blending with the quarry by-products. The concentrations of all metals released during the batch leach tests from the treated dredged materials were below the water quality limits. Column leach tests yielded generally low or non-detectable metal concentrations. The results of the geochemical modeling indicated that the leaching of the analyzed metals was solubility-controlled.

**QUARRY FINES-AMENDED CHESAPEAKE BAY DREDGED SEDIMENTS AS
POTENTIAL HIGHWAY EMBANKMENT MATERIALS**

By

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1 INTRODUCTION

Before 1996, the U.S. Environmental Protection Agency (EPA) designated ocean disposal as one of the main ways of storing sea-bottom dredged materials (Farrah and Pickering, 1993). It was estimated that more than 5 million of tons of dredged materials (DM) were disposed of between 2008 and 2014 (USACE, 2015). According to Maryland Port Authority (MPA), around 1.5 million cubic yards of dredged material is removed annually from the harbor channels and anchorages in Maryland. Hart-Miller Island was initially used for the storage of the material, but the island reached its maximum capacity in 2009. Maryland State law stipulates that DM cannot be placed outside the harbor area and almost all the unconfined placement was ceased by the end of 2010. Starting 2009, the sediments dredged from the Baltimore and Annapolis Harbors were stored in Cox Creek Dredged Materials Containment Facility located south of Scott Key Bridge, on the western shore of Patapsco River. The facility has a total projected capacity of 6 million cubic yards and is expected to reach its maximum capacity by 2023. Because of the running cost of the containment facility and lack of storage area, a plan of action to repurpose the facility was required.

Traditional solutions such as ocean disposal of DM are constrained by national and international regulations. The offshore dumping of the dredged ocean sediments causes many negative impacts on the marine ecosystem and the environment. Such open dumping also causes the long-term damaging pollution due to release of the inorganic pollutants like metal contaminants into the surrounding environment. For the improvement of mechanical and geotechnical properties of DM, commonly used soil stabilization technologies can be adopted. If the stabilized DM is reused, then the environmental impact due to the open disposal of the dredged soil can be avoided.

Alternative solutions, such as land disposal, are costly and require large areas (Beyer et al., 1990; Van Hoof 1991; De Haan et al., 1993; Abriak et al., 2004; Life, 2002). Due to shortages of

natural resources and the sustainable development approach adopted by several countries, the beneficial use of dredged sediments has been considered in civil engineering and agriculture applications (Colin, 2003). In 2004, MPA formed a special committee to study the innovative reuse of DM in Maryland. The committee recommended that the State should aim to manage 500,000 cubic yards of DM through innovative reuse by 2023. The Maryland Dredge Material Management Program selected following 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. An analysis conducted by the Maryland Department of the Environment for MPA indicated that chemically-stabilized DM as a structural fill in highway embankment construction can be a viable option due to its potential to reduce the need for dewatering, and to generate a material with acceptable differential settlement and shrinkage properties (IRDM, 2007).

Beneficial utilization projects for DM have been occasionally documented in the literature. For instance, river sediments from Illinois have been used successfully for urban renewal projects in Chicago and for landscape development in public parks in central Illinois (Darmody and Marlin 2008; Darmody et al., 2004; Ebbs et al., 2006). DM from the Mid-Atlantic States has been successfully amended with other residuals to produce manufactured soils for brownfield redevelopment, gardening, and landscaping applications (Lee, 2001).

Sheehan and Harrington (2012) reported the beneficial use of DM in lieu of topsoil because of its acceptable drainage, adequate nutrient and water retention capabilities and nutrient contents. On the other hand, pH, salinity and water content levels of DM were problematic in the context of topsoil standards and required the stabilization of DM to meet these standards. Adverse effects of metal sulfide oxidation from upland placed dredge materials in Belgium have also been noted by Cappuyns et al. (2008), along with similar reports of acid sulfate soil formation for dredge spoil

materials placed in the Mid-Atlantic United States (Fanning and Fanning, 1989; Demas et al. 2004).

The ex-situ remediation of dredged sediments has been widely applied and shown to have the potential to meet the challenge of ever-increasing quantities of heavily polluted sediment (Peng et al., 2009; Wang et al., 2014). Among several ex-situ remediation methods, chemical stabilization technology has been highly regarded (Song et al., 2013; Li et al., 2001). A variety of materials, e.g., cement, lime, bentonite, have been used to stabilize polluted sediments (Zhang et al., 2011). Both the strength properties of these solidified sediments and concentrations of heavy metals in the leachate of sediments have been monitored to ensure the success of the adopted stabilization technique (Wang et al., 2012; Zentar et al., 2008). Strength tests have shown that sediments could be reused as building and roadbed materials upon their stabilization (Dubois et al., 2009; Wang et al., 2012). Moreover, stabilizing technology is environmentally friendly because heavy metals in the sediment can be chemically stabilized and risks associated with the polluted sediment can be dramatically reduced (Rijkenberg and Depree, 2010; Samara et al., 2009; Tomasevic et al., 2013). However, the effectiveness of different additives used for stabilization of DM varies greatly, and leached concentrations of some heavy metals can be still high upon treatment of DM (Alpaslan and Yukselen, 2002; Kumpiene et al., 2008).

Physical and chemical characteristics of marine sediments are considerably different from those of natural soils. Dredged marine sediments contain very high proportions of organic matter, carbonates, sulfides, and chlorides (Peng et al., 2009; Zagula, 1993). The unique characteristics of dredged sediments directly influence the mobility of heavy metals, and the organic matter combining with heavy metals forms a very stable metal–organic complexes (Thoming et al., 2000; Mulligan et al., 2001).

The application of dewatered and stabilized dredged materials in landscaping, agriculture, construction, restoration of previous industrial sites and covering of landfills is a valuable beneficial utilization methodology (Strubbe et al., 1993). However, before any field application, it should be verified via laboratory testing that the pollutants present in DM will not affect the surrounding environment in the short, medium and long-term of the constructed facility (Bradshaw, 1993). The behavior and fate of heavy metals are governed by various physicochemical processes, which dictate their availability and mobility in soil and sediment systems (Tack and Verloo, 1995). Depending on their binding forms, these metals associated with the sediments are available for mobilization and subsequent uptake by plants and living organisms (Förstner, 1989; Lund, 1990; Ramos et al., 1994).

Singh et al. (2000) investigated the leaching potential of DM collected from three different confined disposal sites in Gent, Belgium through laboratory experiments. Leachates derived from the tests were analyzed for different metals (As, Cu, Cr, Co, Cd, Ni, Zn, Pb, and Mn). Potential and actual leachability varied widely among metals in the sediments studied. Potential leachability, which is expressed as a percentage of total metal content, decreased in the following order: Zn>Cd>Mn>Co>Ni>As>Cu>Pb>Cr while the cumulative leachability (expressed as the percentage of potentially leachable metal pool) decreased in the order: As>Cu>Cr>Ni>Zn>Mn>Cd>Co>Pb. Measured leaching data indicated that there is a low risk of surface and groundwater contamination. The same study revealed that carbonates and Fe and Mn oxides in dredge sediments acted as a major scavenger for Cd, Co, Mn, Ni, and Zn, while the organic matter appeared to be an important carrier for Cr, Cu, and Pb.

Ho et al. (2012) performed 96 h pHstat-leaching tests to examine the leaching behavior of elements at pre-set pH values (2, 4, 6, 8, 9 and 11) on the dredged sediments collected from Cam

River in Vietnam. The pH-dependent leaching behavior of As, Cd, Cu, Mn, Pb, and Zn reflected an asymmetric V-shaped pattern in which they leached at high concentrations under highly-acid conditions (pH 2) or highly-alkaline conditions (pH 11), and minimum leachabilities were obtained at pH 6–8. Under the effect of oxidation, the leachability of heavy metals (Cd, Cu, Mn, Pb, and Zn) and As decreased in the studied pH-range, except for Cd and Cu at pHs 2–8 and Pb at pH 2 the leachability increased.

Grubb et al. (2010) investigated the heavy metal leaching from DM and blends of DM-steel slag fines after 365 days of aging using the Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP). Arsenic leaching from the 100% DM, 100% slag fines, and the DM-slag fines blends was extremely low based on the expected concentrations of total As (up to 100 g/kg). 100% DM containing up to ~125 mg/kg of As did not leach above the SPLP detection limit of 0.05 mg/L.

Naganthan et al. (2013) analyzed the leachate behavior of fresh and hardened cementitious slurry consisting of a mixture of fine aggregate or filler made up of quarry dust obtained from a quarry plant in Malaysia. The slurry showed no corrosive characteristics and the metal leaching after 126 days were below the limiting values.

Approximately 175 million tons of quarry by-products are being generated in the United States annually, mostly from crushed stone production operations, creating another waste disposal problem nationally. Quarry by-products are materials that are produced from the crushing operations and contain large percentages of fine particles that pass through the No. 200 sieve. Quarry by-products may be dry screenings collected from below the last decks in dry or wet or screenings, usually obtained from washing aggregates or collected from settling ponds.

Quarry by-products have been used to improve the geotechnical properties of soils (Sridharan et al., 2006). Usually, the parent rock type and production sources determine the physical and chemical composition and mineralogy of quarry by-products but are relatively consistent at each quarry location. Quarry by-product amended soils can be used in embankment, backfill, and subbase construction due to their high CBR values (Soosan et al., 2001). Marginal differences in the gradation of the material and its compaction characteristics have been observed in past studies depending on the source of quarry by-products (Soosan et al., 2005).

Addition of quarry by-products increases the maximum dry unit weight and decreases the optimum moisture content of expansive soils. Amending quarry by-products to expansive soils increases the angle of internal friction and decreases cohesion (Okafor et al., 2012; Agapitus, 2014). Quarry by-products are considered as an alternative to sand due to their availability, acceptable mechanical and hydraulic properties, insensitivity to changes in moisture during construction, and cost (Naik and Kumar, 2003).

Maryland Port Administration (MPA) and Maryland State Highway Administration (SHA) are in need for a pragmatic solution for two compelling long-term problems in the State: the disposal of dredged sediments and beneficial use options for quarry fines, a by-product of the aggregate mining process. The MPA has major challenges maintaining long-term disposal capacity in its confined disposal facilities. In addition, SHA has emphasized the use of quarry fines, potentially a good investment in beneficial use markets. About DM disposal, while the construction industry may be interested in mining the gravel and/or sand fraction from confined disposal facilities, most of the DM in these facilities typically classifies as ML, MH, and CH soil, which are commonly recognized as being among the poorest earthwork construction materials. Hence, the construction industry has shown little interest in them except for landfill cover.

A potentially cost-effective solution to both recycling challenges can be provided by blending quarry by-products with DM to improve the geotechnical and workability characteristics of both materials for urban fill applications. Here, the term workability is used to describe the ease of handling, transport, placement, and compaction of the blends. Accordingly, a comprehensive evaluation of DM and the blends should be undertaken to provide a basis for the geotechnical design and construction of highway embankments.

However, one key issue that precludes DM stabilization with quarry fines is the potential for groundwater and other environmental impacts caused by metals in both products. Moreover, no information exists on stabilization of DM with these by-products. To evaluate the environmental suitability of quarry by-product-amended dredged sediments in potential highway applications, a series of batch-scale and long-term column leaching experiments were conducted. These results, along with the data from geotechnical and index property testing conducted at the University of Maryland are presented in this thesis. The research consisted of the following tasks:

1. Determining the physical properties of DM and the blends of DM and quarry by-products.
2. Performing batch leach tests including pH_{stat} -test and Toxicity Characteristics Leaching Procedure (TCLP) test for determination of leaching properties of DM and its blends with quarry by-products.
3. Conducting column leach tests to understand the long-term leaching potential and controlling mechanisms for trace metals originating from DM and blends of DM and quarry by-products.

4. Simulating the fate and transport of metals in surface waters nearby highway systems via a numerical model.
5. Investigating the effect of pH on metal leaching from DM and blends and conducting speciation analysis via geochemical modelling.

Section 2 discusses the physical properties of the materials used in testing and how addition of quarry by-products changes the compaction and strength characteristics of DM. Section 3 and Section 4 evaluates metal leaching potential of dredged material and its blends with quarry by-products as determined through batch leach tests (pH_{stat} leaching tests and sequential column leaching tests) Section 5 consists of transport of metals in surface waters nearby highway systems via a numerical model and geochemical analysis using VisualMINTEQ. Section 6 is a summary of the results and set of recommendations based on the completed tests.

2 PHYSICAL PROPERTIES

2.1 Materials

Dredged material, originating from Baltimore and Annapolis Harbors, Maryland, and stockpiled in Cox Creek Containment Facility for over 10 years, was used in the current study. Top 0.5 to 1 ft of DM was removed before sampling. The DM was stored in air-tight buckets to preserve natural water content of the samples, and debris and foreign materials were removed by hand, or by sieving through the 19-mm sieve upon transporting the buckets to the laboratory. DM samples were classified as elastic silt (MH) according to Unified Soil Classification System (USCS) and A-7-5(18) according to the American Association of State Highway and Transportation Officials (AASHTO) Classification System.

A clayey soil, commonly used in highway embankment construction by the local Department of Transportation, was also included in the environmental testing program (Section 3). This soil is often placed beneath the industrial by-products used in the embankments, per construction guidelines of the Maryland State Highway Administration. The embankment soil (ES named herein) was classified as low to high plasticity clay (CL-CH), according to Unified Soil Classification System (USCS).

Quarry fines (unwashed and washed) were collected from Vulcan Material company quarry site in Havre de Grace, while pond fines were from Bluegrass in Churchville. Unwashed and washed fines are classified as SM (Silty Sand) according to Unified Soil Classification System (USCS), while pond fines are classified as ML (Inorganic Silt).

Geotechnical and geoenvironmental tests were performed on pure DM and the other three quarry fines all mixed with DM at 50% by weight; DM-unwashed fines (D-UW), DM-washed fines (D-W) and DM-pond fines (D-P). D-UW, D-W and D-P samples were classified as clayey

sand (SC), silty sand (SM) and low plasticity clay (CL-ML), respectively according to the USCS and A-2-6(1), A-2-7(2) and A-4(1), respectively, according to the American Association of State Highway and Transportation Officials (AASHTO) Classification System. Table 2.1 summarizes the physical properties of all materials included in the testing program.

2.2 Methods

Atterberg limit tests (ASTM D 4318) and sieve analysis (ASTM C136) and hydrometer analysis (ASTM D7298) were performed to classify the DM and the blends. Sample passing through U.S. Sieve No. 40 were used in the liquid limit and plastic limit tests. Modified Proctor compaction tests (ASTM D1557) were carried out to determine compaction characteristics of the DM and DM amended with unwashed, washed and pond fines at 50-50% by weight. Unconsolidated-undrained (UU) triaxial test and direct shear tests were performed on DM and the three blends using the procedures outlined in ASTM D2850 and ASTM D3080, respectively.

2.3 Results

2.3.1 Index Properties

Figure 2.1 shows the gradation test results for the DM and the blends. Dredged material is mostly silt (61.2%) with low percentages of fine sand (15.4%) and clay (22.6%). Sediments dredged from navigational channels do not naturally contain coarse or medium sand, because sand will settle before it reaches still waters. In addition, sediments typically do not contain high percentages of clay, because clay particles stay in suspension (Maher et al., 1998). The blends of D-UW, D-W and D-P consisted of 34.5% (16.4% silt, 18.1% clay), 35% (16.2% silt, 18.8% clay) and 65.5% (43.4% silt, 22.1% clay) fines, respectively. There is clearly a reduction in the fines percentage of the three blends as compared to the DM.

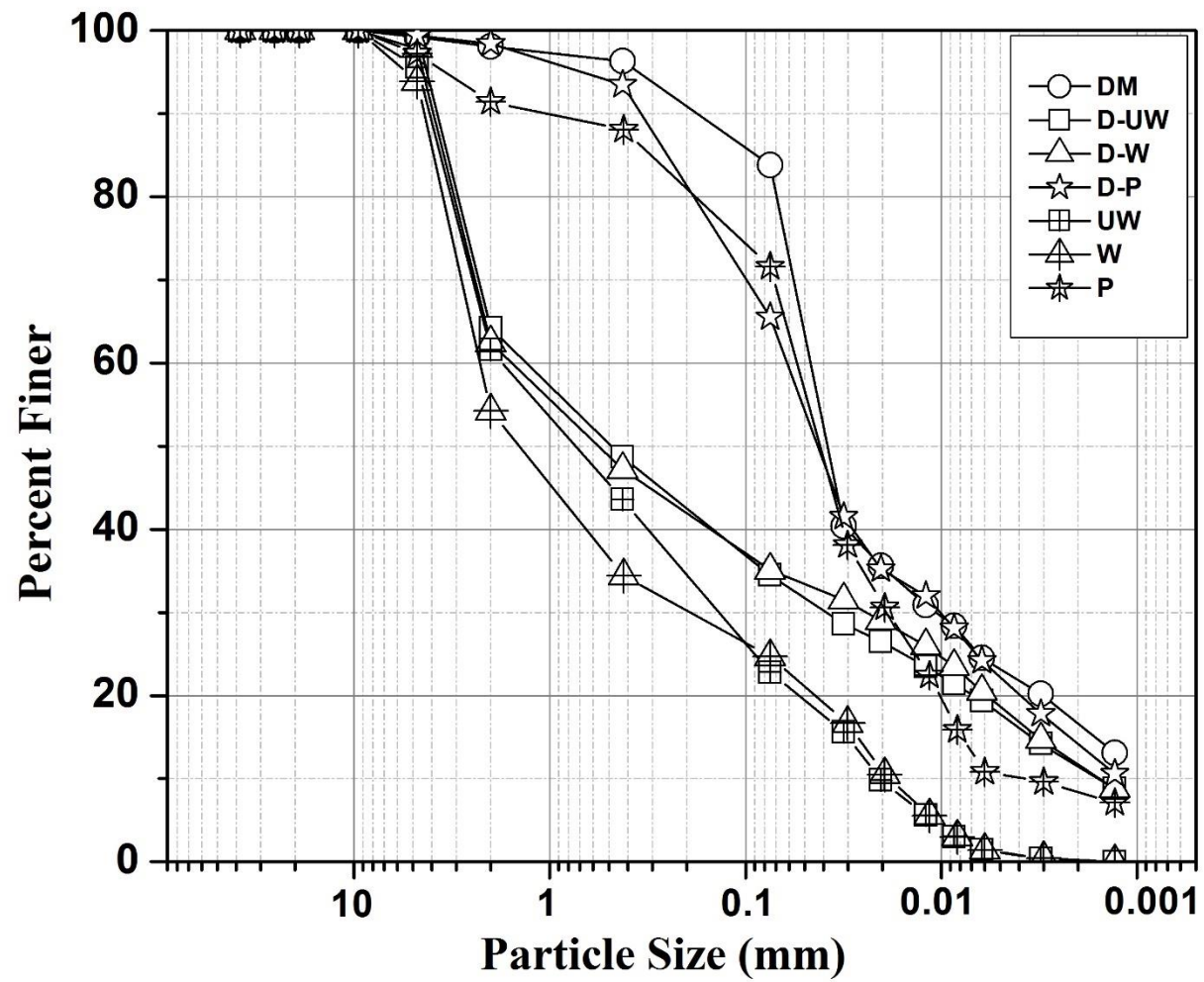


Figure 2.1. Particle size distributions of DM, blends of DM with quarry by-products and only quarry-by-products.

The plasticity indices of D-UW, D-W and D-P are 14, 19 and 4 respectively, per ASTM D4318 (Table 2.1). Addition of unwashed fines or pond fines 50% by weight clearly reduced the plasticity index of DM although there is a slight increase in the plasticity index of D-W blend. The plasticity index decreased from 17 to 4 (reduction of 76%) after the addition of pond fines to DM, thus increasing the workability of the material and reducing the potential for volume change due to variations in moisture content.

DM remains below the A-line and to the right of the liquid limit line ($LL = 54$) on the plasticity chart, and thus classified as elastic silt (MH). There is a clear reduction in the LL of DM after stabilization due to an increase in coarse-sized particles. Prakash et al. (2016) also reported a decrease in consistency limits and plasticity index of DM upon stabilization with quarry dust and related the observed behavior to an increase in coarse-sized particles. Soosan et al. (2001) observed that the liquid limit and plastic limit of a lateritic soil decreased significantly with an increase in the quarry dust content of the mixes.

2.3.2 Compaction Characteristics

Figure 2.2 shows the moisture-unit weight curves for the DM and the blends. Addition of quarry dust leads to an increase in the maximum dry unit weight and a decrease in the optimum moisture content (OMC). The OMC of DM is 24.5% while the OMC of DM-unwashed, DM-washed fines, and DM-pond fines are 16.1%, 15.9%, and 17.5%, respectively. The reduction of OMC in blends is due to formation of coarser solid particles in these mixes (Soosan et al., 2001).

The moisture–unit weight curves for the pure DM exhibit a characteristic convex shape that is typical of MH soils. With the addition of quarry fines at 50% by weight, there is an increase in maximum dry unit weight, and the shape of the compaction curve changes. The maximum dry unit weight of DM is 94.8 pcf [14.9 kN/m^3], while the maximum dry unit weights of D-UW

Table 2.1. Physical properties of the materials tested

Material	Specific Gravity	Gravel (%)	Sand (%)	Fines (%)	Liquid Limit (%)	Plastic Limit (%)	Plasticity Index (%)	USCS Soil Classification
DM	2.68	0.8	15.4	83.8	54	37	17	MH (High plastic silt)
D-UW	2.64	0.3	65.2	34.5	35	21	14	SC (Clayey Sand)
D-W	2.68	2.2	62.8	35.0	48	29	19	SM (Silty Sand)
D-P	2.63	0.6	33.9	65.5	25	21	4	CL-ML (Low plastic clay)
UW	2.77	4.4	72.8	22.8	NP	NP	NP	SM (Silty Sand)
W	2.78	6.2	69.8	24.0	NP	NP	NP	SM (Silty Sand)
P	2.62	0	24.7	75.3	NP	NP	NP	ML (Inorganic Silt)
ES	2.66	1.6	27.2	71.2	50	28	22	CL – CH (High plastic clay)

NP: Non-Plastic

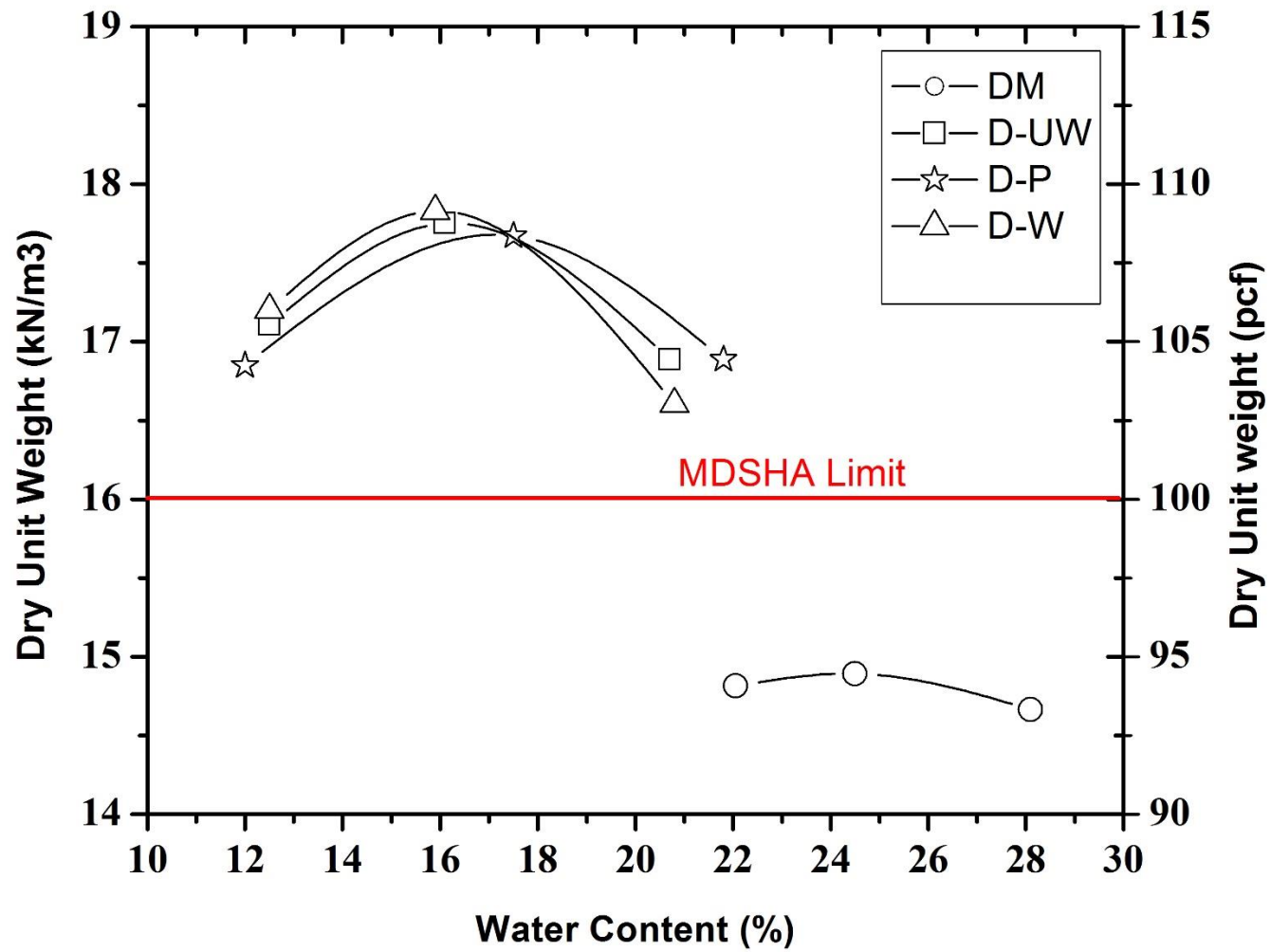


Figure 2.2. Compaction curves of the materials tested

D-W and D-P are 113 pcf [17.7 kN/m³], 113.5 pcf [17.8 kN/m³], and 112.5 pcf [17.7 kN/m³] respectively. Maryland State Highway Administration (SHA) has a minimum acceptable maximum dry unit weight of 100 pcf [15.7 kN/m³] for borrow fill materials used in embankment construction (MDSHA Section 916, 2008). Coarser solid particles and less plastic nature of the blends may have contributed to the increase in maximum unit weights (Nwaiwu et al., 2012). Chetia et al. (2017) also reported an increase in γ_{dmax} and a decrease in OMC of a high plastic silty soil upon stabilization with quarry fines and attributed this change to formation of larger size particles and reduction in clay content.

Shear strength parameters for all the materials are shown in Table 2.2. The effective friction angle for D-UW (45°), D-W (47°), and D-P (38°) are significantly higher than that of DM (30°), as the DM is classified as MH soil while the D-UW, D-W, and D-P are classified as SC, SM, CL-ML, respectively. This significant increase might also be due to an increase in the angularity of the particles in the blends, even though a microscopic analysis was not conducted to confirm this claim. Santamarina and Cho (2004) also showed that the stress–strain response of the sands is strongly influenced by increasing angularity which results in higher peak shear strengths due to an increase in interlocking forces.

Sridharan et al. (2006) studied the shear strength characteristics and failure strain range of soil quarry dust blends and observed that addition of quarry dust to soils reduced the value of cohesion intercept (c) and increased the angle of shearing resistance (ϕ). Prakash et al. (2016) stabilized dredged sediments with the quarry fines. The addition of 50% quarry fines by weight to dredged sediments also increased unconfined compressive strength.

Table 2.2. Compaction and strength parameters of the materials tested

Material	γ_{dmax} (kN/m ³)	OMC (%)	c' (psi)	ϕ'
DM	14.9	24.5	7.20	30
D-UW	17.7	16.1	3.80	45
D-W	17.8	15.9	3.51	47
D-P	17.7	17.5	4.61	38
ES	16.4	26	NT	NT

NT: Not tested.

2.4 Conclusions

A series of geotechnical tests were conducted in the laboratory on DM retrieved from Baltimore and Annapolis Harbors and its blends prepared with quarry by-products. The following conclusions are developed:

- 1) Addition of quarry by-products to dredged material at 50% by weight reduced the value of effective cohesion (c') and increased the angle of internal friction (ϕ'). The increase in ϕ' for blends D-UM, D-W and D-P is 15, 17, and 8 degrees, respectively.
- 2) Stabilization of DM yielded a 20% increase in its dry unit weight coupled with a 36% decrease in OMC. The maximum dry unit weights for the blends prepared with of DM and quarry by-products were above 100 pcf (15.7 kN/m³), a limit set by the local highway department. The results showed that the blends of DM and the quarry by-products have acceptable mechanical values for their potential use in highway embankment construction.
- 3) Engineering properties of DM were improved substantially amending them with the quarry by-products, which has manifested itself in the form of a reduction in liquid limits and plasticity indices.

3 BATCH LEACH TESTS

3.1 Materials

Dredged material (DM) and three different quarry by-products covering a wide range of characteristics were investigated in this study. Blends of DM and quarry by-products were prepared at weight ratios of 50%, and all geotechnical properties were discussed in Section 2 of this report.

Preliminary analysis showed that the material pH of the field-collected DM samples varied from 3.8 to 9.6. Thus, DM with two different pHs, dredged material 1 (D1) with initial pH of 8.18 and dredged material 2 (D2) with initial pH of 7.2, were subjected to a series of batch leach (TCLP and pH_{stat} leaching) tests. The batch leach tests were also performed on the blends of DM with quarry by-products, i.e., unwashed fines (UW), washed fines (W) and pond fines (P).

3.2 Chemical Analysis

ICP-OES (Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometer) was used for the total elemental analysis (TEA) of the materials. As part of the specimen preparation for TEA, 5 mL of HNO₃ was added to 50 mL digestion tubes. The caps of the tubes loosely placed, and the samples were heated at 1200°C for 16 hours. Upon cooling, 1 mL of Hydrogen-Peroxide (H₂O₂) was added to each digestion tube and the tubes were heated on the digestion block for another 30 min, and again removed from the block to cool down. The samples were diluted further at 1:1 ratio and allowed to sit for three hours before the chemical analysis.

The concentrations of all metals for TEA as well as the batch and column leachates were determined using a Varian Vista-MPX CCD Simultaneous ICP-OES (Thermo Jarrell Ash IRIS Advantage Inductively Coupled Plasma Optical Emission Spectrometer). All sampling equipment that contacted the leachate samples was acid-cleaned, dried and stored in clean, sealed bags. A

Table 3.1. Total element analysis of D1, the blends, and the embankment soil

Analyte	D1 (mg/kg)	D1-UW (mg/kg)	D1-W (mg/kg)	D1-P (mg/kg)	ES (mg/kg)	MDL (mg/kg)
Mo	3.3	2.1	2.4	2.3	<2	2
Cu	376.9	208	206.1	220.4	61.7	2
Pb	89.4	55.5	60.1	45.3	<5	5
Zn	277	184	181	154	142	2
Ag	1.1	0.3	0.3	0.6	461	0.5
Ni	409.8	130.6	127	235.7	17.4	2
Co	18.3	16	16.3	30.2	29.1	2
Mn	6817	4206	4594	4312	885	5
Fe	79700	73300	73100	19000	53,700	0.01
As	39	20	23	19	3.24	5
U	3.9	2.5	2.6	2.1	<20	20
Th	11.6	8.4	8.5	5.9	N/A	2
Sr	103	113	118	109	N/A	2
Cd	0.8	0.3	0.3	0.4	<0.4	0.4
Sb	10.6	4.5	6	5.3	N/A	5
Bi	2.30	1.0	1.20	1.20	N/A	5
V	207	176	179	201	138	2
Ca	41000	35300	36900	59700	1940	0.01
P	110	930	940	720	262	0.002
La	38.4	29.2	28.5	20.2	N/A	2
Cr	422	263	260	331	37	2
Mg	15400	19900	19100	32900	6300	0.01
Ba	291	244	239	157	98.6	1
Ti	343	460	464	388	N/A	0.01
Al	56500	62400	62200	66700	47,700	0.01
Na	2980	1615	1683	786	106	0.01
K	14200	10200	10700	8000	2350	0.01
Zr	76	65.4	70.7	49.4	N/A	2
Sn	8	5.10	5.40	4.40	N/A	2
Y	21.1	29.6	27.4	18.3	N/A	2
Nb	21.7	14.8	15.6	12.4	N/A	2
Be	0.7	2.0	2.0	<1	N/A	1
Sc	12	18	18	26	N/A	1
Li	53.6	28.3	28.3	30.5	110	0.1

Table 3.2. Total element analysis of DM, the blends, and the embankment soil

Analyte	D2 (mg/kg)	D2-UW (mg/kg)	D2-W (mg/kg)	D2-P (mg/kg)	ES (mg/kg)	MDL (mg/kg)
Mo	3.2	2.0	2.0	<2	<2	2
Cu	306.5	196	201	216.8	61.7	2
Pb	84.4	51.2	58.7	55.1	<5	5
Zn	252	169	178	161	142	2
Ag	.6	0.2	0.2	0.4	461	0.5
Ni	365.2	140.1	131	25.7	17.4	2
Co	16.0	13.4	14.1	26.1	29.1	2
Mn	8532	4098	4401	4101	885	5
Fe	91000	71300	71500	22000	53,700	0.01
As	35	23	19	17.2	3.24	5
U	3.7	2.1	2.3	2.6	<20	20
Th	10.2	8.1	8.2	6.3	N/A	2
Sr	108	111	110	101	N/A	2
Cd	0.4	0.2	0.2	0.2	<0.4	0.4
Sb	8.3	4.1	5.8	4.1	N/A	5
Bi	1.6	1.0	1.0	1.0	N/A	5
V	252	146	191	193	138	2
Ca	49900	36900	37200	56100	1940	0.01
P	124	920	890	680	262	0.002
La	35.3	22.0	25.5	21.2	N/A	2
Cr	488	271	231	360	37	2
Mg	18400	21000	18200	31100	6300	0.01
Ba	280	231	256	161	98.6	1
Ti	335	466	472	371	N/A	0.01
Al	57200	61800	61900	64600	47,700	0.01
Na	2900	1500	1591	681	106	0.01
K	13900	11300	11700	9200	2350	0.01
Zr	86.6	71.4	72.3	59.1	N/A	2
Sn	8	4.8	4.90	5.20	N/A	2
Y	20.4	31.6	22.4	17.3	N/A	2
Nb	24.3	16.2	14.8	14.1	N/A	2
Be	2	1..3	1.2	<1	N/A	1
Sc	11	20	20	23	N/A	1
Li	47.3	26.4	26.4	29.5	110	0.1

reagent blank was tested every 20 samples and a spiked sample was analyzed every 10 samples for calibration. Minimum detection limits (MDLs) for ICP-OES were determined for each metal, and a set of calibration standards, according to the U.S. Code of Federal Regulations Title 40 was followed. The chemical compositions of the dredged sediments along with the blends are provided in Tables 3.1 and 3.2.

3.3 Methods

3.3.1 pH_{stat} Leaching Test

USEPA Method 1313, a component of the Leaching Environmental Assessment Framework (LEAF) was followed for the pH_{stat} leaching tests. The tests were conducted at different pHs to determine the metal leaching behavior of both dredged materials (D1 and D2) and the blends of DM-quarry by-products. All the equipment used in the laboratory, including the centrifuge tubes, syringes, and filter holders were acid-washed and rinsed with deionized water before usage.

Acid Neutralization Capacity (ANC) curves (i.e., acid-base titration curves) were developed to evaluate the amount of acid or base needed to reach a given pH value for the pH_{stat} tests. Four grams of dry material (particle size < 2 mm) and a liquid-to-solid ratio (L:S) of 10:1 was used. Different volumes of acid (2N/3N Nitric Acid) and 2N sodium hydroxide (NaOH) were added to vary the pH from 2 to 13. Due to space problems, reaction vessels of 50 mL polypropylene centrifuge tubes were used. The samples were rotated through a tumbler at a rate of 28±2 rpm for 48 hours, and additional rotation was performed at 4000±100 rpm for 10 minutes. Titration curves were obtained by plotting the pH values against the required volume of acid or base.

All pH_{stat} leaching tests were also conducted at L:S of 10:1 and a pH range of 2-13. The batches prepared at different pHs were then rotated through a tumbler at a rate of 28±2 rpm for 48

hours. After collection, the batches were centrifuged at 4000 ± 100 rpm for 10 minutes. Centrifugation helped all the major solid particles to settle in the centrifuge tube. To separate the solid and liquid phase, the leachate was then filtered through a $0.45\text{-}\mu\text{m}$ paper filter. pH, electrical conductivity and oxido-reduction potential (ORP) were recorded for each sample. The pH and ORP were measured using an Orion 520A meter model equipped with a sure-flow model pH probe. The electrical conductivity (EC) was measured using a YSI Model 35 conductance meter. The filtered eluate was acidified with nitric acid at $\text{pH} < 2$ and refrigerated at 4°C for further analysis.

3.3.2 Toxicity Characteristics Leaching Procedure (TCLP)

The toxicity characteristics leaching procedure (TCLP), also known as the EPA Method 1311, is a leaching test method developed by the U.S. EPA to determine hazardous characteristic of solid wastes and has been recommended by the Maryland Department of Environment (MDE) for assessing the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. This test involves a simulation of leaching through a landfill and can provide a rating that can prove if the waste is dangerous to the environment or not.

The test was used in the current study to determine whether the DM or blends of DM-quarry by-products can be classified as a hazardous waste or not. The material was leached with an acidic solution, and the resulting leachate quality was used to assess the potential of toxic constituents in a waste material to contaminate groundwater and cause environmental or health concerns.

Sieve number 10 (2 mm) was used to sieve DM and the other blends. An acetate buffer with a pH of 4.93 ± 0.05 was used as the extraction fluid. The liquid-to-solid ratio (L:S) was 20:1. Mixture of extraction fluid with DM and the other blends were rotated at 28 ± 2 rpm using a tumbler for 18 hours. Beckman Coulter Allegra X-22 model was used to centrifuge the samples for 10

minutes at a rate of 4000 ± 100 rpm to allow the solid particles to settle. The leachate was then filtered through a 0.75-micrometer glass fiber filter. Electrical conductivity and pH of the samples were measured upon filtration. All samples were acidified by adding nitric acid at $\text{pH} < 2$ before storing them at 4°C for the ICP-OES analysis.

3.4 Results

3.4.1 pH_{stat} Leaching Test

Figure 3.1 shows the ANC curves for pure dredged materials (D1 and D2) and their corresponding blends with the quarry by-products. Similar neutralization behavior can be observed for the dredged materials and the blends. Addition of large amounts of acid is required to lower the pH, whereas a small amount of base shows a drastic increase in the pHs. This also suggests that quarry by-products do not significantly change the buffering capacity of the DMs tested.

The pH_{stat} test effluents were analyzed for aluminum (Al), arsenic (As), calcium (Ca), iron (Fe), copper (Cu), potassium (K), magnesium (Mg), manganese (Mn), nickel (Ni), and zinc (Zn). Due to their potential risk to the environment and their behavior with the change in pH, six metals selected for further discussion were: aluminum (Al), arsenic (As), copper (Cu), iron (Fe), Nickel (Ni) and Zinc (Zn). Effluent concentrations of most of the other metals were either below detection limits or did not present any relevant leaching pattern worth discussing. Some of the metals like calcium(Ca) and magnesium(Mg) occasionally showed elevated concentrations but they did not present any serious environmental concern as no EPA Water Quality Limit (WQL) was available for them.

In general, four different leaching patterns can be observed during pH_{stat} leaching tests (Figure 3.2). The leaching patterns for the six elements listed above are of two types; cationic or amphoteric. In a cationic pattern, pH and metal concentrations are inversely proportional, i.e., the

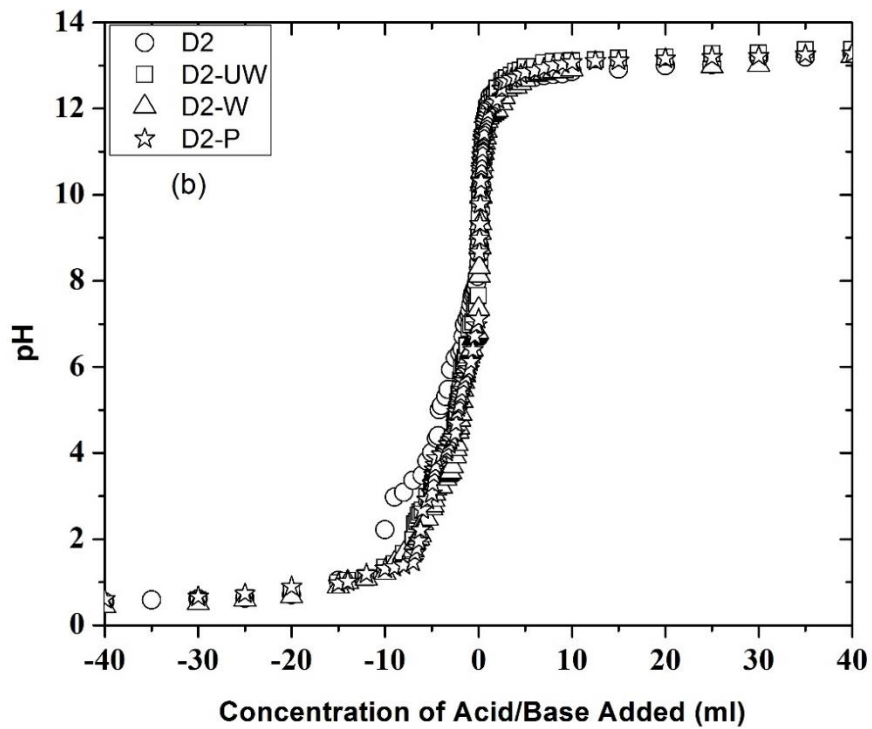
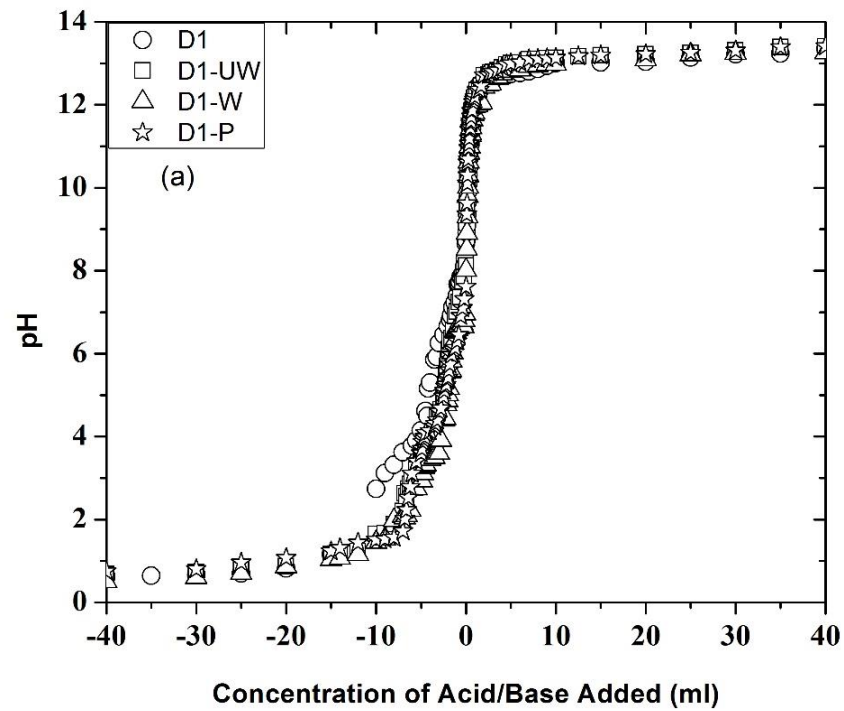


Figure 3.1. Acid Neutralization Capacity (ANC) curves for the (a) D1 and (b) D2 and their blends with the quarry by-products.

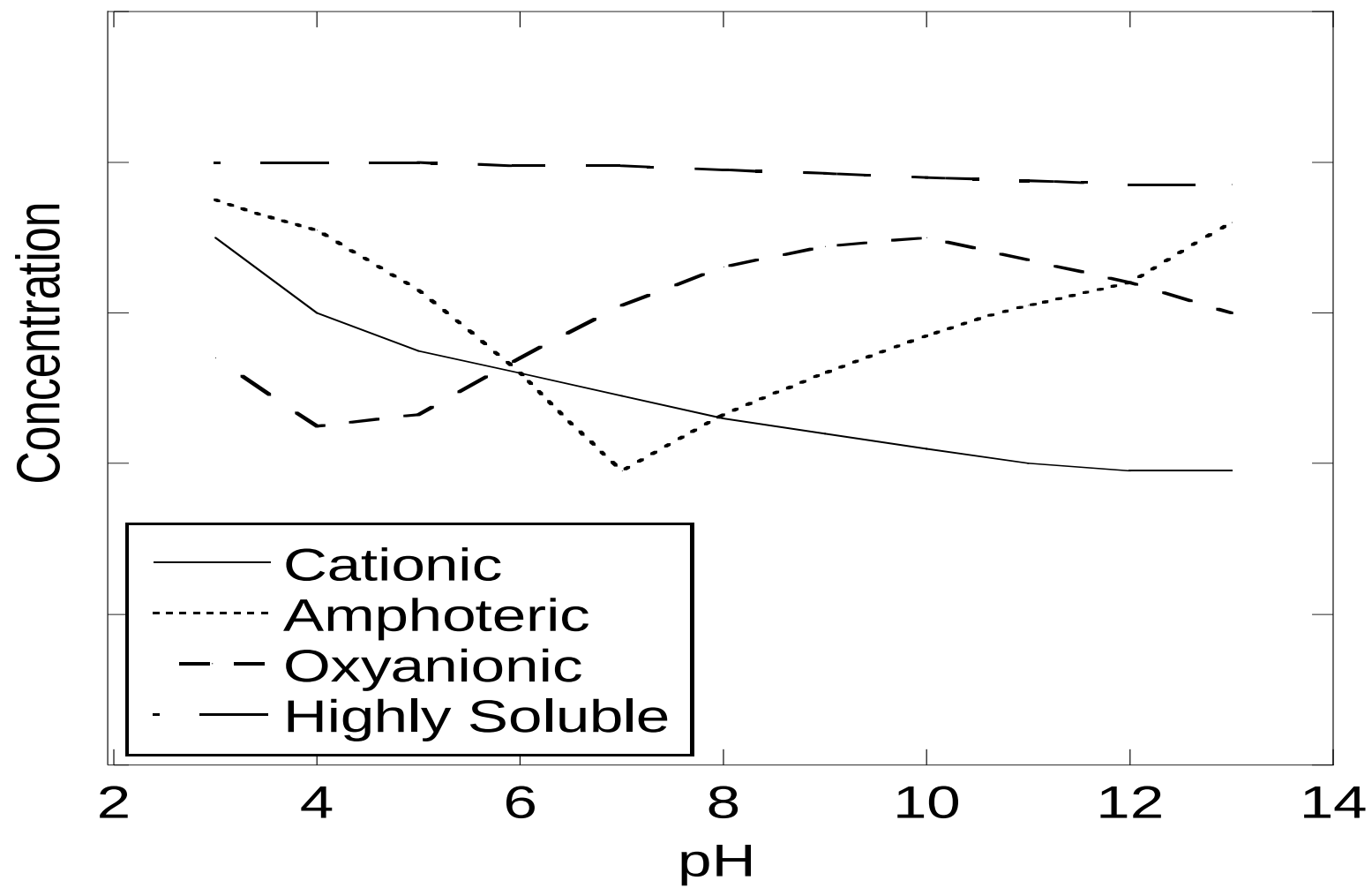


Figure 3.2. Liquid solid partitioning as a function of pH (adapted from Kosson et al. 2002)

metal concentrations decrease with increasing pH, while in amphoteric pattern there is higher leaching of metal concentrations at extreme pHs as compared to those at near neutral pHs. Duplicates were performed for every sample (D1 and D2), so the concentration of metals in pH_{stat} test is the average of concentration of metals in each trial.

Leaching of Aluminum

An amphoteric leaching pattern of Al is observed for both dredged materials and their blends in pH_{stat} leaching tests (Figure 3.3.). Al concentrations for all samples are below the EPA WQL at drinking water pHs (pH 6.5-9). D1 and D2 leach more aluminum than their corresponding blends under acidic and basic pHs, suggesting that the quarry by-products can immobilize the Al present in the dredge material. Al is strongly leached at pH 2 and pH 11, and the lowest concentrations are obtained at pH 5–8, most probably due to formation of $\text{Al}(\text{OH})_3$ in this pH range (Gitari et al., 2008). Cappuyns and Swennen (2008) also reported a V-shaped (amphoteric) pattern for Al leaching from river sediments. Zevenbergen and Comans (1994) and Meima and Comans (1997) suggested that slowly dissolving aluminosilicate minerals may control Al leaching at different pH values. The concentrations of Al presented in Figure 3.3 remain below the EPA WQL (0.75 ppm) at drinking water pHs (pH 6.5-9) and above the WQL at extreme pH values. However, it should be recognized that Al is listed only in the secondary drinking water regulations of EPA and a minimum limit for Al is not listed in Maryland Aquatic Toxicity Limit (ATL) specifications.

Leaching of Arsenic

An amphoteric pattern can be observed for As leaching from D1 and D2 while the leaching from the blends can be described with a cationic pattern (Figure 3.4). The amphoteric leaching pattern for arsenic for dredged materials is well reported in literature (Cappuyns and Swennen 2008;

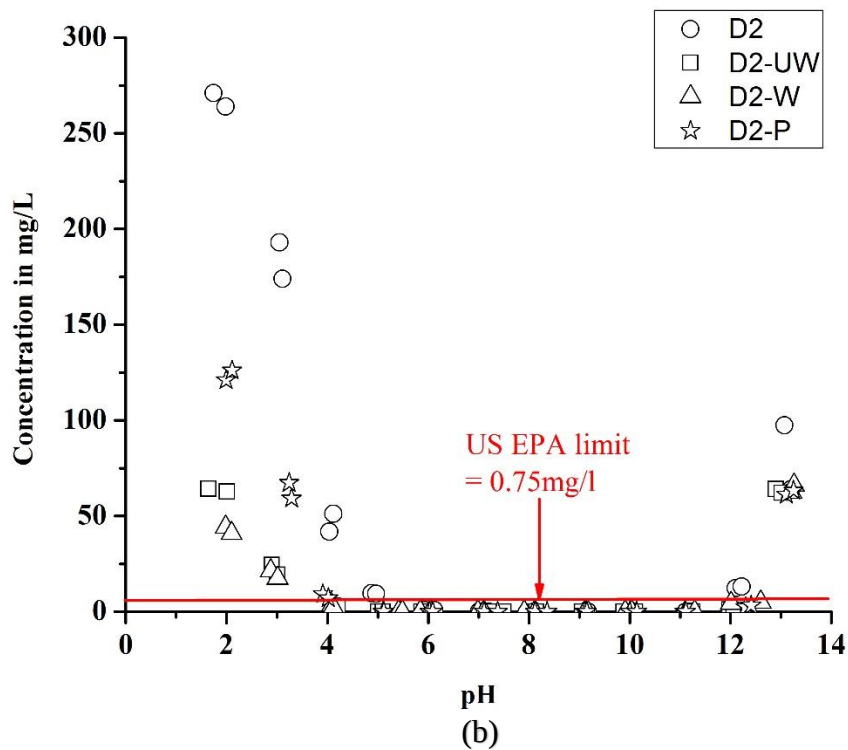
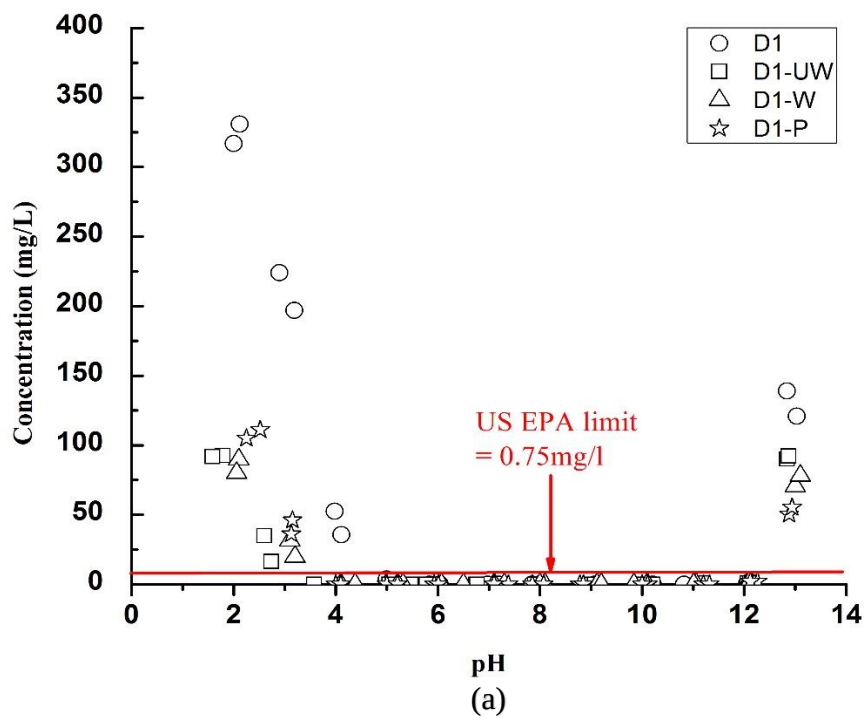


Figure 3.3. Concentrations of Al as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

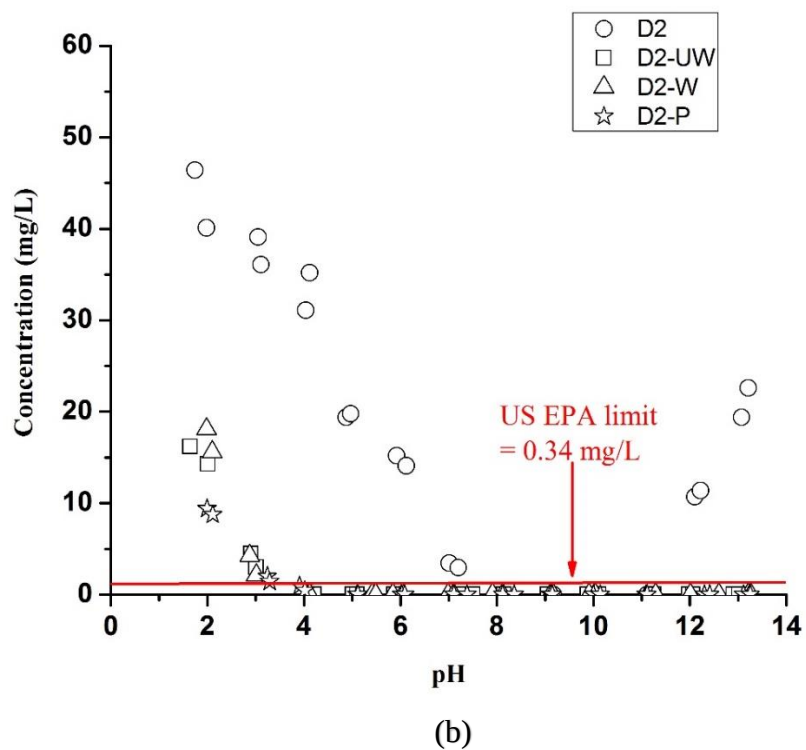
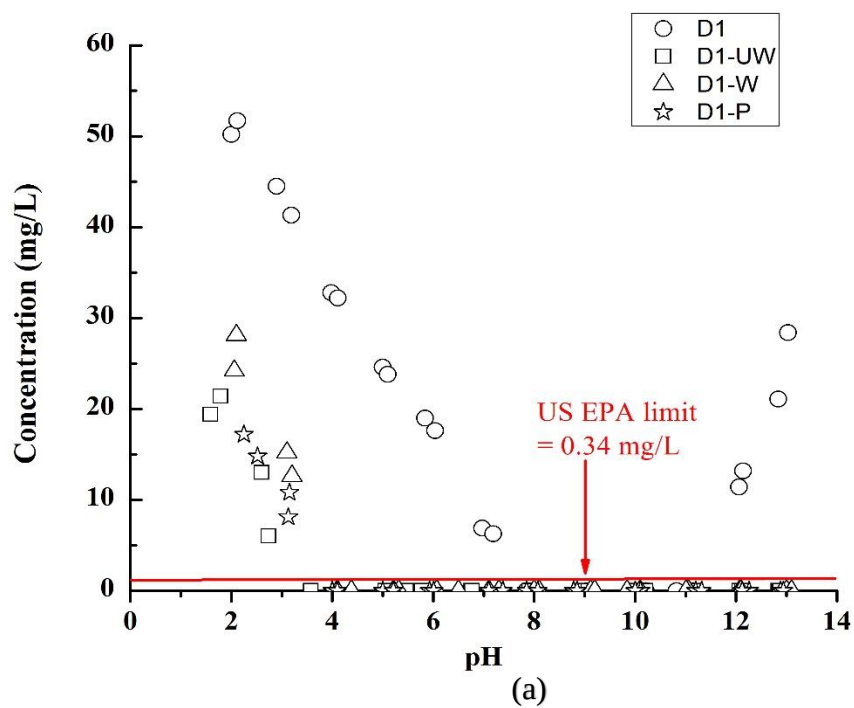


Figure 3.4. Concentrations of As as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

Ho et al., 2012; Lager, 2005; Rubinos et al., 2011; Tack et al., 1995 and Herreweghe et al., 2002). Arsenic concentrations for both D1 and D2 are above the EPA WQL for As (0.34 mg/L) within the EPA recommended drinking water pH range (6.5 to 9), while there is no detectable leaching of As from the blends at this pH range. One of the reasons for measuring no As in the neutral pH range may be due to the maximum sorption of Arsenic(V) on goethite and lepidocrocite at pH 6 and on hematite between pH 7 and pH 8 (Bowell, 1994). Since As occurs as arsenate in oxidized soils and sediments, a higher solubility is expected as pH increases (Cappuyns and Swennen, 2008). The increase in leachability of As at pH>10 could be due to a variation in surface charge as a function of pH. Arsenic occurs in nature mainly as an oxyanion, thus under alkaline conditions the sediment surface is usually negative. This leads to a decrease in the anion retention capacity of the sediment, and therefore, an increase in the leaching of As (Cappuyns and Swennen, 2008). However, the considerable leached amounts of As at pH 2–4 can be due to the dissolution of arsenic in hydroxides, sulfates, phosphates, carbonates and clay minerals at low pH (Van Herreweghe et al., 2002; Cappuyns and Swennen, 2008; Rubinos et al., 2011).

TEA results show that the As concentrations in DM are higher than the ones in the blends (Table 3.1), therefore As leaching is expected to be higher for pure DM. The mobility of As in a soil is mainly controlled by adsorption/desorption processes and co-precipitation with metal oxides. Arsenic have a high adsorption affinity to oxides and hydroxides of Fe and Al (Langmuir et al., 1999; Sracek et al., 2004).

Therefore, the most extensively studied amendments for As immobilization are oxides of Fe and, to a lesser extent, Al and Mn (Kumpiene et al., 2008). The strong leaching of Al and Fe in the current study (Figures 3.3 and 3.6) has probably led to the mobilization of formerly

adsorbed arsenic (Lager et al., 2005). One of the reasons for no leaching of As from the blends at pH>10 may be attributed to the fact that no leaching of Fe was observed at pH>10.

Leaching of Copper

Figure 3.5 shows an amphoteric leaching pattern for Cu for the dredged materials (D1 and D2) as well as their blends prepared with the quarry by-products. Similar observations were made by Martín-Torre et al. (2013) and Cappuyns et al. (2008) during testing of marine sediments. The leached concentrations of Cu are below the U.S EPA WQL (0.013 mg/L) for all samples within the regulated drinking water pH range (6.5-9). At highly acidic and basic pHs, the Cu concentrations leaching from the DM amended with quarry by-products are lower than the ones leaching from pure DM, suggesting that the quarry by-products are able immobilize Cu from DM.

Copper is mainly bound to organic matter and sulphides (Forstner, 1989), and mobility of copper is therefore controlled by redox-related decomposition of oxidisable fraction. Leaching of Cu is reported to be solubility-controlled by the dissolution precipitation reactions of CuO and Cu(OH)₂ (Apul et al., 2005; Komonweeraket et al., 2015). Under acidic conditions, Cu becomes more mobile with decreasing pH because the dissolution of metal hydroxides and carbonates increases and the adsorption at cation exchange surfaces of sediments decrease, while solubility of Cu decreases from the dissolution of sulfide minerals under basic conditions (Van Herreweghe et al., 2002; Rubinos et al., 2011). Copper is known to have a strong tendency to form hydroxo complexes (Tamura and Furuichi, 1997).

The mobility of Cu is usually the lowest at slightly alkaline pH but can increase under highly alkaline conditions (>10) due to the formation of OH complexes (Sloot et al., 1997). High

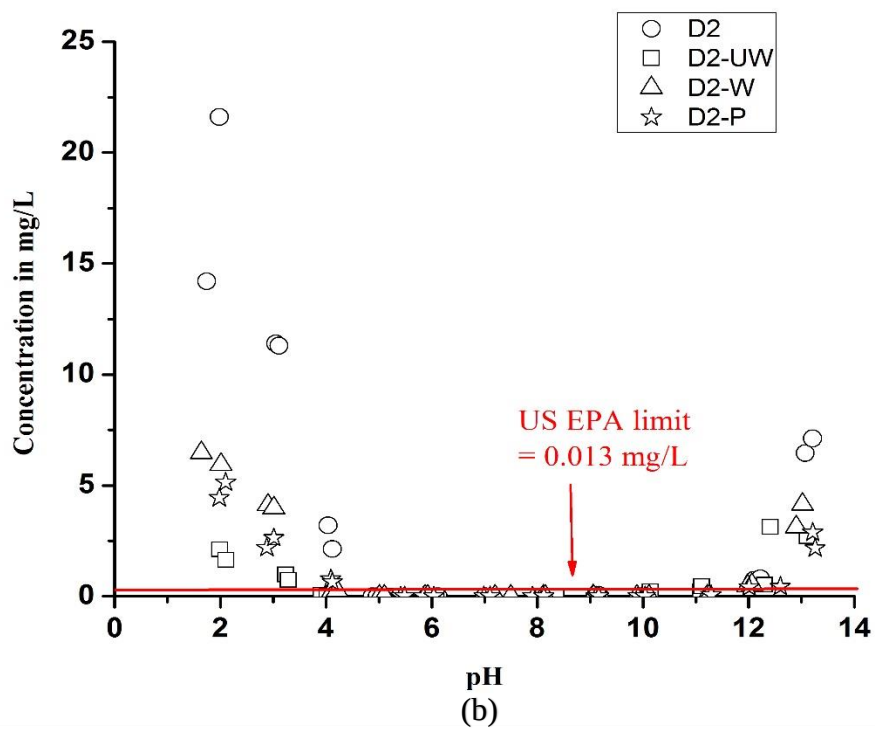
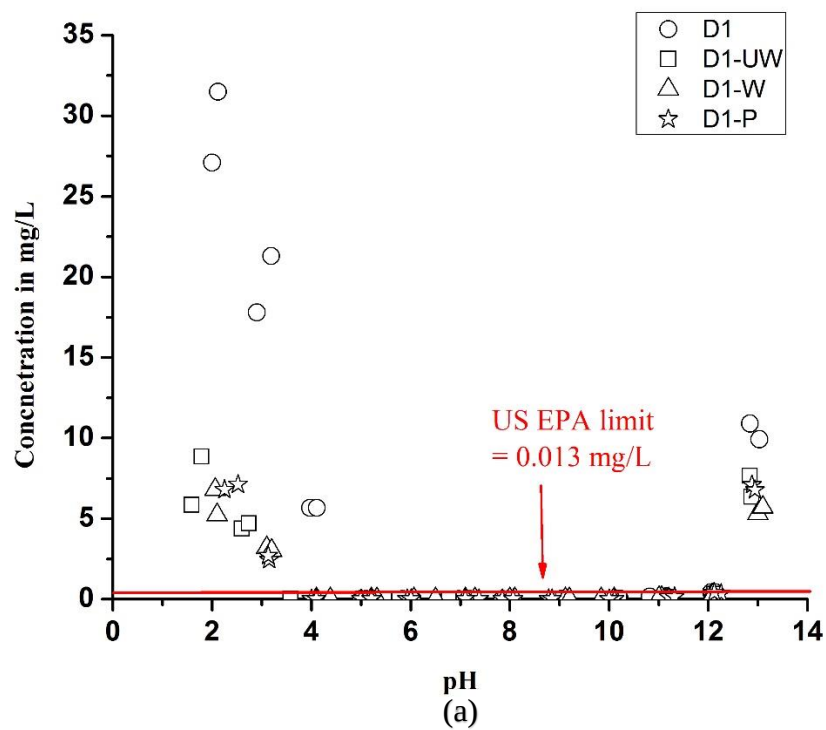


Figure 3.5. Concentrations of Cu as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

leaching of copper under alkaline conditions, which was probably due to the formation of hydroxo complexes, was also reported by van Herreweghe et al. (2002).

Leaching of Iron

Leaching of Fe shows an amphoteric pattern for D1 and D2 while a cationic pattern can be seen for their blends prepared with the quarry by-products (Figure 3.6). In general, heavy metals display the highest mobility at low pH values and the mobility decreases with increasing pH. The sulphides/polysulphide formation by sulphate reducing bacteria has the potential to greatly affect Fe metal concentrations in sediments (Cappuyns and Swennen, 2008). Iron is released from reducible minerals (e.g., oxides/oxyhydroxides) within the sedimentary layers, which generates sulphide precipitates to give ferrous Fe (Billon et al., 2001). Iron is also mobilized when their sulphides are moved into oxidizing environments where they are unstable (Moore et al., 1998).

The presence of Fe in the leachate may be because of complex formation of Fe-dissolved organic carbon (DOC) complexes or the reduction of Fe-oxide. At pH 2, the dissolution of poorly stable Fe- oxides can be responsible for the leaching of Fe, while at pH 10, Fe might be present in the complexed form, probably with DOC as Fe has a high affinity for DOC (Cappuyns and Swennen, 2008). In the current study, the DM-quarry by-product blends leach less Fe as compared to pure DM (D1 and D2) under acidic and alkaline conditions. It is important to note that even though Fe does not have a U.S EPA WQL, the Fe concentrations in the leachates of D1 and D2 and their corresponding blends with the quarry by-products are below the U.S EPA maximum concentration limit for drinking water (10 ppm) for iron between pH 6.5 and 9.

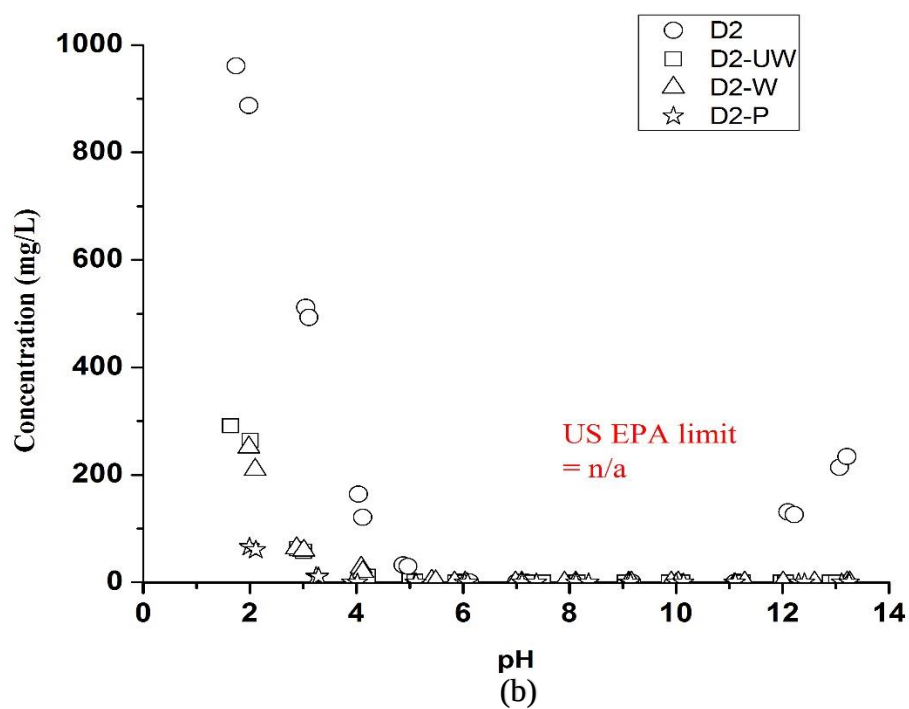
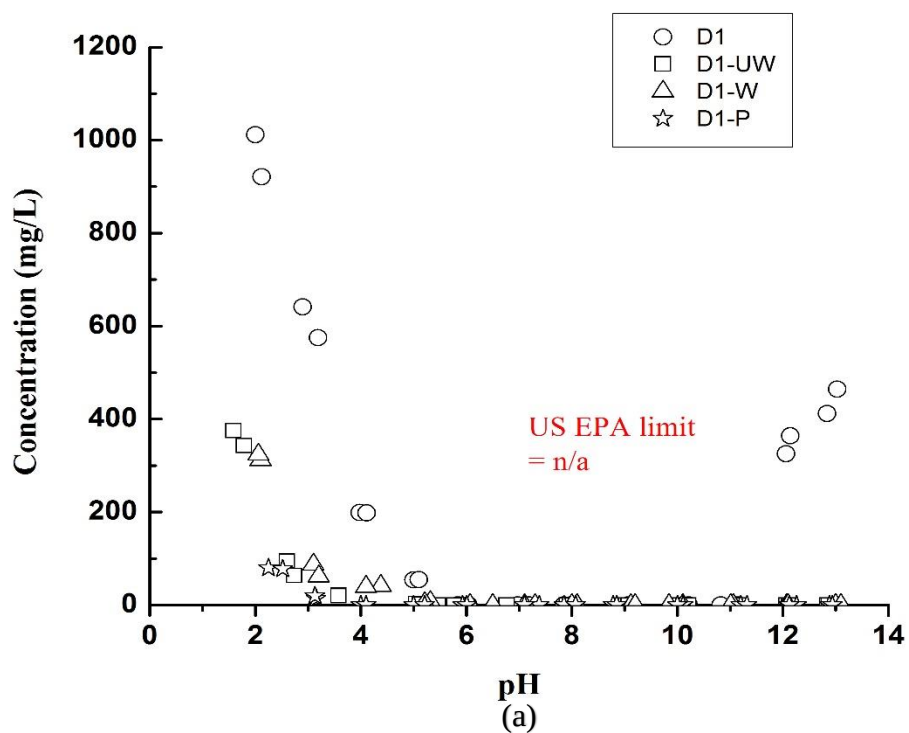


Figure 3.6. Concentrations of Fe as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

Leaching of Nickel

Ni follows an amphoteric pattern for the D1 and D2 and a cationic pattern for their corresponding blends with quarry by-products (Figure 3.7). There is a significant drop in Ni concentrations at pH 6 to 8, which may be due to sorption of the metals on the DM and its blends (Tack et al., 1996; Lager et al., 2005). Trace metals like Ni can co-precipitate or adsorb to Fe/Mn oxides. Nickel was reported to primarily co-precipitate with Mn oxides in salt marsh sediments (Zwolsman et al., 1993). The leaching of heavy metals from soils and sediments is to a large extent determined by the release of DOC. Organic carbon can bind metals and organic contaminants, whereas DOC can mobilize metals and organic contaminants. Generally, the solubility of DOC increases with increasing pH; however, aquatic sediments contain a higher proportion of fulvic acids than terrestrial soils and sediments (Cappuyns and Swennen, 2008).

A possible explanation of the release of Ni under alkaline conditions is the dissolution of organic matter and the complexation of dissolved Ni by DOC. TEA results indicate that there is higher amount of Ni in a DM than its corresponding blends (Table 3.1), therefore Ni leaching at extremely low pHs is expected to be higher for both DMs as compared to the blends. However, around near-neutral pHs (~7-8), there is negligible leaching of Ni from D1 and D2 and the blends. Nickel leaching from the dredged materials and the blends are below the EPA WQL (0.47 ppm) within the EPA recommended drinking water pH range (6.5 to 9).

Leaching of Zinc

As illustrated in Figure 3.8, the Zn concentrations in the leachates are below the U.S EPA WQL (0.12 ppm) within the regulated drinking water pH values (pH 6.5-9). Leaching of Zn shows a

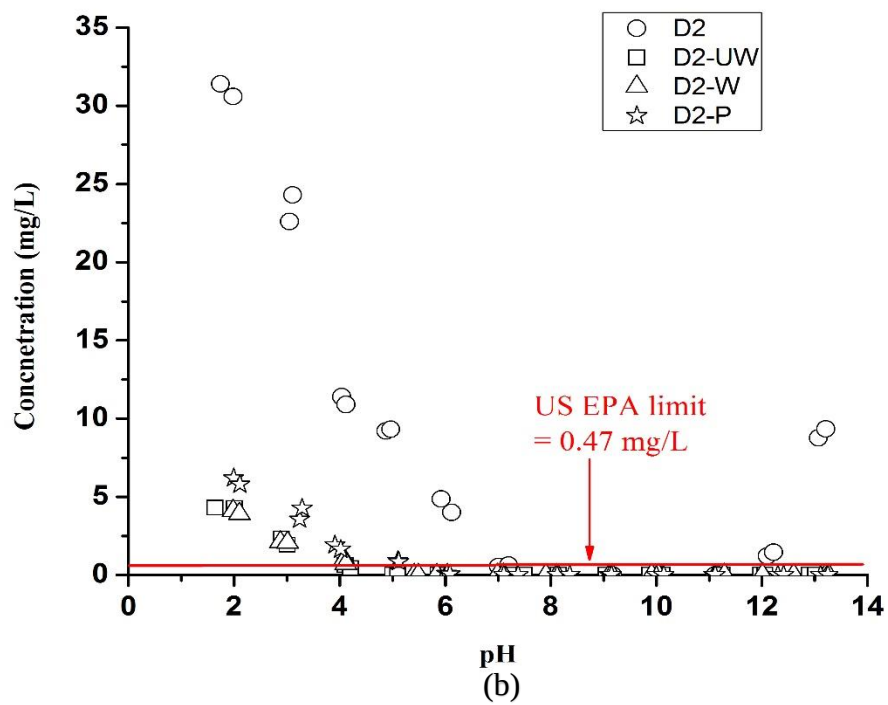
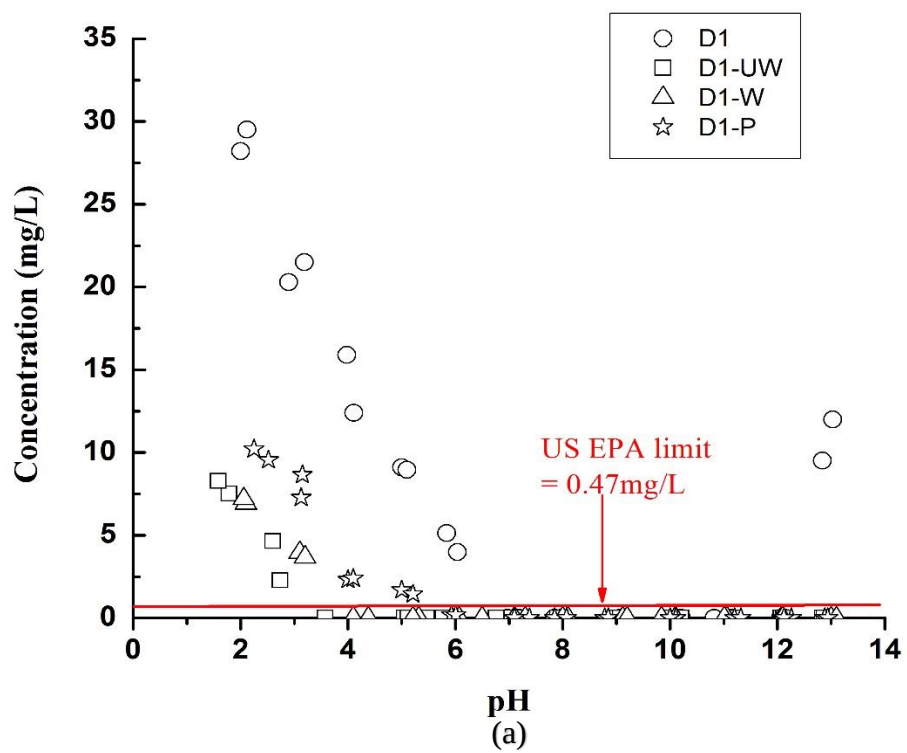
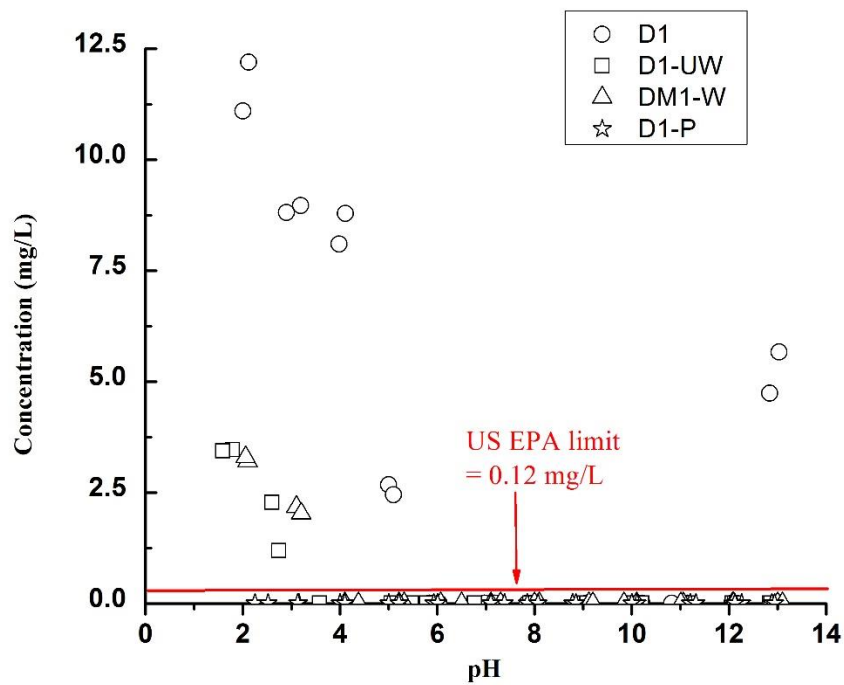
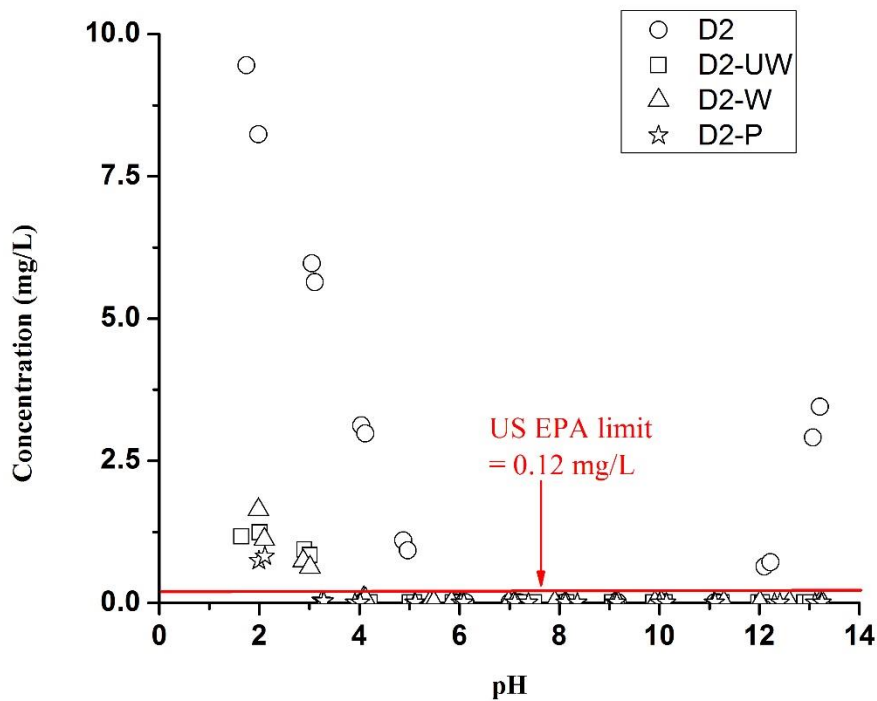


Figure 3.7. Concentrations of Ni as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.



(a)



(b)

Figure 3.8. Concentrations of Zn as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

cationic behavior for the blends, and an amphoteric leaching pattern is evident for D1 and D2, like the observations made by Cappuyns and Swennen (2008) and Martín-Torre et al. (2013). Although the Zn in the DM and blends is in the range of 244– 154 mg/kg (Table 3.1), the leaching patterns seem to be strongly dependent on the pH of the solution. The amphoteric characteristics of Zn leaching is observed because of its high solubility at both low and high pH values, and when pH is higher than 12, the solubility increases mainly due to the formation of hydroxide complexes (Quina et al., 2003). Zn starts precipitating as Zn(OH)_2 and dissolves completely as Zn(OH)_3^- under highly alkaline pH conditions (Cotton and Wilkinson, 1999). Zn can precipitate with hydroxides, carbonates, phosphates, sulfides, molybdates and several other anions and form complexes with organic ligands (Kiekens, 1995). It is known that heavy metals (e.g., Cd, Cu, Mn, Pb and Zn) have great affinity for organic matter because of their capacity to form stable complexes with humic material (Dijkstra et al., 2006), thus an increase of organic matter released in the solution can lead to an increase in metal leaching (Centioli et al., 2008). One of the reasons for observing a cationic leaching pattern for Zn in the blends may be since the organic matter in blends is less than that in DM.

The leached concentrations of all these six metals are the highest under acidic conditions ($\text{pH} < 4$) as compared to natural ($\text{pH} 6\text{--}8$) and basic conditions ($\text{pH} > 11$). The leaching of heavy metals is highly mobilized at $\text{pH} < 4$ because of the presence of H^+ ions in the acid which replaces the cations from their binding sites, and thus increases leaching ability of metals. Therefore, as the pH increases, lower metal concentrations are recorded due to the low presence of H^+ ions to break the cations binding sites, thus favoring adsorption. On the other hand, the precipitation under alkaline conditions involves the reaction of the cations with the hydroxide ion (OH^-) to form metal hydroxides at high pH ($\text{pH} > 12$).

3.4.2 TCLP Test Results

The toxicity characteristic leaching procedure (TCLP) method was used to analyze metal leaching from the dredged sediments and their blends with the quarry by-products. The pH of the TCLP effluents ranges from 5.88 to 6.33, as shown in Figure 3.3. Concentrations of Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, V and Zn leached from both the dredged materials and the blends, and the data is presented in Table 3.3. Both the dredged materials and their blends show no detectable metals (except for Mn) in TCLP leachates, which may indicate that these metals may be associated with the other sediment matrixes, such as organic matter fraction, Fe–Mn oxides fractions, and/or residual fractions (Chen et al., 2015; Guevarariba et al., 2004; Passos et al., 2010; Morillo et al., 2004 and Cuong et al., 2006). Elevated concentrations of Mn can be observed even though there is no EPA limit listed for this metal. Mn complexes with free OH⁻ ions and precipitates as Mn (hydro)oxides in aqueous solution at neutral and alkaline pHs (Cetin et al., 2012). Mixing D1 with quarry by-products shows a reduction in Mn leaching like the observations made by Kadir et al. (2017) during testing of quarry dust amendment into clay bricks.

Table 3.3. TCLP effluent metal concentrations for D1 and D2 and the blends prepared with the quarry by-products

TCLP	TCLP pH	Al (mg/L)	As (mg/L)	Ba (mg/L)	Cu (mg/L)	Mn (mg/L)	Zn (mg/L)
D1	6.33	BDL	BDL	BDL	BDL	11.2	BDL
D1-UW	6.11	BDL	BDL	BDL	BDL	9.81	BDL
D1-W	5.88	BDL	BDL	BDL	BDL	7.81	BDL
D1-P	6.01	BDL	BDL	BDL	BDL	7.85	BDL
D2	6.47	BDL	BDL	BDL	BDL	BDL	BDL
D2-UW	6.32	BDL	BDL	BDL	BDL	BDL	BDL
D2-W	6.13	BDL	BDL	BDL	BDL	BDL	BDL
D2-P	5.84	BDL	BDL	BDL	BDL	BDL	BDL
U.S EPA WQL (mg/L)	6.5-9	0.75	0.15	NA	0.06	NA	0.12
MDL (mg/L)		0.001	0.001	0.001	0.001	0.02	0.005
TCLP Regulatory Limits		NA	5	100	NA	NA	NA

Table 3.3. (cont'd) TCLP effluent metal concentrations for D1 and D2 and the blends prepared with the quarry by-products

Specimen Name	TCLP pH	Na (mg/L)	Ni (mg/L)	P (mg/L)	Pb (mg/L)	Fe (mg/L)	V (mg/L)
D1	6.33	BDL	BDL	BDL	BDL	BDL	BDL
D1-UW	6.11	BDL	BDL	BDL	BDL	BDL	BDL
D1-W	5.88	BDL	BDL	BDL	BDL	BDL	BDL
D1-P	6.01	BDL	BDL	BDL	BDL	BDL	BDL
D2	6.47	BDL	BDL	BDL	BDL	BDL	BDL
D2-UW	6.32	BDL	BDL	BDL	BDL	BDL	BDL
D2-W	6.13	BDL	BDL	BDL	BDL	BDL	BDL
D2-P	5.84	BDL	BDL	BDL	BDL	BDL	BDL
U.S EPA WQL (mg/L)	6.5-9	NA	0.052	NA	0.065	1	NA
MDL (mg/L)		1	0.01	0.01	0.01	0.01	0.01
TCLP Regulatory Limits		NA	NA	NA	5	NA	NA

Table 3.3. (cont'd) TCLP effluent metal concentrations for D1 and D2 and the blends prepared with the quarry by-products

Specimen Name	TCLP pH	B (mg/L)	Cd (mg/L)	Co (mg/L)	Cr (mg/L)	K (mg/L)	Mg (mg/L)
D1	6.33	BDL	BDL	BDL	BDL	BDL	BDL
D1-UW	6.11	BDL	BDL	BDL	BDL	BDL	BDL
D1-W	5.88	BDL	BDL	BDL	BDL	BDL	BDL
D1-P	6.01	BDL	BDL	BDL	BDL	BDL	BDL
D2	6.47	BDL	BDL	BDL	BDL	BDL	BDL
D2-UW	6.32	BDL	BDL	BDL	BDL	BDL	BDL
D2-W	6.13	BDL	BDL	BDL	BDL	BDL	BDL
D2-P	5.84	BDL	BDL	BDL	BDL	BDL	BDL
U.S EPA WQL (mg/L)	6.5-9	0.75	0.002	NA	0.011	NA	NA
MDL (mg/L)		0.001	0.001	0.001	0.001	1	1
TCLP Regulatory Limits		NA	1	NA	0.2	NA	NA

3.5 Conclusions

A series of batch leaching (pH_{stat} and TCLP) tests were conducted to investigate the environmental impacts of pure and quarry by-product-amended DM in a highway environment. The following conclusions can be warranted based on the findings:

pH_{stat} leaching test

- Both dredged materials (D1 and D2) and their blends with the quarry by-products showed a similar neutralization behavior, suggesting a very small difference in the amounts of acid or base that was needed to reach a near-neutral pH value for the DM and its blends.
- Leaching of Al, As, Cu, Fe, Ni and Zn followed a mix of cationic and amphoteric patterns.
- The concentrations of all six metals (except for As) leached from the pure dredged materials were below the U.S EPA WQL within the drinking water pH range (pH = 6.5-9).
- The concentrations of all six metals leached from the blends of DM and quarry by-products were below the U.S EPA WQL within the drinking water pH range (pH = 6.5-9).

TCLP tests

- Elevated concentrations of Mn were observed in the TCLP effluents of D1 and its blends with the quarry by-products. The addition of quarry by-products generally caused a reduction in the Mn concentrations.
- The TCLP concentrations of all contaminant metals listed by EPA were below the U.S EPA WQL.

4 SEQUENTIAL COLUMN LEACH TESTS

4.1 Method

To simulate flow through a highway embankment constructed with DM or blends of DM with quarry by-products and a thin layer of embankment soil (ES), a series of sequential column leach tests (SCLTs) were conducted. The SCLT setup is shown in Figure 4.1.

The polyvinyl chloride (PVC) columns having a diameter of 4.0 in. [152 mm] and a height of 4.1 in. [155 mm] were operated in an up-flow mode using a peristaltic pump on the influent line. 0.02 M NaCl solution prepared with ASTM Type II water (resistivity > 1 Megaohm-cm, ASTM D1193) at near-neutral pH (pH 6-7) was pumped into the columns. The column specimens were prepared at 2% dry value of their optimum corresponding moisture value using the modified Proctor compaction effort (ASTM D 1557). The effluent tubing of the first column, which contained pure or treated DM, was connected to the second column which contained the embankment soil. On the effluent end of the column, leachates were collected in 50 mL tubes. pH and electrical conductivity (EC) of effluent samples were recorded immediately after sample collection. The leachate samples were filtered using a 0.2- μ m membrane filter and acidified to pH<2 using 2% HNO₃ before storing them at 39°F [4°C] for further analysis.

An inflow rate of 12.5 mL/hr. was used in all SCLTS. Naka et al. (2016) tested the effect of flow rates on pH, EC and the release of inorganic ions on five different types of soils. The two flow rates chose in that research project (12 and 36 mL/h) had little or no effect on the release of cations and anions. Lopez Meza et al. (2010) studied the effect of contact time on the release of inorganic components from bottom ash and demolition waste. The contact times (2.5, 5, and 16 hr) had negligible effect on leaching of copper, chromium, sulfate, and chloride.

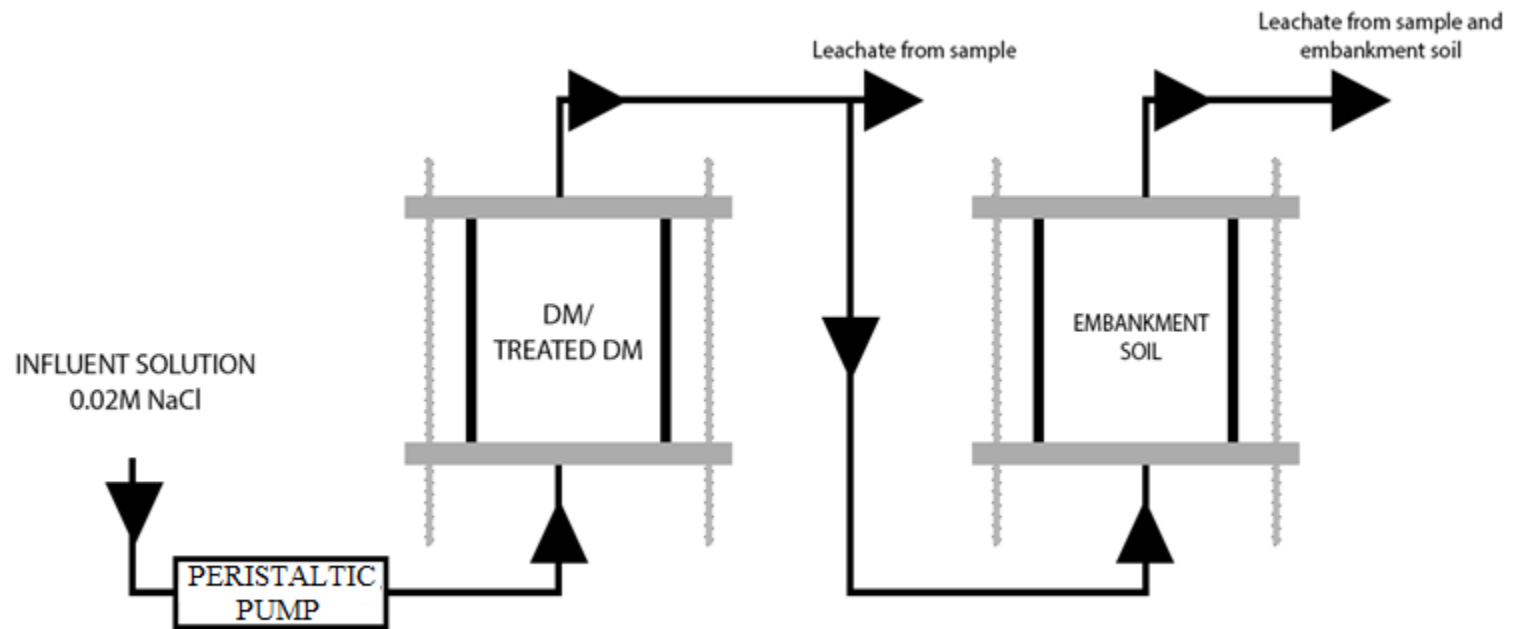


Figure 4.1. Sequential Column Leach Test (SCLT) setup

4.2 Results

4.2.1 pH and Electrical Conductivity

The pH of effluent solution from pure D1 is slightly alkaline (pH 7-8.2), most probably due to the initial pH of D1 (pH = 8.18) while the pH of the effluent solution from pure D2 was in the range of 7.2 to 7.6. The blends of D1 and quarry by-products also show comparable pH values (pH 6.8-8.2), whereas the pH of effluent solution from the blends of D2 and quarry by-products was in the range of 6.8 to 7.8. The effluents originating from the sequential column (effluent from ES) exhibit near-neutral behavior (pH 6-8) for both the DM and its blends with quarry by-products (Figure 4.2). It should be noted that the collecting method did not allow one to avoid contact with air, but gaseous CO₂ exchange may have occurred, with a possible modification of the solution pH.

Lions et al. (2007) performed column leach tests on 5-year-aged DM from France. The effluent pH remained between 6.9 and 7.5 whereas the initial pH of DM was around 7.0. According to them the strong buffer-capacity of the natural DM provided an important resource of acidity while exchangeable cations (Ca, Mg, K) and carbonates contributed to alkalinity. Comparable effluent pH values of ~7.5 were reported by Couvidat et al. (2015) during long-term column testing of dredged sediments.

The electrical conductivity (EC) of column leachates for both the DM and the blends show typical washout trends (Figure 4.3). Since EC is a measure of dissolved ions, a washout curve that monotonically decreases is expected. Myers (1999), Payan et al. (2012) and Couvidat et al. (2015) witnessed the same trends for EC during testing of marine dredged sediments. EC elution curves for DM and blends tested in the current study show no evidence of nonideal flow during testing, i.e., a sudden increase in the EC value followed by rapid declination.

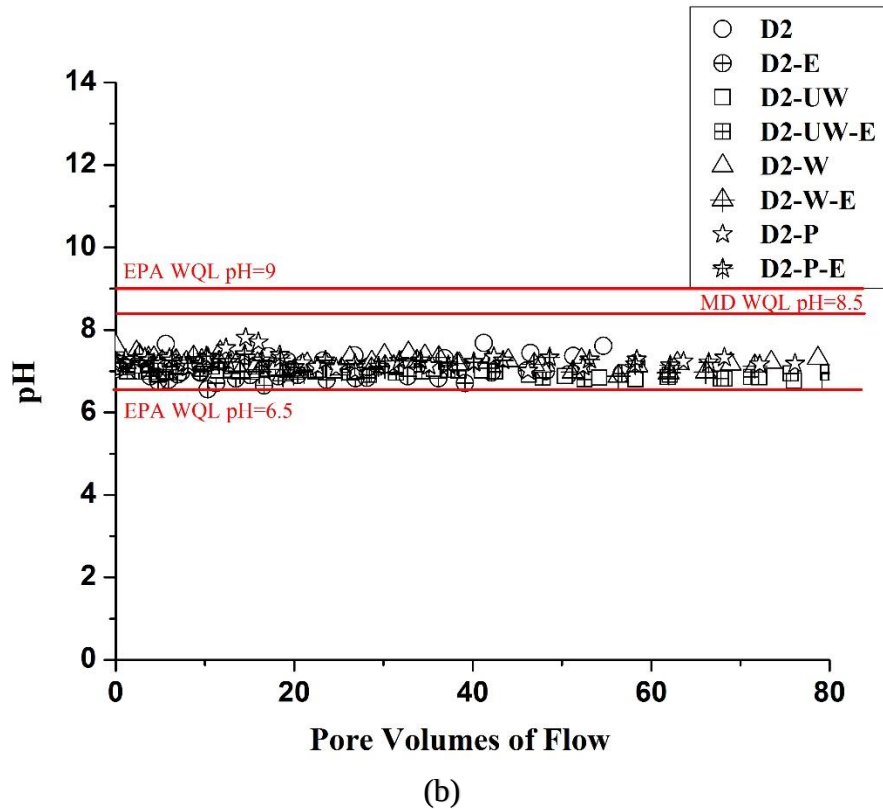
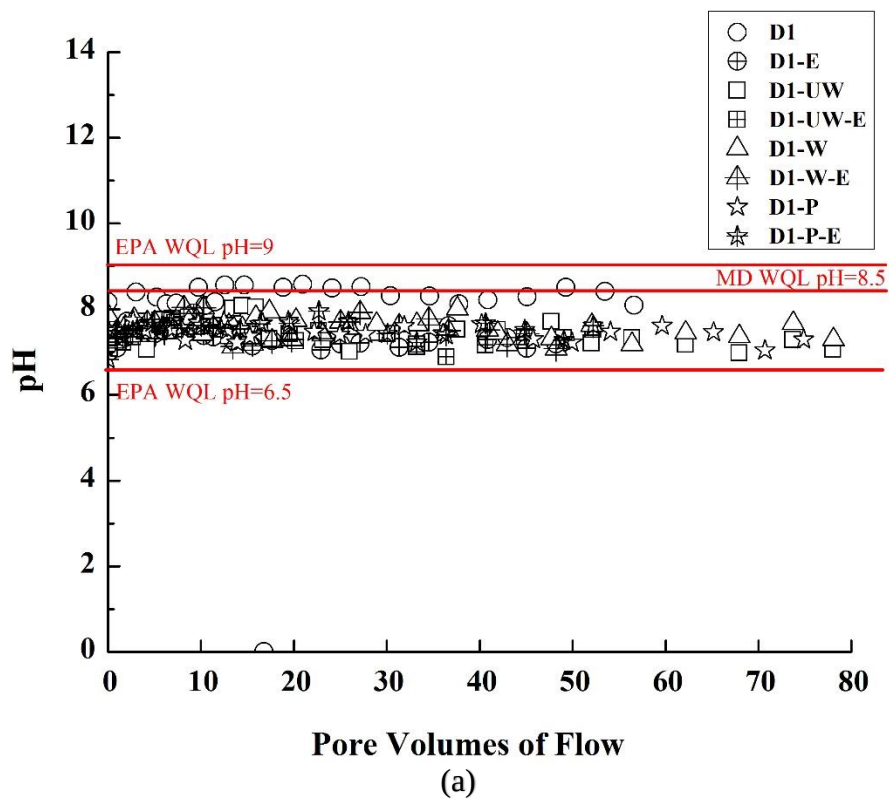


Figure 4.2. pH of effluents for (a) D1 and (b) D2 and its blends with quarry by-products.

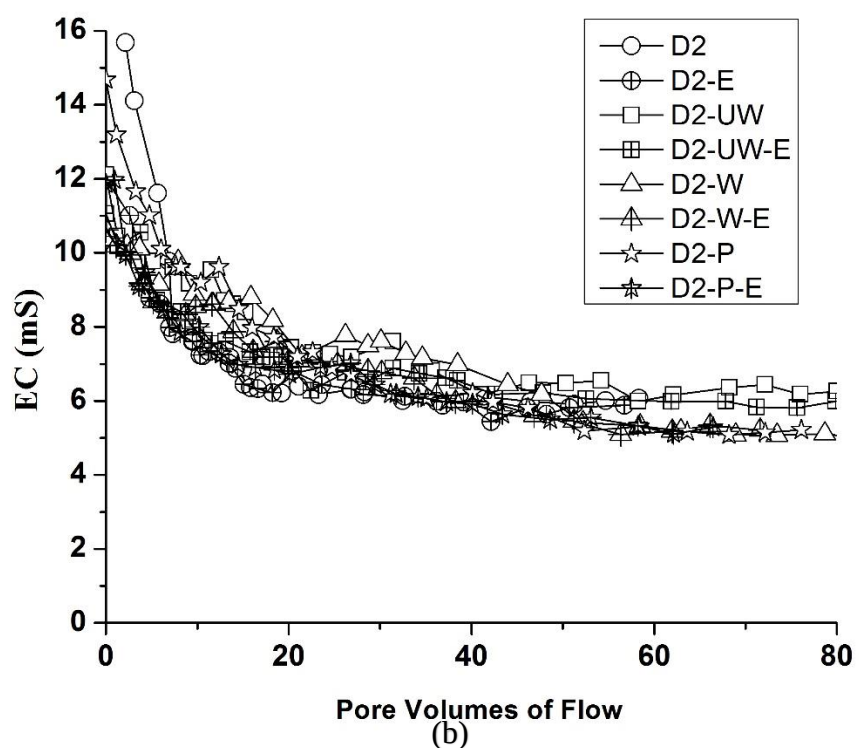
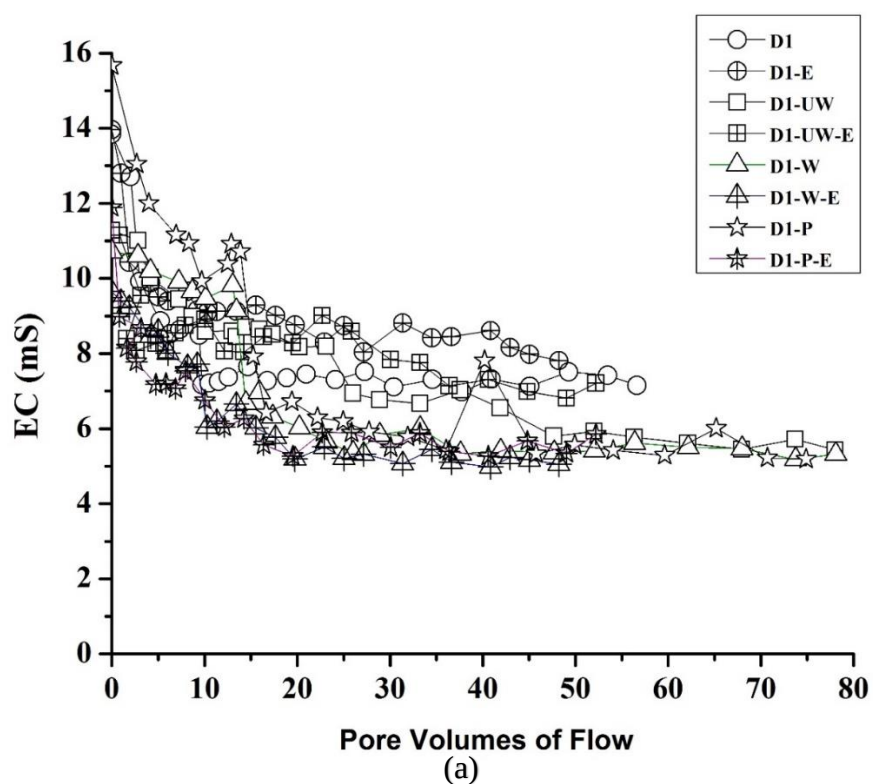


Figure 4.3. EC of effluents in for (a) D1 and (b) D2 and its blends with quarry by-products

4.2.2 Trace Metal Leaching

Water soluble concentrations of inorganic elements (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Na, Ni, Pb, V, and Zn) in these materials, as analyzed by the ICP-OES. Of the elements, As, B, Ba, Cd, Co, Cr, Mn, Pb, and V concentrations in the DM and blends filtrates are below the MDLs. Table 4.1 presents the peak SCLT concentrations for Cu, Fe, Zn and Ni while Figures 4.4 to 4.7 provide the elution curves. The SCLT test was stopped after 80-85 pore volumes as no significant leaching of metal contaminants was observed in the leachates. In general, the metal elution curves, except for Fe, showed a tendency for initial concentrations to decrease, and in several cases rapidly, to steady-state levels.

Leaching of Copper

Copper concentrations in column leachates collected from both the D1 and D2 exceed the U.S. EPA WQL of 0.13 mg/L in the first two and five pore volumes of flow, respectively, but immediately drop to acceptable levels after therein (Figure 4.4). For the blends of both the DM (D1 and D2) with the quarry-by-products, most copper concentrations are below the EPA WQL of 0.13 mg/L after first two pore volumes. Cu concentration in D1, D2 and their corresponding blends with quarry by-products is below the detection limit of 0.001 mg/L after 10 pore volumes.

Myers (1999) also witnessed similar patterns for leaching of Cu in column leach tests conducted on Hamlet City Lake dredged sediments and suggested that the initial Cu leaching was due to the release of Cu from the pore water of sediment cores. As he expected that the leachable Cu was stored in pore water of sediment. After the sediment pore water was eluted, copper release was negligible.

First flush pattern of Cu in DM column leach test was also observed by Couvidat et al. (2015). According to them the first flush pattern might be because of the initial leaching of Cu

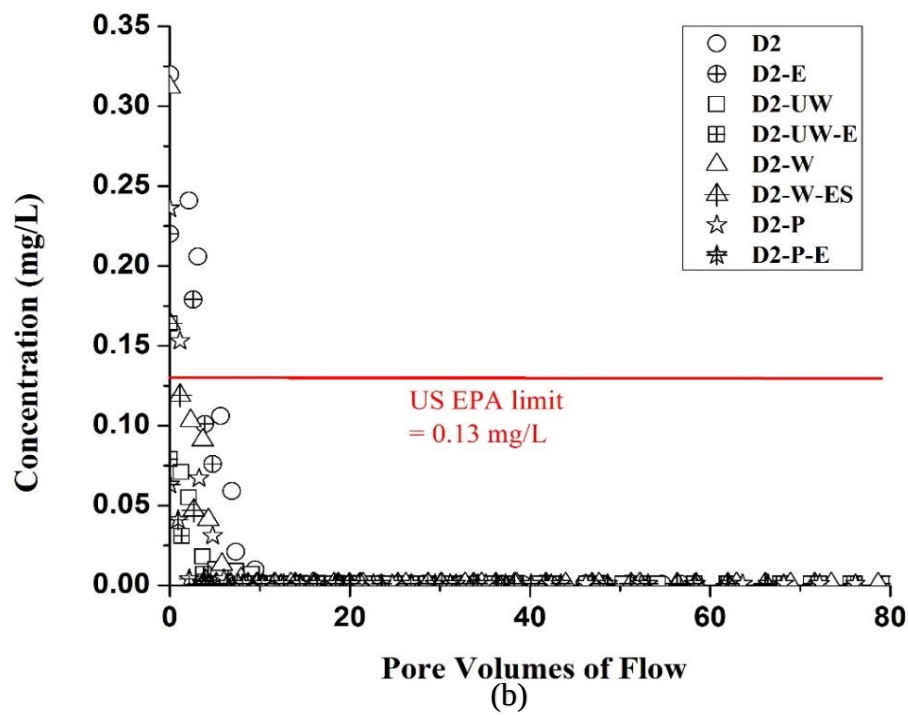
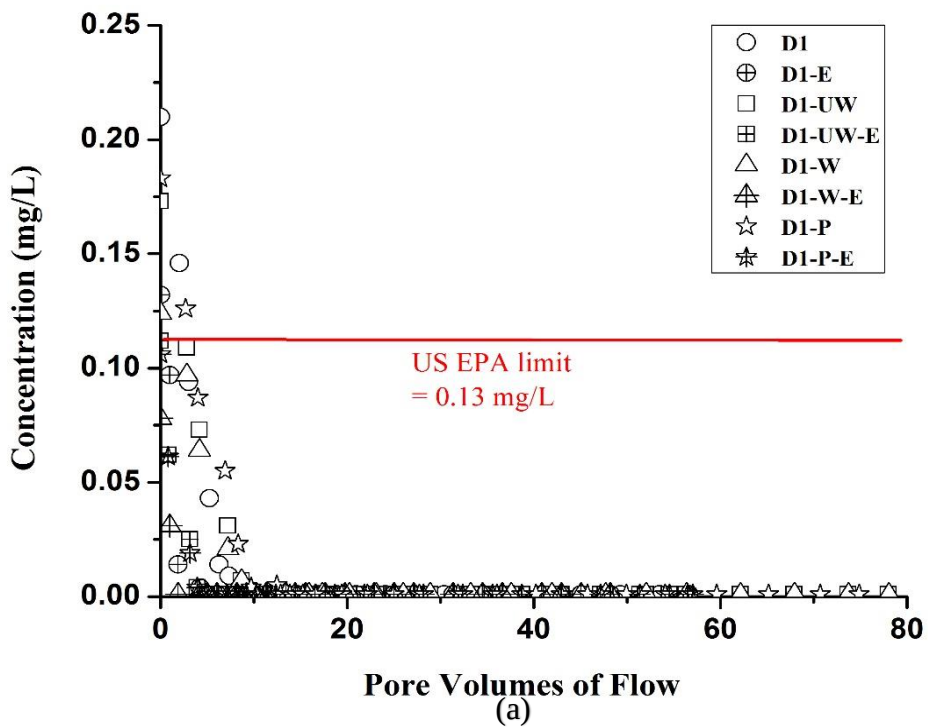


Figure 4.4. SCLT elution curve for Cu for (a) D1 and (b) D2 and its blends with quarry by-products

from the organo-clays aggregate (organic matter physically associated with fine clay grains), as the organo-clay aggregates are associated with minerals, organic matter, and trace metals like Cu and Zn.

Copper leaching can be influenced by the mobility of sulfides (Forstner et al., 1981). The stability of sulfide bound Cu as the stable sulfide-bound metals (such as CuS and pyrite) are unlikely to be oxidized in the short-term due to their slower oxidation kinetics, which eventually results in low Cu concentrations. Organic matter also plays an important role in metal binding in dredged sediments, and the complexation of Cu with dissolved organic carbon (DOC) has been registered as an important factor (Caetano et al., 2002, Stephens et al., 2001). Although DOC measurements were not carried out during the experiments, it is speculated that this parameter has largely influenced the Cu release at the registered pH values.

Leaching of Iron

A lagged pattern can be observed for Fe leaching from the both the DM (D1 and D2) and its blends prepared with the quarry by-products (Figure 4.5), similar to the observations made by Couvidat et al. (2015). In case of pure D1, a sudden increase in Fe concentrations can be observed between five and seven pore volumes of flow while in case of D2 a spike in concentration can be seen after seven pore volumes. The concentration of Fe in D1 increases from 0.12 ppm at four pore volumes to 0.52 ppm at seven pore volumes, while for D2 the concentration increases from 0.11 ppm to 0.41 ppm at seven pore volumes after which the concentrations drop and ultimately to levels below the detection limit of 0.001 ppm after seventeen and eighteen pore volumes, respectively. The maximum Fe concentrations leached from the three blends of both the DM are lower than the

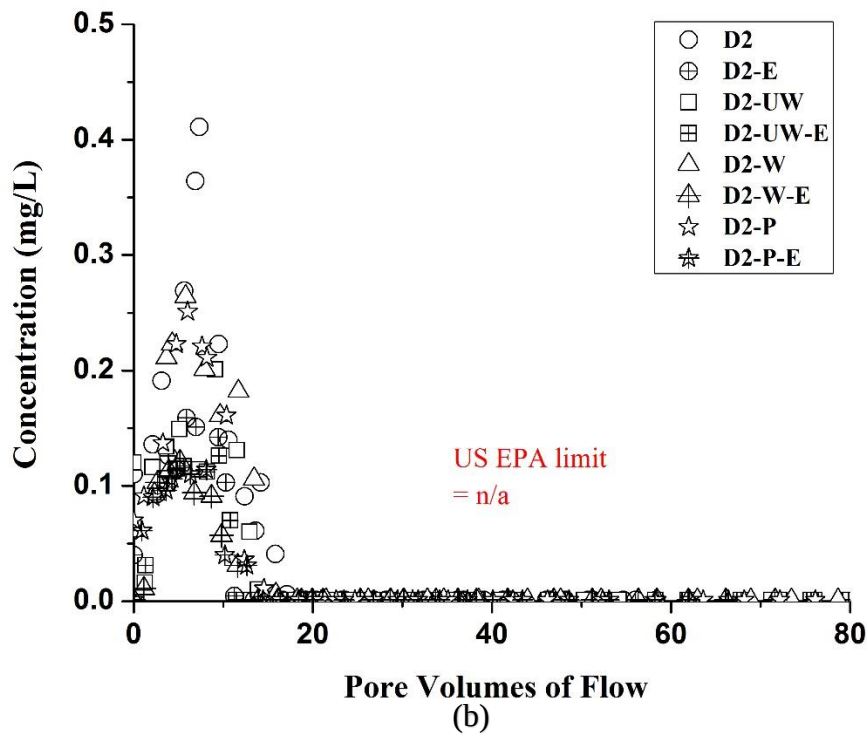
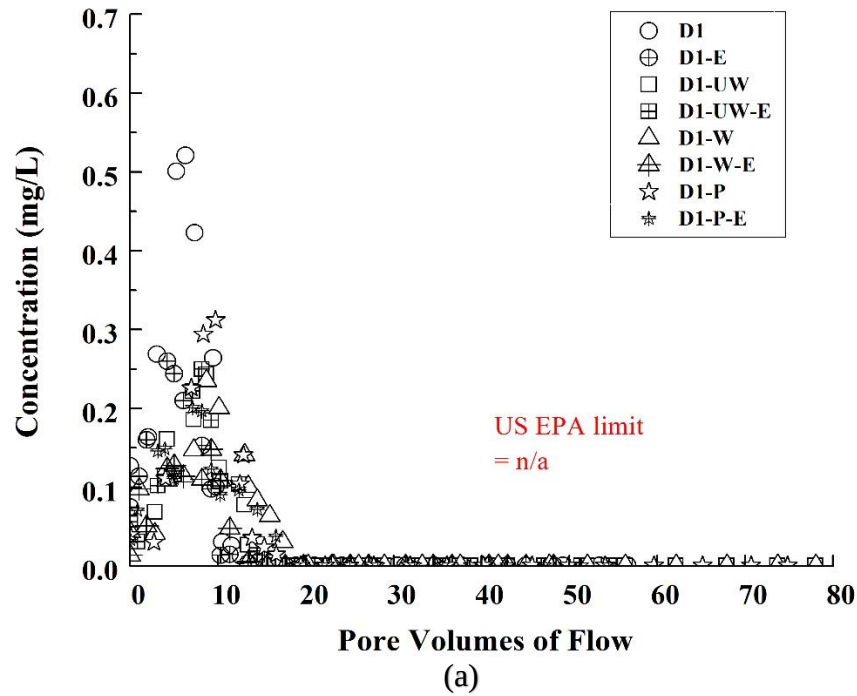


Figure 4.5. SCLT elution curve for Fe for (a) D1 and (b) D2 and its blends with quarry by-products

leached Fe concentration from DM. These findings clearly suggest that the quarry by-products can immobilize Fe from DM.

Myers (1999) also found that Fe concentrations in column leachate from Hamlet City Lake sediments increased to peak values of 35-40 mg/L within the first few pore volumes and dropped immediately afterwards. Myers (1999) suggested that the reservoir of leachable iron was mobilized during the beginning stages of the column test, and that the iron concentrations were replenished by a leachable reservoir capable of maintaining iron concentrations for a long period of time. A column leach test, according to the European standards was performed on dredged sediments by Cappuyns and Swennen, 2008. They noticed an increase in the release of Fe concentration towards the end of test, suggesting that the leaching of Fe was due to release of Fe complexed with DOC.

Metal mobility depends on several processes, such as discrete sulfide phase precipitation, complexation with bisulfides, polysulfides or organic matter, and adsorption or co-precipitation within iron sulfides (Diaz et al., 1998). Furthermore, pyrite (FeS_2) and iron monosulfide (FeS) can play a central role in the iron and sulfur cycles in marine sediments (Schippers and Jorgensen, 2002). It is believed that a combination of these factors has played an integral role in Fe leaching in the current study, even though a separate analysis was not conducted to study these factors.

Leaching of Zinc

Figure 4.6 shows the first-flush pattern of zinc (Zn) for both the dredged material and its blends with quarry by products. Zn concentrations further reduce once the leachate passes through the embankment soil. Zinc concentrations in column leachate from D1 declined from 0.62 ppm to below the minimum detection limit of 0.005 ppm by the time eleven pore volumes were eluted

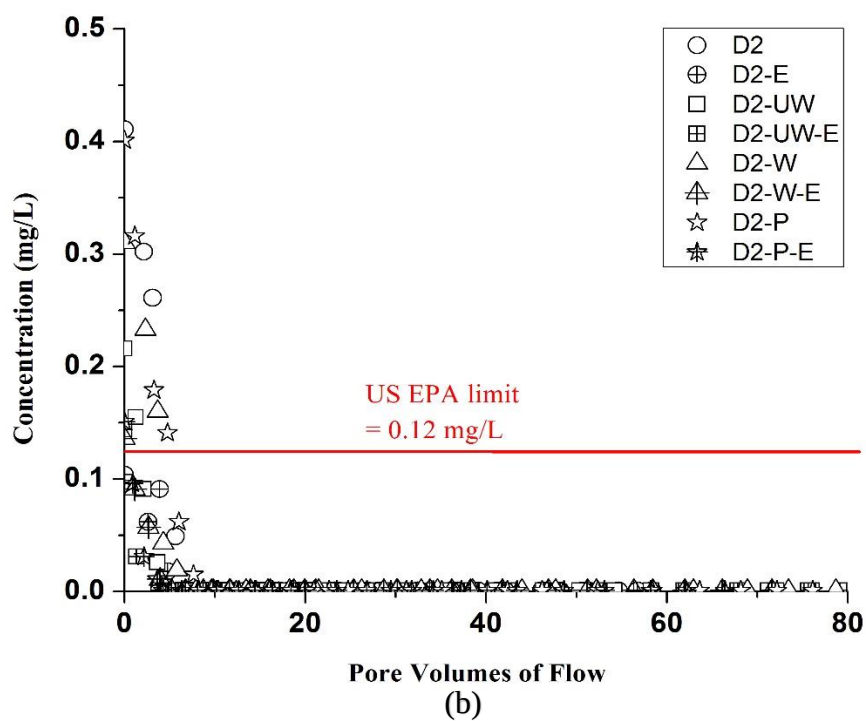
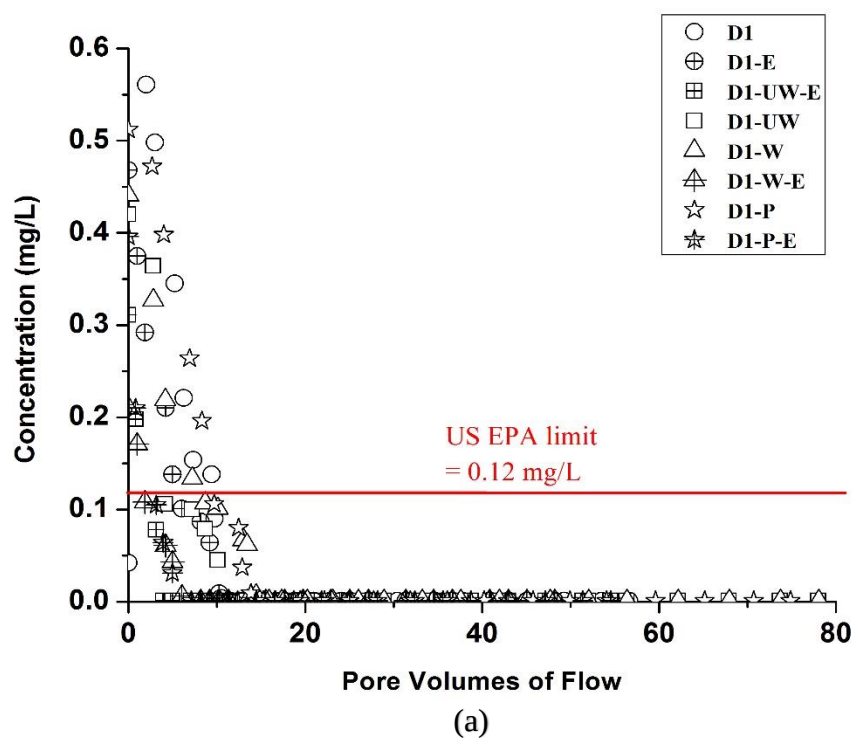


Figure 4.6. SCLT elution curve for Zn for (a) D1 and (b) D2 and its blends with quarry by-products

while in case of D2, the Zn concentration decreases from 0.42 ppm to below detection limit after seven pore volumes were eluted. It takes nine and three pore volumes for the concentrations of Zn to drop to levels below the U.S. EPA WQL of 0.12 mg/L (ppm) for D1 and D2, respectively. The Zn concentrations in D1 and its blends with quarry-by-products decline below U.S. EPA WQL of 0.12 mg/L after three, seven and nine pore volumes for D1-UW, D1-W and D1-P, respectively. In case of D2 and its blends with quarry by products the concentration of Zn reduces below the U.S. EPA limit after two, three and five pore volumes for D2-UW, D2-W and D2-P, respectively.

Zn shows the highest mobilization during the initial stages of the elution when dissolution and surface wash-off processes play a predominant role (Al-Abed et al., 2008; Tiruta-Barna et al., 2004; Payán et al. 2013). The Pourbaix diagram of zinc species clearly shows the amphoteric nature of zinc and indicates that higher leachate pH (>12) may lead to increased zinc leaching (Pourbaix, 1974). This could be one of the reasons for observing low Zn concentrations in column effluents at the near-neutral pHs.

Myers (1999) also witnessed a similar leaching pattern for Zn during testing of dredged sediments, and suggested that just like Cu, the first flush pattern of Zn might be because of the presence of Zn in the sediment pore water and as pore water was eluted, zinc leaching was negligible. Couvidat et al. (2015) also reported a first-flush pattern for Zn leaching from marine sediments. The reduction in the concentration of Zn after first few flush might be because Fe-oxi-hydroxides phases and phyllosilicates have been found to reduce Zn mobility after sulfides oxidation (Isaure, 2002; Isaure et al., 2005). However, the initial leaching of Zn at the near-neutral pH can also be attributed to the fact that Zn^{2+} is a stable divalent cation and has strong affinity for OM as well as towards carbonates (Sauvé et al., 2000)

Leaching of Nickel

The mobility of nickel in the SCLT leachates is very low (Figure 4.7). The concentration of Ni in leachate from the embankment soil (ES) further reduces the concentration of nickel originating from DM and the blends (Figure 4.7). A first-flush leaching pattern is evident for both the DM and their corresponding blends with quarry by products. The maximum concentration of Ni in the leachate from D1, D2 and their corresponding blends with quarry-by-products is below the U.S. EPA limit of 0.47 ppm. The maximum concentration of Ni in D1 and D2 is 0.42 ppm and 0.36 ppm, respectively. After approximately twelve and seven pore volumes, the concentration of Ni was below the detection limit for D1 and D2, respectively. In both the cases the concentration of Ni leaching from blends is less than the concentration of Ni leaching from pure DM.

Liu et al. (2018) evaluated the leaching behavior of heavy metals in soil columns under effects of simulated rainwater on the dredged sediment of Meiliang Bay (China). The leaching experiments were performed for a testing duration that is equivalent to 2 years of precipitation in the field and a first-flush pattern was observed for Ni leaching, similar to the observations made by Myers (1999) during testing of dredged river sediments.

The Ni portion bound to the organic/sulfidic phase may be low due to low amounts of organic matter in the Chesapeake Bay sediments (OM = 10% by weight), which may be one of the reasons for the low mobility of Ni in the DM and the blends tested in the current study. Higher amounts of Ni bound to this phase were found in water bodies where sediments contained higher amounts of organic matter (Sekhar et al., 2003; Loska and Wiechuła, 2003). The organic/suphidic phase is moderately mobile and was reported to be released from this phase due to decomposition of organic matter and oxidation of sulfides to SO_2^- (Calmano et al., 1993).

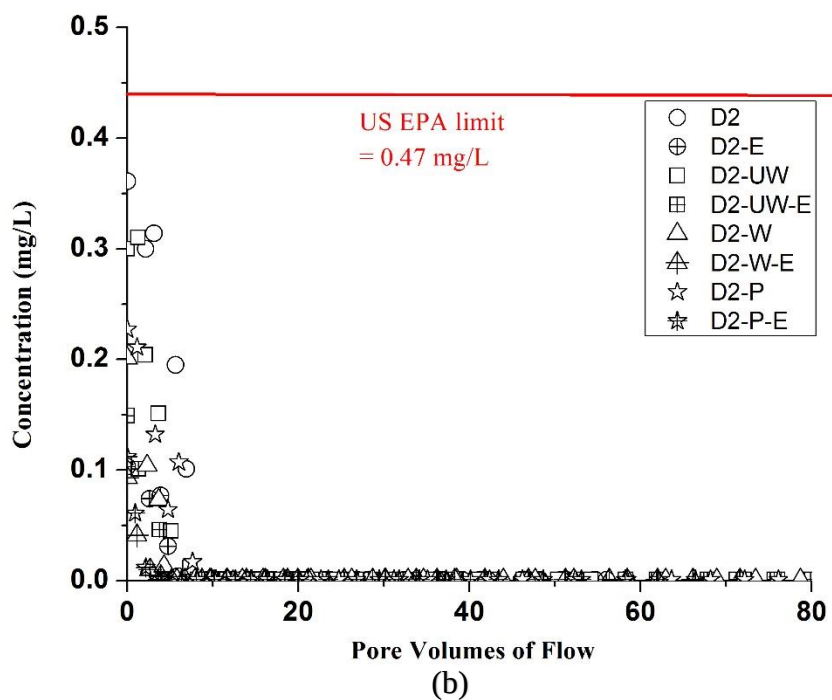
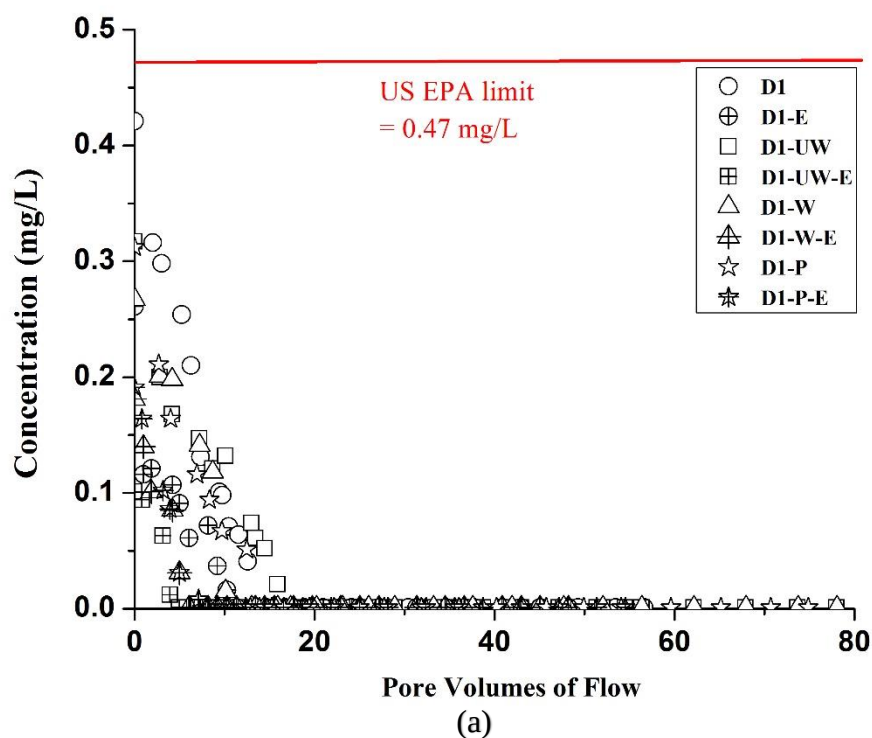


Figure 4.7. SCLT elution curve for Ni for (a) D1 and (b) D2 and its blends with quarry by-products

Another possible reason for recording relatively lower Ni concentrations for the DM-quarry by-product blends may be attributed to higher sand content of the blends (Table 2.1), which is also in agreement with the nickel analyses conducted by Czaplicka-Kotas et al. (2008) on dredged sediments. Low levels of Ni leaching observed in earlier work was attributed to the higher adsorption affinity of this pollutant to soil or complexation of Ni with Fe, Mn, and Al at near-neutral pHs (Voegelin et al., 2003; Szarek-Gwiazda et al., 2011). The high portion of Ni bound to stable geochemical phases in the current study suggests that there is a limited potential for Ni mobility. Therefore, Ni leaching from the Chesapeake Bay sediments poses a low toxicological risk to aquatic organisms.

Numerous researchers in the past have proved that content of clay fraction and of organic matter is the chief measure of the capacity of bottom sediments to accumulate contaminants (Farkas et al., 2007; Czerniawska and Kusza, 2011). Factors like adsorption/desorption processes, salinity, presence of sulfur and carbonates, pH have affected the metal mobility in sediments (Du Laing et al., 2009). Sediments from the Baltimore Harbor as compared to blends had a relatively high concentration of organic matter (10% versus 4%-5% by weight), which might have influenced the solubility and mobility of the heavy metals in the organisms. Because of the presence of numerous negatively charged groups, organic matter has high capacity to form complex with them. The studied sediments are rich in organic matter as compare to blends, therefore the formation of potential mobile metal-dissolved organic carbon complexes under oxidizing conditions prevents metals from co-precipitation with or adsorbing to Fe (hydr)oxides (Rinklebe and Shaheen, 2014).

The initial rapid release of various elements may have originated from the exchangeable fraction, as this fraction was easily released once rinsed with water. Because of the continuous input of hydrogen ions during the leaching period, it would lead to an increase of hydrogen ions

Table 4.1. Peak effluent concentrations from SCLT. Concentrations exceeding EPA WQL are in bold.

Sample	pH	Cu	Fe	Zn	Ni
D1	8.58	0.21	0.521	0.612	0.421
D1-E	7.91	0.132	0.244	0.468	0.261
D1-UW	8.08	0.173	0.243	0.42	0.317
D1-UW-E	7.77	0.112	0.222	0.3	0.101
D1-W	7.85	0.124	0.235	0.441	0.267
D1-W-E	8.04	0.078	0.128	0.21	0.181
D1-P	7.72	0.183	0.312	0.512	0.312
D1-P-E	7.95	0.106	0.201	0.396	0.191
D2	7.66	0.32	0.411	0.420	0.36
D2-E	7.22	0.22	0.159	0.104	0.103
D2-UW	7.21	0.164	0.201	0.216	0.3
D2-UW-E	7.11	0.08	0.126	0.144	0.15
D2-W	7.61	0.312	0.261	0.310	0.201
D2-W-E	7.34	0.164	0.121	0.136	0.093
D2-P	7.81	0.236	0.251	0.401	0.227
D2-P-E	7.41	0.063	0.114	0.151	0.112
WQL	6.5-9	0.13	N/A	0.12	0.47
BDL	--	0.001	0.001	0.005	0.001

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

in the soil solution, thus strengthening the competitive adsorption of metal elements. At the same time, the carbonate fraction and organic- sulfide fraction of heavy metals would be slowly released under the effects of simulated rainwater, thereby explaining the slow release phase of these elements (Liu et al., 2018).

4.3 Conclusions

A series of laboratory sequential column leach tests (SCLTs) was conducted to investigate the leaching characteristics of Dredged Material and its blends with quarry by-products. The following observations were made:

- 1) First flush pattern was observed for Cu, Zn and Ni while Fe exhibited a lagged response for the dredged materials and its blends with quarry by-products.
- 2) Column leach tests conducted on pure D1 with initial pH=8.18 produced leachates with a pH range of 7.71-8.56 while for D2 with initial pH=7.2 produced leachates with a pH range of 6.96-7.66. Peak effluent concentrations of As was below the minimum detection limits for both D1 and D2, while the concentration of Ni was below the U.S. EPA WQL throughout the test. Cu and Zn concentrations in both D1 and D2 exceeded the EPA WQLs; however, they immediately decreased to levels below after few pore volumes.
- 3) In case of blends of DM and quarry by-products the peak concentration of metals leached during the SCLT test was less than peak concentration of pure DM. Just like pure DM, the Cu and Zn concentrations in the blends of both D1 and D2 exceeded the EPA WQLs but after few pore volumes they immediately decreased below the WQL.
- 4) Embankment soil further helped in reducing the concentration of Cu, Zn, Fe and Ni as compare to the concentration of these metals leached form pure DM and their blends with quarry by-products.

5 MODELING OF SURFACE WATER CONTAMINATION AND GEOCHEMISTRY

5.1 Modeling of Contaminant Transport in Surface Waters

5.1.1 Methodology

The usage of DM and its blends with quarry by-products increases the concern of contamination of surface water bodies like rivers and streams. To evaluate the transportation of contaminants in surface waters, analytical solutions of the advective-dispersive equation (ADE) and related models are usually used. The ADE takes into consideration advective transport and dispersive/diffusive transport. UMDSurf, a numerical model that predicts the distribution of metal concentrations in surface waters as a function of distance away from the edge of DM-amended highway embankment, was used.

The solute flux for one-dimensional transport, J_s , is expressed as follows,

$$J_s = uC - D_x \frac{\partial C}{\partial x} \quad (5.1)$$

where u is the longitudinal fluid flow velocity, C is the solute concentration given in mass per unit volume of water, D_x is the longitudinal dispersion coefficient that accounts for the combined effects of ionic or molecular diffusion and hydrodynamic dispersion, and x is the longitudinal coordinate.

Next, the mass balance equation is formulated based on the accumulation of solute in a control volume over time caused by the divergence of flux (i.e., net inflow or outflow),

$$\frac{\partial C}{\partial t} = -\nabla \cdot J_s - R_s + R_w C_e \quad (5.2)$$

where t and R_s represent time and arbitrary sources or sinks of solute, respectively. When $R_s < 0$ it means there is consumption of solute, and when $R_s > 0$ it means that there is feeding of solute. The last term in the equation denotes the injection (>0) or pumping (<0) of water with constituent concentration C_e at a rate R_w . A typical ADE equation, however, excludes the last two terms and is written as

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial x} \quad (5.3)$$

In this study, a numerical one-dimensional solution of ADE with a third-type inlet ($\omega = 1$) and the boundary conditions provided below were used.

$$C(x, 0) = f(x) \quad (5.4)$$

$$\left(uC - \omega D_x \frac{\partial C}{\partial x} \right)_{x=0^+} = ug(t) \quad (5.5)$$

$$\frac{\partial C}{\partial x}(\infty, t) = 0 \text{ or } \frac{\partial C}{\partial x}(L, t) = 0 \quad (5.6)$$

A semi-infinite domain with the uniform initial concentration, $f(x) = C_i$, and no production/decay were assumed to exist. The inlet concentration function of the pulse type, $g(t)$, with the constant concentration C_0 is formulated as

$$g(t) = \begin{cases} C_0, & 0 < t \leq t_0 \\ 0, & t \geq t_0 \end{cases} \quad (5.7)$$

Finally, the solution to Equation 5.3 is then given as

$$C(x, t) = \begin{cases} C_i + (C_0 - C_i)A(x, t), & 0 < t \leq t_0 \\ C_i + (C_0 - C_i)A(x, t) - C_0A(x, t - t_0), & t \geq t_0 \end{cases} \quad (5.8)$$

Where,

$$A(x, t) = \frac{1}{2} \operatorname{erfc} \left[\frac{x - ut}{\sqrt{4D_x t}} \right] + \sqrt{\frac{tu}{\pi D_x}} \exp \left[-\frac{(x - tu)^2}{4D_x t} \right] - \frac{1}{2} \left(1 + \frac{ux}{D_x} + \frac{tu^2}{D_x} \right) \exp \left(\frac{ux}{D_x} \right) \operatorname{erfc} \left[\frac{x + tu}{\sqrt{4D_x t}} \right] \quad (5.9)$$

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

5.1.2. Results

UMDSurf was used to predict concentrations of Cu, Fe, Ni and Zn in surface water bodies at 20, 50, 100, 200, 500, and 1000 meters away from the source. Figures 5.1 through Figure 5.8 illustrate the forecasted concentrations of Cu, Fe, Ni and Zn at different horizontal distances in surface waters from the point of contact for both the DM and blends of DM-quarry by-products leachates passing through the natural formation composed of CL or CL-ML. Maximum (peak) concentrations of metals from the sequential column leach tests were used as the input concentrations at $t = 0$ sec. The instantaneous injection ($t = 10$ sec) of 2.2 lb [1 kg] solute in the main channel of a stream having a cross-sectional area of 107 ft^2 [10 m^2], an average flow velocity of 3.2 ft/s [1 m/s], and a dispersion coefficient of $54 \text{ ft}^2/\text{s}$ [$5 \text{ m}^2/\text{s}$] was considered (De Smedt et al., 2005; van Genuchten, 2013). Concentration of metals modeled at $t = 0$ (initial point) are much lower than peak concentration of the metals observed in SCLTs. As the leachate passes through the subgrade and natural soil to reach surface water, the metal concentrations are retarded. Two different subgrade soils were assumed to exist below the highway embankment.

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

The concentration of metal decreases significantly with time and horizontal distance from the surface of pure dredged material, quarry by-products amended dredged material and quarry by-products amended dredged material – embankment soil system. In surface waters, concentrations of all metals leached from all the systems are significantly lower than the WQLs. Even though the peak SCLT concentrations of Zn and Cu were above the WQLs for some systems, they drop to the levels below the WQLs after travelling through the natural formation. The decrease in the concentrations immediately at the entrance into the surface waters is more clearly pronounced for the CL-ML formation than for the CL formation due to the higher pH approaching neutral levels (6.3 versus 5.9) and higher retardation factors.

Leaching of Copper

The peak concentration of Cu from SCLT of D1 and D2 is 210 µg/L and 320 µg/L, respectively. However, upon exiting from the CL type formation the concentration in the surface water reduces to 17.6 µg/L and 26.8 µg/L, respectively, while the same concentrations are 2.79 µg/L and 4.27 µg/L, respectively, if the formation is CL-ML type. The point of entrance concentration of Cu for the blends (D1 or D2 amended with quarry by-products) is in the range of 10-15 µg/L and 13-62 µg/L for CL type formation while the ranges are 1.75-2.5 µg/L and 2-3 µg/L for the

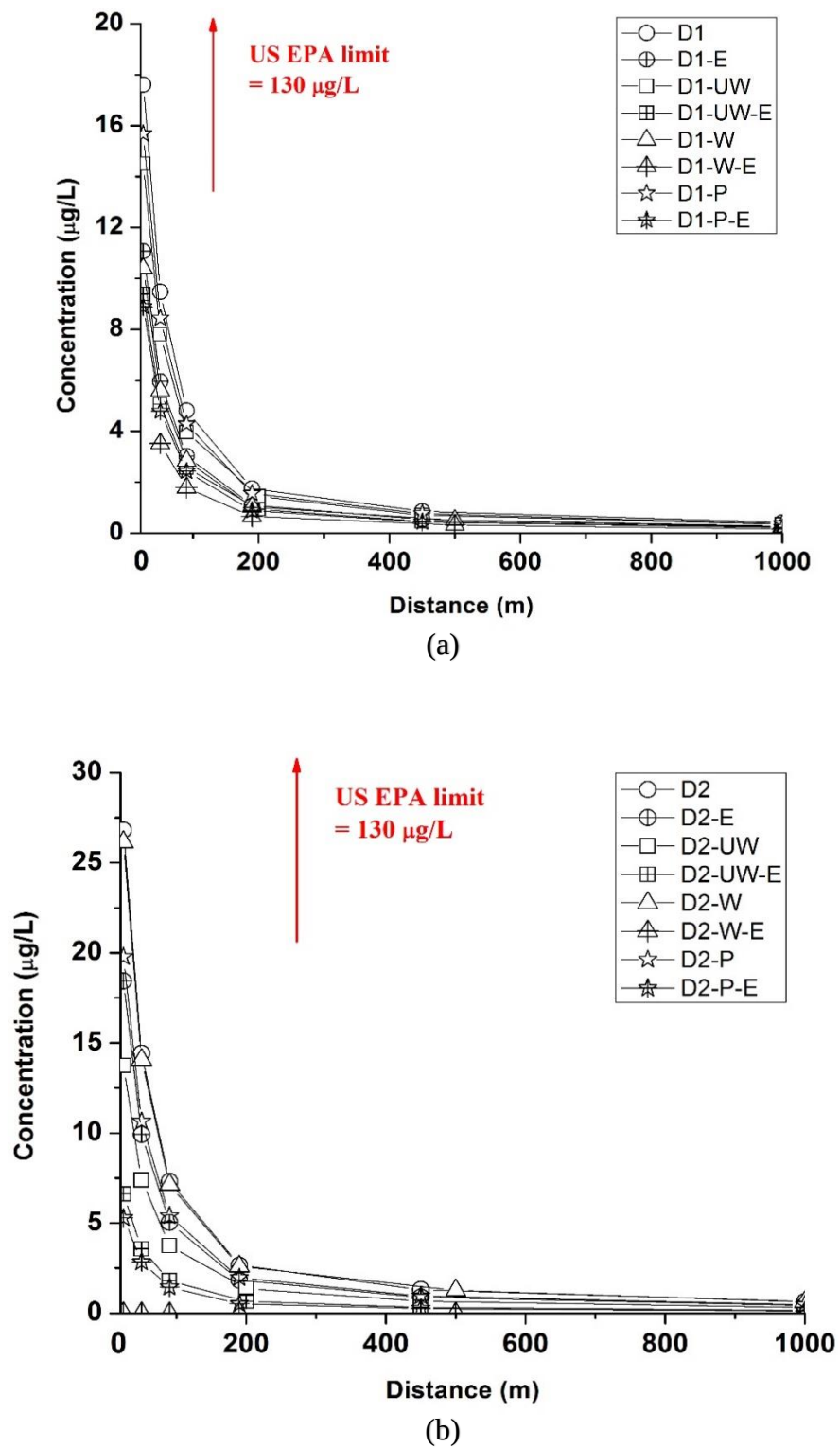


Figure 5.1. Surface water contamination of Cu in (a) D1 and (b) D2 and the blends prepared with the quarry by-product as a function of horizontal distance (**CL type formation, RF=7**)

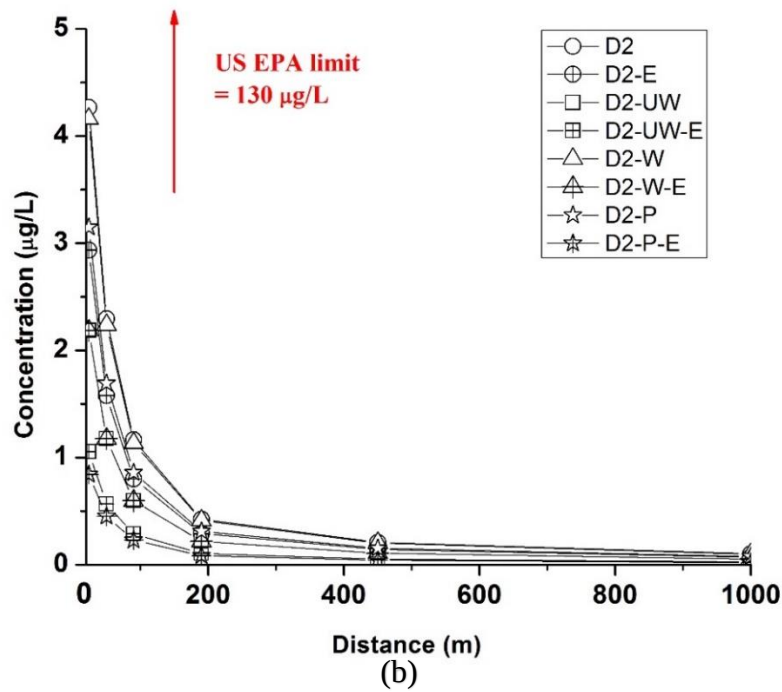
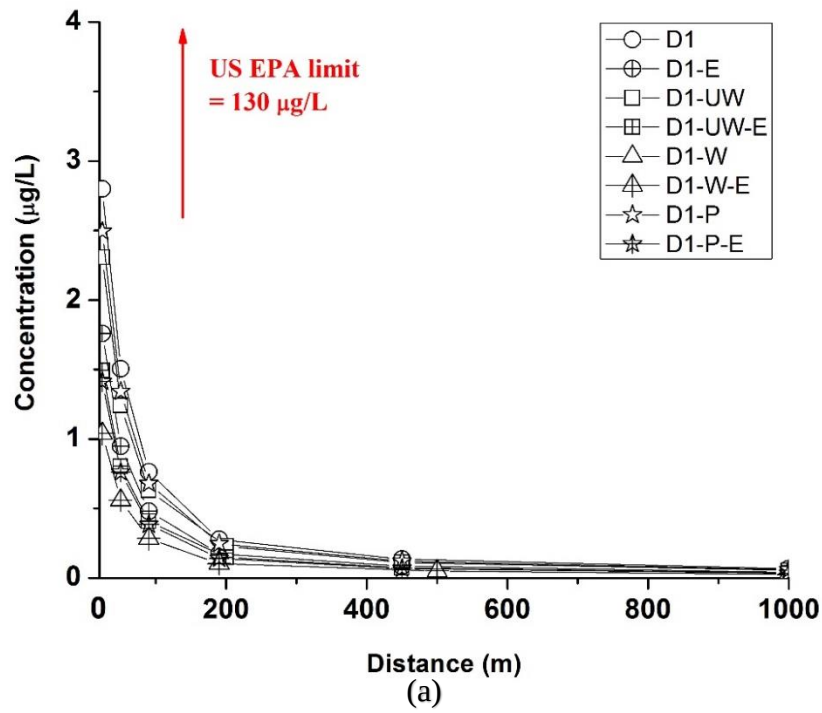


Figure 5.2. Surface water contamination of Cu in (a) D1 and (b) D2 and the blends prepared with the quarry by-product as a function of horizontal distance (**CL-ML type formation RF=44**)

Table 5.1. UMDSurf Results for Copper (CL formation)

Sample	UMDSurf C_{peak} ($\mu\text{g/L}$)	Dist. reqd. to reach C_{50} (m)	Dist. reqd. to reach DL (m)	DL ($\mu\text{g/L}$)	U.S. EPA WQL ($\mu\text{g/L}$)
D1	17.6	50	300	1	130
D1-E	11.0	50	190	1	130
D1-UW	14.5	50	240	1	130
D1-UW-E	9.4	50	150	1	130
D1-W	6.5	50	190	1	130
D1-W-E	8.04	50	130	1	130
D1-P	15.7	50	240	1	130
D1-P-E	8.89	50	160	1	130
D2	26.8	50	450	1	130
D2-E	18.4	50	240	1	130
D2-UW	13.7	50	300	1	130
D2-UW-E	6.6	50	140	1	130
D2-W	26.1	50	420	1	130
D2-W-E	13.1	50	230	1	130
D2-P	19.7	50	400	1	130
D2-P-E	5.3	50	140	1	130

C_{peak} : peak concentration in UMDSurf; C_{50} : 50% of C_{peak} ; DL: ICP detection limit.

Table 5.2. UMDSurf Results for Copper (CL-ML formation)

Sample	UMDSurf C_{peak} ($\mu\text{g/L}$)	Dist. reqd. to reach C_{50} (m)	Dist. reqd. to reach DL (m)	DL ($\mu\text{g/L}$)	U.S. EPA WQL ($\mu\text{g/L}$)
D1	2.8	50	90	1	130
D1-E	1.75	50	50	1	130
D1-UW	2.3	50	70	1	130
D1-UW-E	1.5	50	35	1	130
D1-W	2.03	50	60	1	130
D1-W-E	1.03	50	25	1	130
D1-P	2.5	50	70	1	130
D1-P-E	1.41	50	35	1	130
D2	4.26	50	130	1	130
D2-E	2.9	50	70	1	130
D2-UW	2.18	50	70	1	130
D2-UW-E	1.05	50	24	1	130
D2-W	4.15	50	130	1	130
D2-W-E	2.18	50	70	1	130
D2-P	3.14	50	80	1	130
D2-P-E	0.84	50	10	1	130

C_{peak} : peak concentration in UMDSurf; C_{50} : 50% of C_{peak} ; DL: ICP detection limit.

CL-ML type formation, respectively. Cu concentrations decrease by more than 50% at 50 m away from the entrance point. The concentration of copper is below the detection limit (1 µg/L) after 300 m and 450 m into the surface for D1 and D2, respectively, for the CL type of formation (Figure 5.1), while in the CL-ML type formation the concentration reaches below the detection limit (1 µg/L) after 90 m and 130 m for D1 and D2 (Figure 5.2). In case of the blends prepared with D1, the concentration reaches below the detection limit (1 µg/L) after 190-240 m and 35-70 m into the surface water for CL and CL-ML type formations, respectively. The same ranges are 300-450 m and 60-70 m for the blends prepared with D2.

Leaching of Iron

The peak concentration of Fe from SCLT of D1 and D2 is 521 µg/L and 411 µg/L, respectively. However, upon exiting from the CL type formation the concentration in the surface water reduces to 35.28 µg/L and 34.44 µg/L, respectively, while the same concentrations are 4.93 µg/L and 4.82 µg/L, respectively, if the formation is CL-ML type. The point of entrance concentration of Fe for the blends (D1 or D2 amended with quarry by-products) is in the range of 10-26 µg/L and 12-22 µg/L for CL type formation while the ranges are 1.5-2.8 µg/L and 1.7-3 µg/L for the CL-ML type formation, respectively. Fe concentrations decrease by more than 50% at 50 m away from the entrance point. The concentration of iron is below the detection limit (1 µg/L) after 700 m and 600 m into the surface for D1 and D2, respectively, for the CL type of formation (Figure 5.3), while in the CL-ML type formation the concentration reaches below the detection limit (1 µg/L) after 120 – 130 m for both the D1 and D2 (Figure 5.4). In case of the blends prepared with D1, the concentration reaches below the detection limit (1 µg/L) after 410-600 m and 40-70 m into the

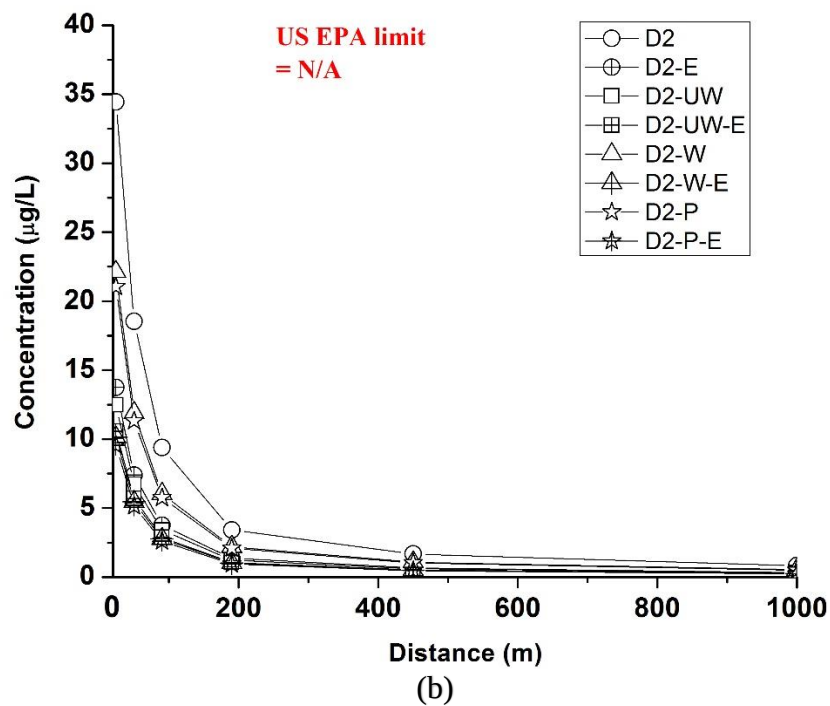
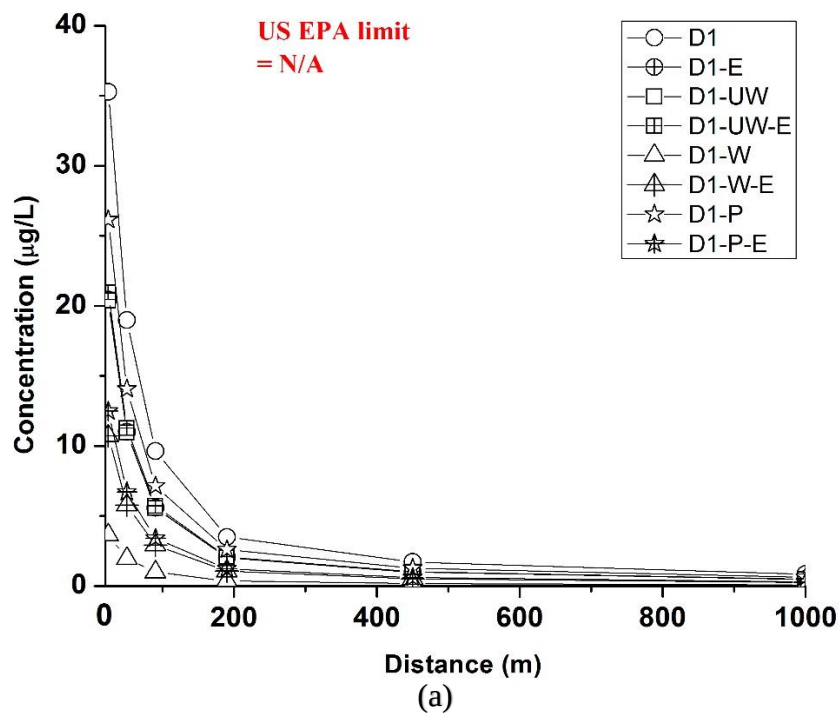
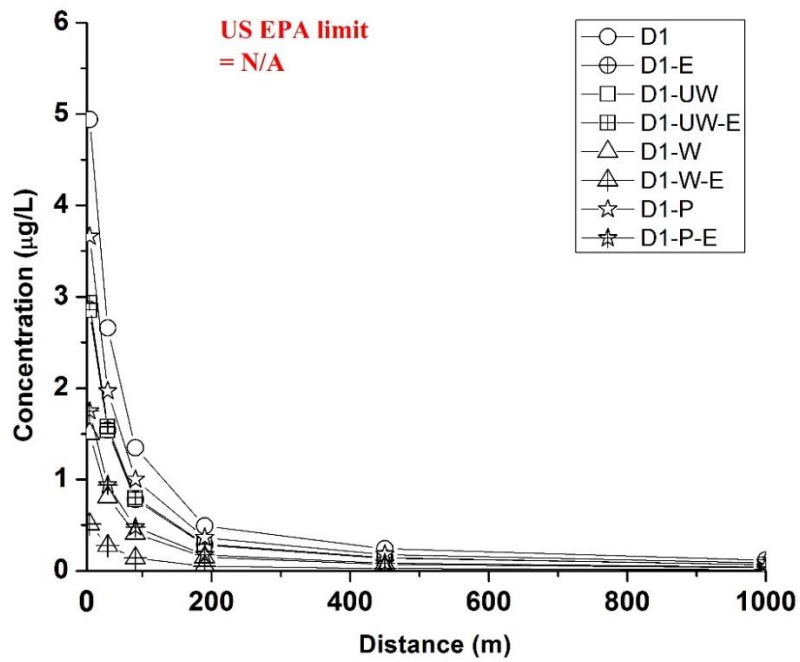
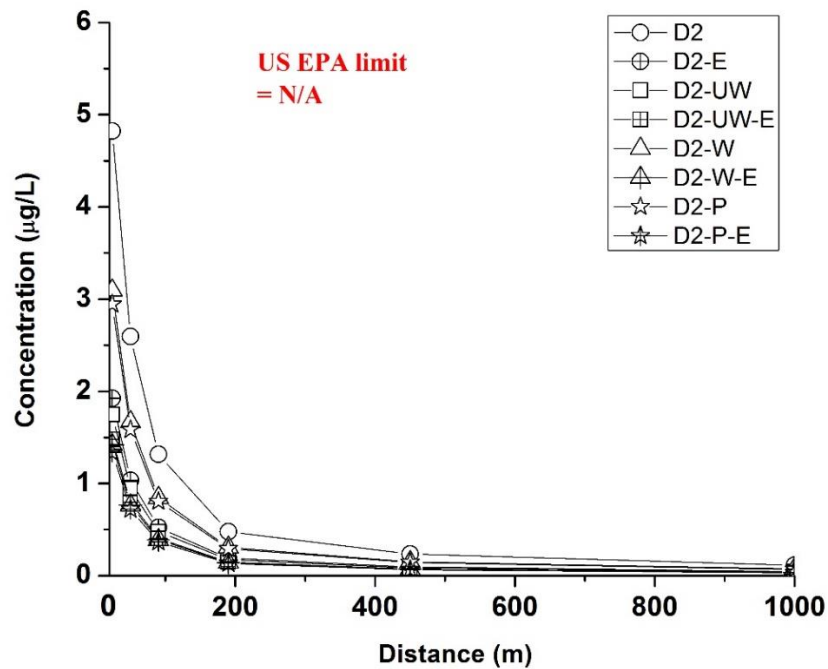


Figure 5.3. Surface water contamination of Fe in (a) D1 and (b) D2 and the blends prepared with the quarry by-product as a function of horizontal distance (**CL type formation, RF=7**)



(a)



(b)

Figure 5.4. Surface water contamination of Fe in (a) D1 and (b) D2 and the blends prepared with the quarry by-product as a function of horizontal distance (**CL-ML type formation RF=50**)

Table 5.3. UMDSurf Results for Iron (CL formation)

Sample	UMDSurf C_{peak} ($\mu\text{g/L}$)	Dist. reqd. to reach C_{50} (m)	Dist. reqd. to reach DL (m)	DL ($\mu\text{g/L}$)	U.S. EPA WQL ($\mu\text{g/L}$)
D1	35.28	50	700	1	N/A
D1-E	20.45	50	450	1	N/A
D1-UW	20.36	50	440	1	N/A
D1-UW-E	18.1	50	430	1	N/A
D1-W	10.72	50	190	1	N/A
D1-W-E	3.1	50	90	1	N/A
D1-P	26.15	50	600	1	N/A
D1-P-E	12.5	50	320	1	N/A
D2	34.44	50	600	1	N/A
D2-E	13.74	50	370	1	N/A
D2-UW	12.5	50	300	1	N/A
D2-UW-E	10.6	50	190	1	N/A
D2-W	22.1	50	450	1	N/A
D2-W-E	10.1	50	190	1	N/A
D2-P	21.0	50	450	1	N/A
D2-P-E	9.56	50	180	1	N/A

C_{peak} : peak concentration in UMDSurf; C_{50} : 50% of C_{peak} ; DL: ICP detection limit.

Table 5.4. UMDSurf Results for Iron (CL-ML formation)

Sample	UMDSurf C_{peak} ($\mu\text{g/L}$)	Dist. reqd. to reach C_{50} (m)	Dist. reqd. to reach DL (m)	DL ($\mu\text{g/L}$)	U.S. EPA WQL ($\mu\text{g/L}$)
D1	4.93	50	120	1	N/A
D1-E	2.86	50	80	1	N/A
D1-UW	2.85	50	70	1	N/A
D1-UW-E	2.8	50	70	1	N/A
D1-W	1.5	50	40	1	N/A
D1-W-E	0.51	50	10	1	N/A
D1-P	3.6	50	90	1	N/A
D1-P-E	1.75	50	40	1	N/A
D2	4.8	50	130	1	N/A
D2-E	1.9	50	70	1	N/A
D2-UW	1.74	50	40	1	N/A
D2-UW-E	147	50	40	1	N/A
D2-W	3.09	50	70	1	N/A
D2-W-E	1.41	50	30	1	N/A
D2-P	2.94	50	70	1	N/A
D2-P-E	1.33	50	30	1	N/A

C_{peak} : peak concentration in UMDSurf; C_{50} : 50% of C_{peak} ; DL: ICP detection limit.

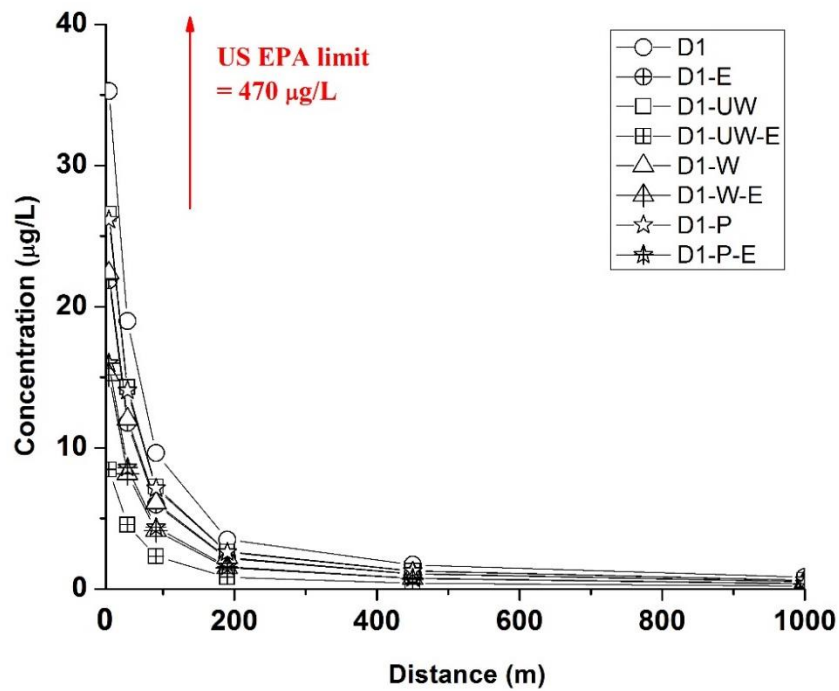
surface water for CL and CL-ML type formations, respectively. The same ranges are 300-450 m and 50-70 m for the blends prepared with D2.

Leaching of Nickel

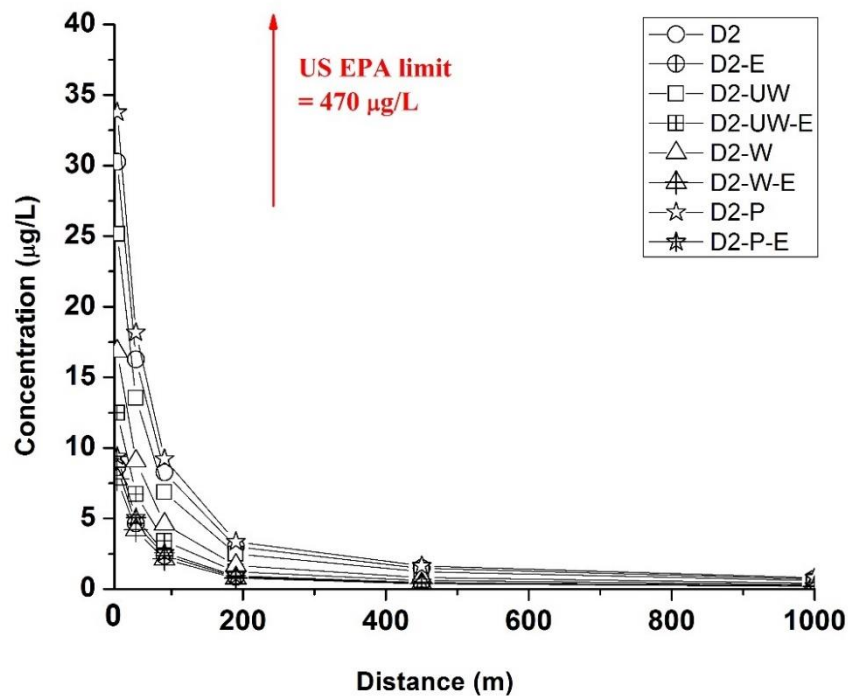
In the case of Ni, the peak from SCLT for all the system was below the U.S. EPA WQL (470 µg/L). The peak concentration of Ni from SCLT of D1 and D2 is 421 µg/L and 360 µg/L, respectively. However, upon exiting from the CL and CL-ML type formation the concentration in the surface water reduces to 35.28 µg/L and 30.25 µg/L, respectively. The point of entrance concentration of Ni for the blends (D1 or D2 amended with quarry by-products) is in the range of 22-26 µg/L and 16-32 µg/L for both the CL and CL-ML type formation (Figure 5.5 and Figure 5.6). Ni concentrations decrease by more than 50% at 50 m away from the entrance point. The concentration of nickel is below the detection limit (1 µg/L) after 700 m into the surface for the D1 and D2 for the CL as well as CL-ML type formation. In case of the blends prepared with D1, the concentration reaches below the detection limit (1 µg/L) after 600 m into the surface water for both the CL and CL-ML type formations. The same ranges are 400-700 m for the blends prepared with D2.

Leaching of Zinc

In the case of Zinc, the peak concentration of SCLT for all the system is above the U.S. EPA WQL (120 µg/L). The peak concentration of Fe from SCLT of D1 and D2 is 612 µg/L and 420 µg/L, respectively. However, upon exiting from the CL type formation the concentration in the surface water reduces to 51.28 µg/L and 34.44 µg/L, respectively, while the same concentrations are 22.4



(a)



(b)

Figure 5.5. Surface water contamination of Ni in (a) D1 and (b) D2 and the blends prepared with the quarry by-product as a function of horizontal distance (**CL type formation, RF=7**)

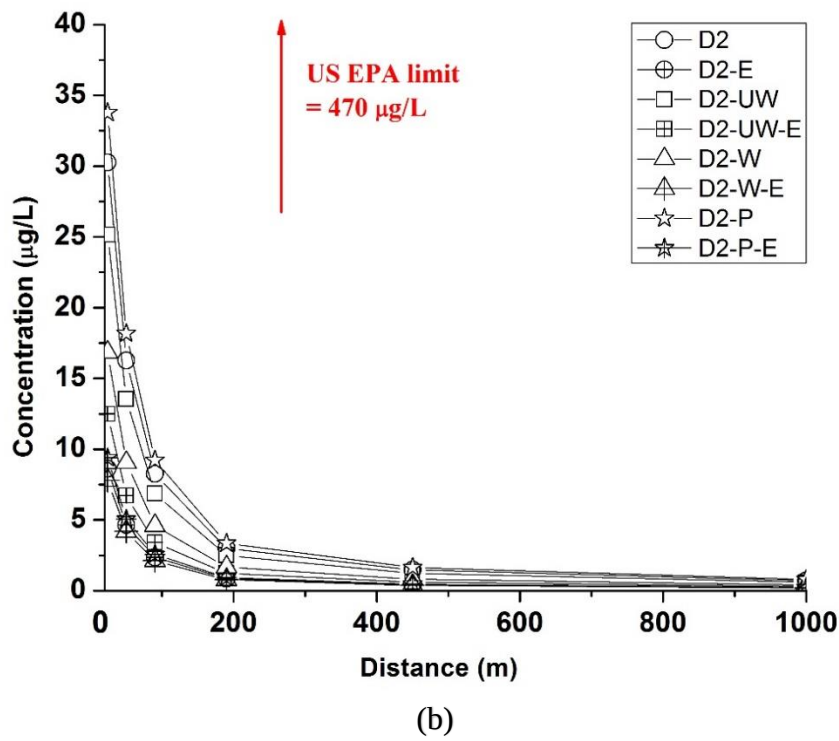
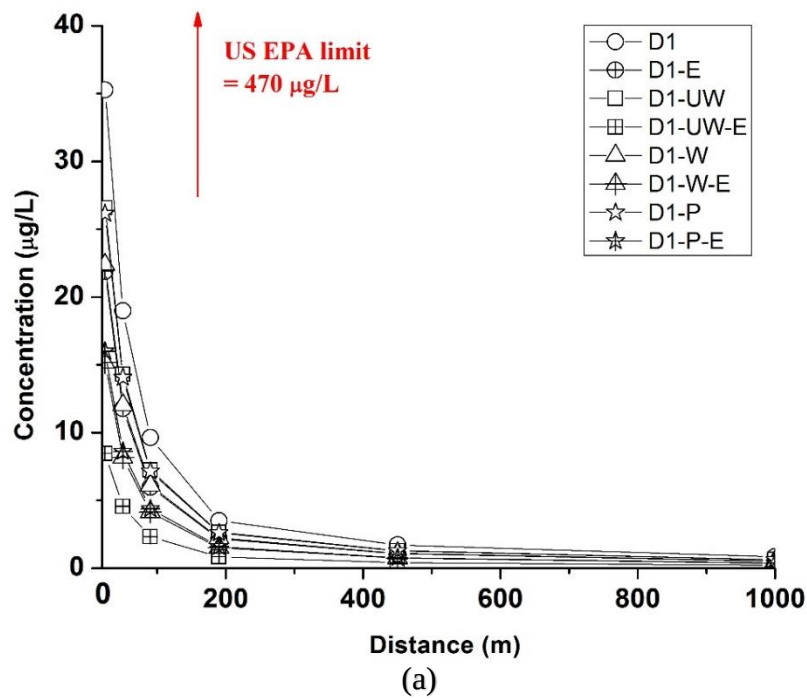


Figure 5.6. Surface water contamination of Ni in (a) D1 and (b) D2 and the blends prepared with the quarry by-product as a function of horizontal distance (**CL-ML type formation RF=7**)

Table 5.5. UMDSurf Results for Nickel (CL formation)

Sample	UMDSurf C _{peak} (µg/L)	Dist. reqd. to reach C ₅₀ (m)	Dist. reqd. to reach DL (m)	DL (µg/L)	U.S. EPA WQL (µg/L)
D1	35.28	50	700	1	470
D1-E	21.87	50	450	1	470
D1-UW	26.5	50	600	1	470
D1-UW-E	8.4	50	150	1	470
D1-W	22.3	50	600	1	470
D1-W-E	15.16	50	300	1	470
D1-P	26.14	50	600	1	470
D1-P-E	16.00	50	300	1	470
D2	30.25	50	700	1	470
D2-E	8.632	50	140	1	470
D2-UW	25.14	50	600	1	470
D2-UW-E	12.5	50	320	1	470
D2-W	16.84	50	400	1	470
D2-W-E	7.8	50	150	1	470
D2-P	33.7	50	700	1	470
D2-P-E	9.4	50	140	1	470

C_{peak}: peak concentration in UMDSurf; C₅₀: 50% of C_{peak}; DL: ICP detection limit.

Table 5.6. UMDSurf Results for Nickel (CL-ML formation)

Sample	UMDSurf C _{peak} (µg/L)	Dist. reqd. to reach C ₅₀ (m)	Dist. reqd. to reach DL (m)	DL (µg/L)	U.S. EPA WQL (µg/L)
D1	35.28	50	700	1	470
D1-E	21.87	50	450	1	470
D1-UW	26.5	50	600	1	470
D1-UW-E	8.4	50	150	1	470
D1-W	22.3	50	600	1	470
D1-W-E	15.16	50	300	1	470
D1-P	26.14	50	600	1	470
D1-P-E	16.00	50	300	1	470
D2	30.25	50	700	1	470
D2-E	8.632	50	140	1	470
D2-UW	25.14	50	600	1	470
D2-UW-E	12.5	50	320	1	470
D2-W	16.84	50	400	1	470
D2-W-E	7.8	50	150	1	470
D2-P	33.7	50	700	1	470
D2-P-E	9.4	50	140	1	470

C_{peak}: peak concentration in UMDSurf; C₅₀: 50% of C_{peak}; DL: ICP detection limit.

$\mu\text{g/L}$ and $15.06 \mu\text{g/L}$, respectively, if the formation is CL-ML type. The point of entrance concentration of Zn for the blends (D1 or D2 amended with quarry by-products) is in the range of $35 - 43 \mu\text{g/L}$ and $18-33 \mu\text{g/L}$ for CL type formation while the ranges are $15-19 \mu\text{g/L}$ and $8-15 \mu\text{g/L}$ for the CL-ML type formation, respectively. Zn concentrations decrease by more than 50% at 50 m away from the entrance point. The concentration of zinc is below the detection limit ($5 \mu\text{g/L}$) after 950 m and 800 m into the surface for D1 and D2, respectively, for the CL type of formation (Figure 5.7), while in the CL-ML type formation the concentration reaches below the detection limit ($5 \mu\text{g/L}$) after 450 m and 400 m for D1 and D2 (Figure 5.8). In case of the blends prepared with D1, the concentration reaches below the detection limit ($5 \mu\text{g/L}$) after 700-900 m and 270-300 m into the surface water for CL and CL-ML type formations, respectively. The same ranges are 400-700 m and 150-300 m for the blends prepared with D2.

For all four metals, the UMDSurf concentrations decrease by more than 50% at ~ 50 m away from the entrance point, and the rate of decrease is greater for higher initial concentrations as indicated by steeper slopes. Due to high retardation factors, the embankment soil and the natural formation absorb the metals as the leachate passes through their structure, thus minimizing the transport of the contaminants into surface waters.

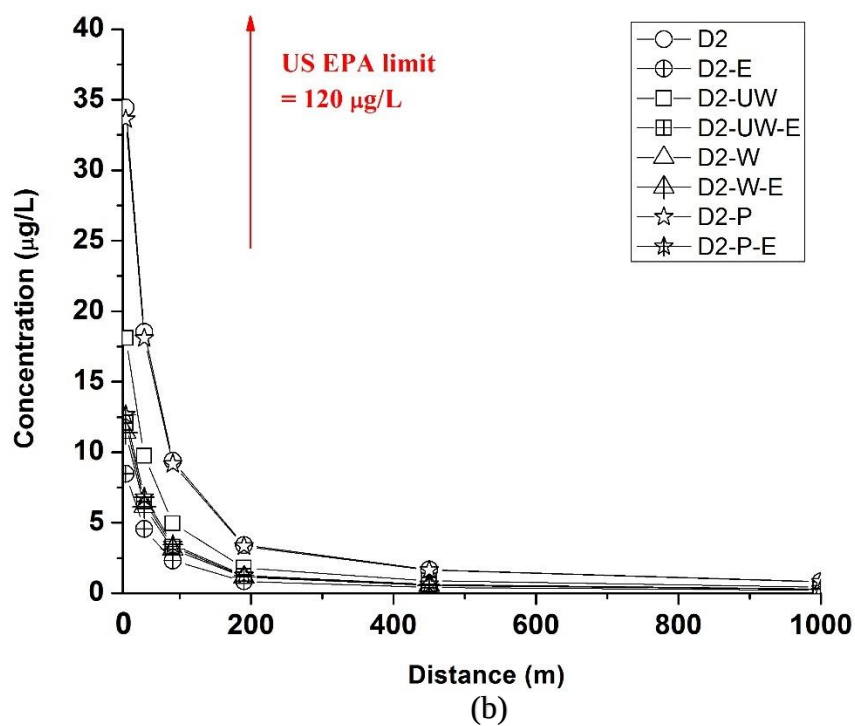
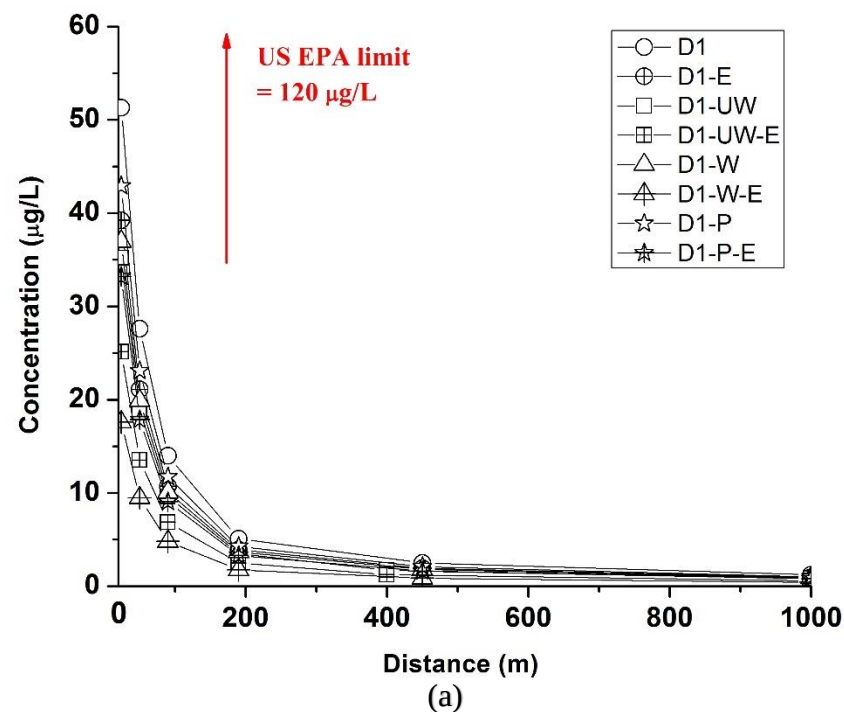
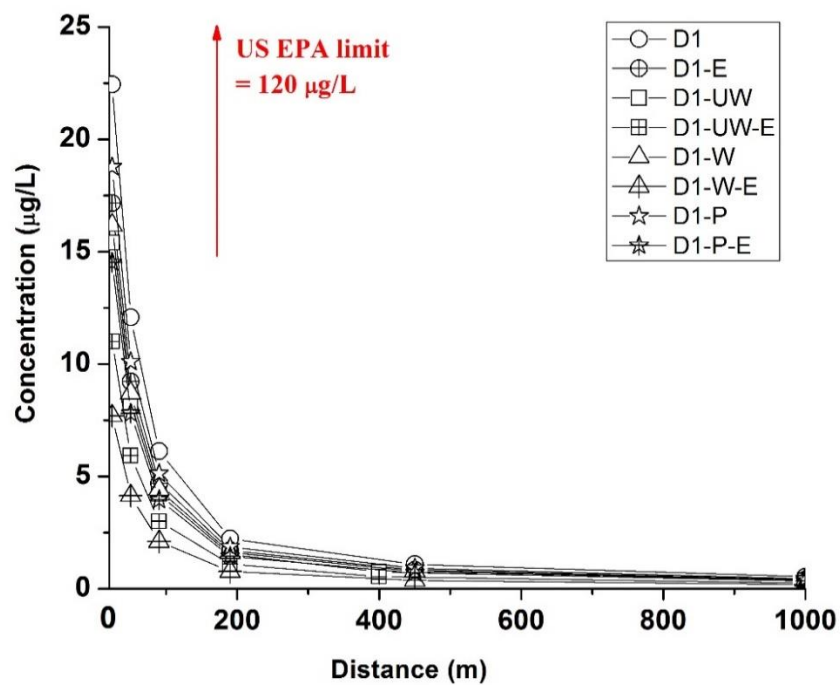
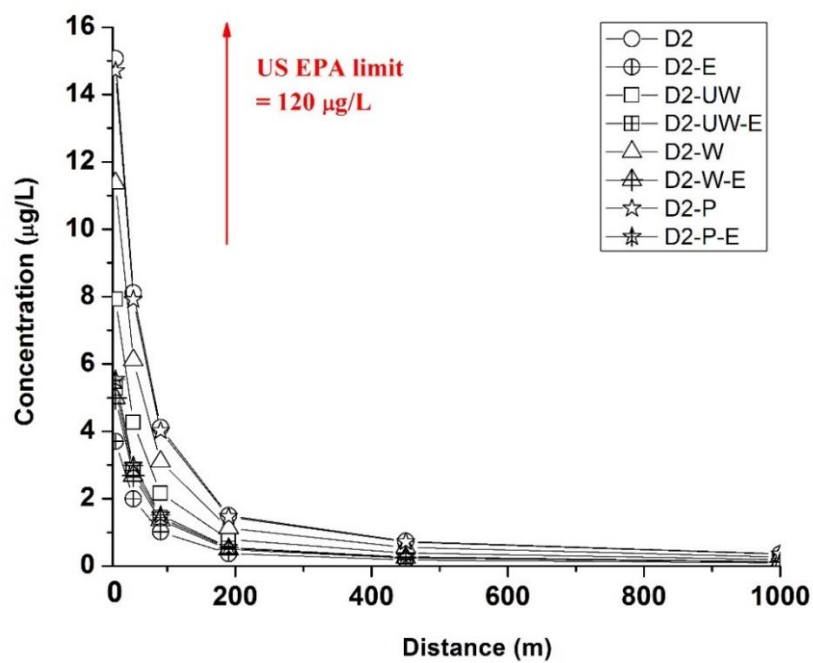


Figure 5.7. Surface water contamination of Zn in (a) D1 and (b) D2 and the blends prepared with the quarry by-product as a function of horizontal distance (**CL type formation, RF=7**)



(a)



(b)

Figure 5.8. Surface water contamination of Zn in (a) D1 and (b) D2 and the blends prepared with the quarry by-product as a function of horizontal distance (**CL-ML type formation RF=16**)

Table 5.7. UMDSurf Results for Zinc (CL formation)

Sample	UMDSurf C _{peak} (µg/L)	Dist. reqd. to reach C ₅₀ (m)	Dist. reqd. to reach DL (m)	DL (µg/L)	U.S. EPA WQL (µg/L)
D1	51.3	50	950	5	120
D1-E	39.2	50	750	5	120
D1-UW	35.2	50	700	5	120
D1-UW-E	25.14	50	650	5	120
D1-W	36.95	50	750	5	120
D1-W-E	17.6	50	400	5	120
D1-P	43	50	900	5	120
D1-P-E	33.2	50	650	5	120
D2	34.44	50	800	5	120
D2-E	8.42	50	140	5	120
D2-UW	18.14	50	400	5	120
D2-UW-E	12.07	50	200	5	120
D2-W	26	50	650	5	120
D2-W-E	11.4	50	300	5	120
D2-P	33.6	50	700	5	120
D2-P-E	12.65	50	350	5	120

C_{peak}: peak concentration in UMDSurf; C₅₀: 50% of C_{peak}; DL: ICP detection limit.

Table 5.8. UMDSurf Results for Zinc (CL-ML formation)

Sample	UMDSurf C _{peak} (µg/L)	Dist. reqd. to reach C ₅₀ (m)	Dist. reqd. to reach DL (m)	DL (µg/L)	U.S. EPA WQL (µg/L)
D1	22.43	50	450	5	120
D1-E	17.16	50	250	5	120
D1-UW	15.4	50	270	5	120
D1-UW-E	10.9	50	190	5	120
D1-W	16.17	50	300	5	120
D1-W-E	7.7	50	130	5	120
D1-P	18.78	50	300	5	120
D1-P-E	14.51	50	250	5	120
D2	15.06	50	400	5	120
D2-E	3.7	50	120	5	120
D2-UW	7.91	50	150	5	120
D2-UW-E	5.3	50	100	5	120
D2-W	11.37	50	250	5	120
D2-W-E	4.98	50	120	5	120
D2-P	14.7	50	300	5	120
D2-P-E	5.5	50	130	5	120

C_{peak}: peak concentration in UMDSurf; C₅₀: 50% of C_{peak}; DL: ICP detection limit

5.2 Geochemical Analysis

The pH-dependent leaching of major and trace elements from the different materials, measured using a pH-static system, enables conclusions on the main release-controlling parameters and on the chemical speciation of the potential contaminants. For both the dredged materials (D1 and D2) and their blends with quarry by-products, geochemical modelling has resulted in the identification of solubility-controlling phases in these matrices. The geochemical speciation model Visual MINTEQ v. 3.1 was used to calculate the element speciation in the solutions obtained from pH-stat leaching tests.

VisualMINTEQ was run in two steps. In the first step, pH and E_h data was used to determine the predominant oxidation states from the analyzed metals while in the second step, the aqueous concentrations of metal species in the leachates as well as the dominant control mechanisms were determined. In this study, geochemical analysis was conducted on D1 and D2 and their corresponding blends with quarry by-products to determine the dominant oxidation state of the leached metals and determine whether leaching of these elements are solubility-controlled or sorption-controlled. The output database includes the saturation index (SI), which allows to predict the main phases that control the solubility of the components of interest (Cornelis et al., 2008).

5.2.1 Results of Geochemical Analysis

The goal of this research was to simultaneously consider surface complexation, surface precipitation, and solubility controls for multiple components. Modelling of leaching was done in the presence of multiple analytes as opposed to modeling each element in isolation from other species because the nature of metal speciation on solid surfaces is a function of not only pH but

also, of surface coverage, competitive adsorption, ionic strength, and aqueous phase complexation (Criscenti and Sverjensky, 2003).

5.2.2 Predominant Oxidation States

Input mass concentration for each component (Al, As, Cu, Ni, Fe, and Zn) is based on the initial concentration from pH_{stat} leaching experiment. Pentavalent arsenic [As(V)] was reported to be the dominant oxidation state for arsenic in all the leachates (Fathollahzadeh et al., 2014; Maity et al., 2011). The form of As(III) is thermodynamically unstable in aerobic conditions; hence, it oxidizes easily to the less mobile form of As(V). Arsenic(V) is the dominant dissolved arsenic-species in natural waters, i.e. under oxic and natural pH conditions (Lager et al., 2005). In case of iron, Fe(III) is the dominating species as desiccation of dredged material results in an increase of insoluble iron(III)(hydr)oxides due to the oxidation of dissolved Fe²⁺ and of FeS_x (Smolders et al., 2005). For the two metals included in the redox analysis, the predominant oxidation state for Al, Cu, Zn and Ni in the samples were Al (III), Cu (II), Zn(II) and Ni(II) respectively.

5.2.3 Aqueous Phase Composition and Saturation Index Calculation

First, the predominant oxidation states of metals were determined by inputting in Visual MINTEQ the aqueous ion concentrations and the pH and Eh values measured in pH_{stat} leaching experiments and allowing only redox and aqueous complexation reactions. Second, saturation indices (of 206 solids included in Visual MINTEQ database) were calculated by inputting in Visual MINTEQ the aqueous concentrations of ions measured in pH dependent leaching experiments and allowing only aqueous complexation reactions (Apul et al., 2005).

Based on the major crystalline phases of the sediment under study, the input data consisted of the total concentration of the following major components Al^{3+} , As(V) , Ni^{2+} , Zn^{2+} , Cu^{2+} and Fe^{3+} and the following inorganic metal binding ligand SO_4^{2-} . Furthermore, model input files were composed of the total concentrations of the elements of interest in the pH range of 2-13. It is assumed that equilibrium was reached between the leachates and the potential solubility-controlling minerals in a 25°C open system. Because of the exposure of CO_2 to the atmosphere, the leachates were assumed to be in equilibrium with the partial pressure of atmospheric CO_2 at 32.N/m² (3.162×10^{-4} atm; Langmuir, 1997) during filtration and chemical analysis. Possible solid phases were selected to calculate the leachate composition in equilibrium.

VisualMINTEQ provides the concentration and the activities of species present in the aqueous solutions. The computation of the activity of the solutions requires the use of Davies equation.

$$\log \gamma_i = -A z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \quad (5.10)$$

where γ_i is the activity coefficient for ion i ; A is a constant dependent on the dielectric constant of water and temperature (~ 0.5 at 20 °C); z is the charge of ion; and I is the ionic strength of the solution (Stumm and Morgan, 1996). The ionic strengths (I) were computed by multiplying the EC values by 0.013, which is a number empirically derived from many river water samples to determine the ionic strength of aqueous solutions (Griffin and Jurinak, 1973).

Saturation indices calculated using VisualMINTEQ helps in explaining the controlling mechanism for leaching of metals. Those saturation indices were determined while accounting for the minerals and solid phases in VisualMINTEQ database. Depending upon the Saturation Index (SI) value, the mechanism of leaching can be solubility or sorption controlled. Usually, the high positive SI values are shown by the oversaturated metals, while the undersaturated ones shows

highly negative SI value, thus suggesting that leaching of a metal is controlled by another mineral or solid phase. If the mineral is in equilibrium with the element, then the SI values = 0 will be near the solubility line of the mineral or solid phase. And as the distance between the activities of metals and solubility line increases, the metal is either controlled by the solubility of another mineral or is not solubility-controlled. Solubility lines were also plotted on the same graph to visualize if the leached metal was solubility- or sorption-controlled.

5.2.4 Mechanism Controlling Leaching

Concentrations of Al, Cu, Ni, Fe, and Zn in the leachates from both the DM and their blends with quarry by-products are found to be consistent with the dissolution/precipitation of solid/minerals. Table 5.9 summarizes the dominant oxidation state and controlling-solids for each element of interest. Oxide hydroxide and carbonate minerals appear to control the leaching of these metals. Leaching of As was not solubility-controlled and no geochemical reactions were elucidated from the results in the research reported in this study. Fathollahzadeh et al. (2014) also witnessed the same. According to them, as the species of As, as arsenate (V), usually dominated by oxidized form, mainly HAsO_4^{2-} without any organic complexation, were mainly associated with oxide and hydroxides of Fe and Mn. According to Ho et al. (2013), for As no minerals are saturated, which indicates that the secondary minerals of As are too soluble to control their dissolved concentrations in the studied sediments.

TABLE 5.9 Controlling solids for elements

Element	Speciation	Solubility-Controlling Solids	Dredge Material Specimens Controlled by the Solids
Al	Al(III)	Gibbsite $[\text{Al}(\text{OH})_3]$ amorphous	D1, D2, D1-UW, D2-UW, D1-W, D2-W, D1-P, D2-P
As	As(V)	None	None
Cu	Cu(II)	$\text{Cu}(\text{OH})_2$	D1, D2, D1-UW, D2-UW, D1-W, D2-W, D1-P, D2-P
Fe	Fe(III)	Ferrihydrite $[\text{Fe}(\text{OH})_3]$	D1, D2, D1-UW, D2-UW, D1-W, D2-W, D1-P, D2-P
Ni	Ni(II)	$\text{Ni}(\text{OH})_2$	D1, D2, D1-P, D2-P
		NiCO_3	D1, D2, D1-UW, D2-UW, D1-W, D2-W, D1-P, D2-P
Zn	Zn(II)	Smithsonite $[\text{Zn}(\text{CO})_3]$	D1, D2, D1-UW, D2-UW, D1-W, D2-W, D1-P, D2-P

The VisualMINTEQ calculations show that the Al in the leachate is solubility controlled for both the Dredged Material (D1 and D2) and their respective blends with quarry fines. The log-activities of the dissolved Al species in the leachate of DM and its blends with quarry by-products is in proximity of mineral named Gibbsite $[\text{Al}(\text{OH})_3]$ (Figure 5.9). Reynolds (2006), Astrup et al. (2006), and Komonweeraket et al. (2015) also reported gibbsite as the minerals controlling the solubility of Al. The pH_{stat} leaching of Al is adequately described over a large pH range by the solubility behaviour of Al (hydr)oxide forms such as gibbsite, in agreement with Meima and Comans (1997). Meima and Comans (1997) also suggested that at near-neutral pH's three minerals act simultaneously as pH- and solubility-controlling phases for Al, Ca and SO_4 ; gibbsite ($\text{Al}(\text{OH})_3(\text{s})$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}(\text{s})$). The leaching of Al from the untreated dredged sediments agreed well with $\text{Al}(\text{OH})_3(\text{s})$ at high and low pH, similar to the observations made by Gardner et al. (2007). At $\text{pH} > 12$ Al might be controlled by more amorphous Al (hydr)oxide forms (amorphous $\text{Al}(\text{OH})_3$) suggesting that Al concentrations may continue to rise as the pH is increased (Dijkstra et al., 2006). Zevenbergen and Comans (1994) and Meima and Comans (1997) also showed that slowly dissolving aluminosilicate minerals could control Al leaching at higher pH values.

The dominant oxidation state of Cu leached from DM or from the blends prepared with the quarry by-products was determined to be Cu(II). For Cu, the controlling phase of Cu is $\text{Cu}(\text{OH})_2$ (Figure 5.10). Cu shows high affinity for organic matter in soils and sediment, particularly humic acids and formation of carbonate and hydroxyl soluble complexes (Dijkstra et al., 2004; Nordmyr et al., 2008). $\text{Cu}(\text{OH})_2(\text{s})$ is known as a solid phase that controls the leaching of Cu metals

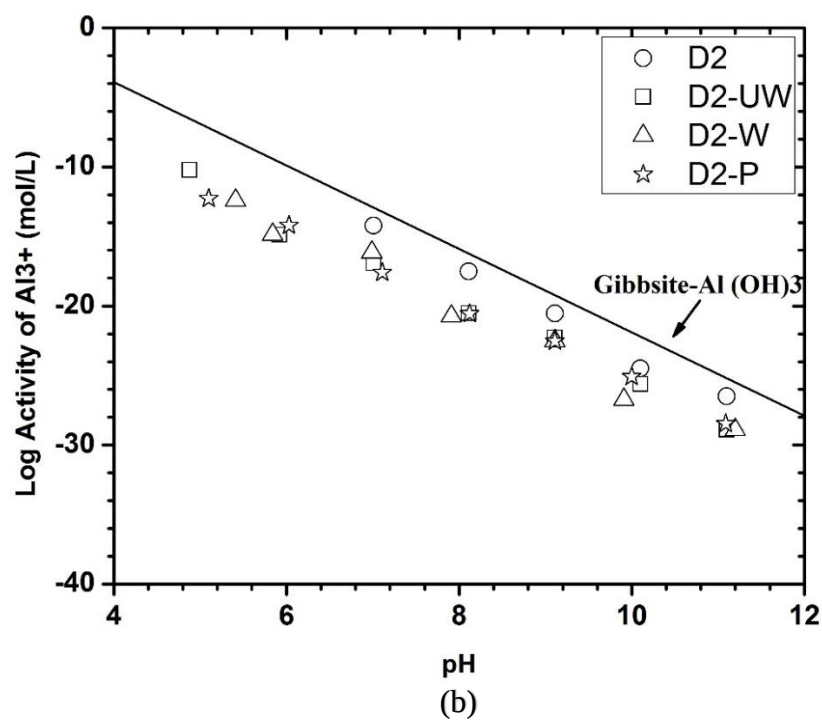
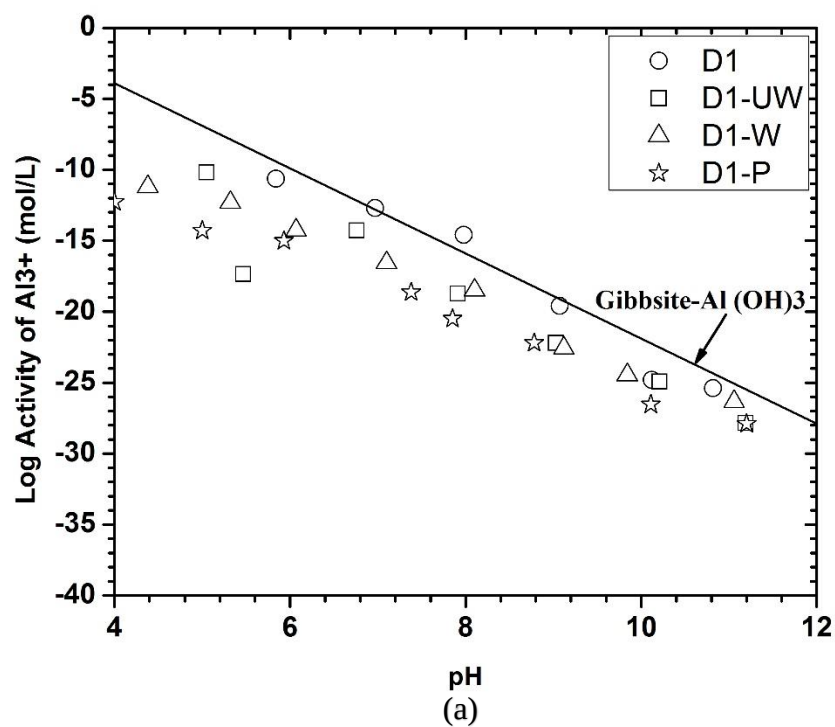


Figure 5.9 Log activities of Al versus pH in leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

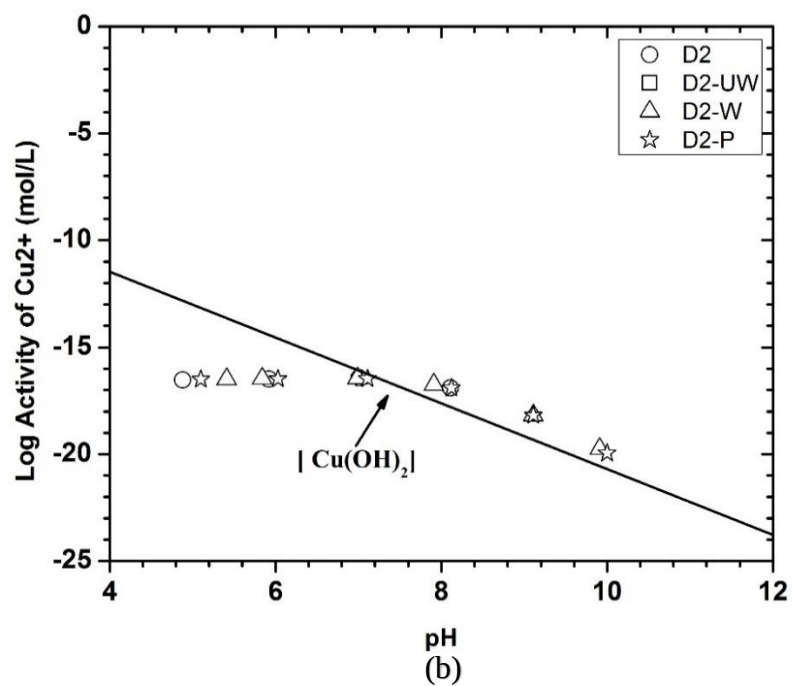
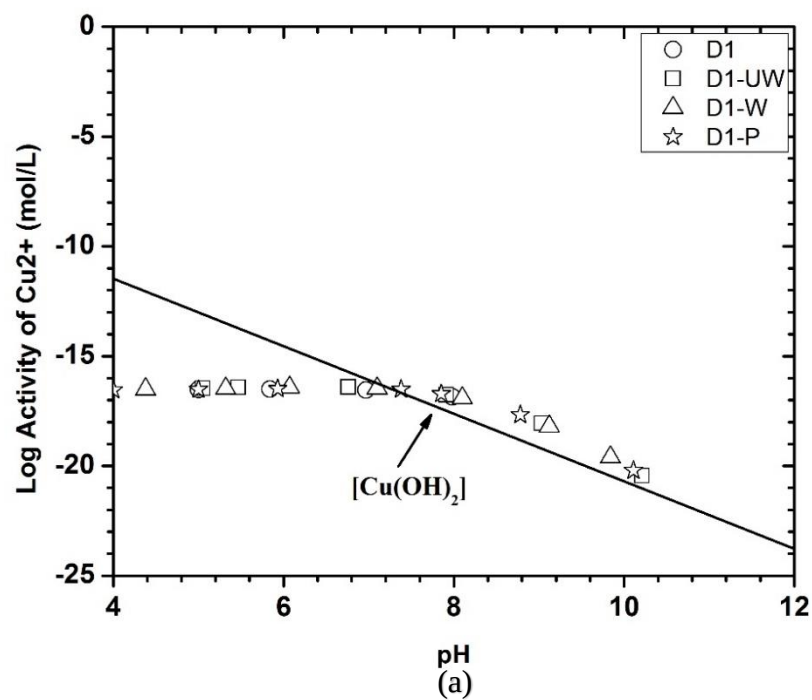
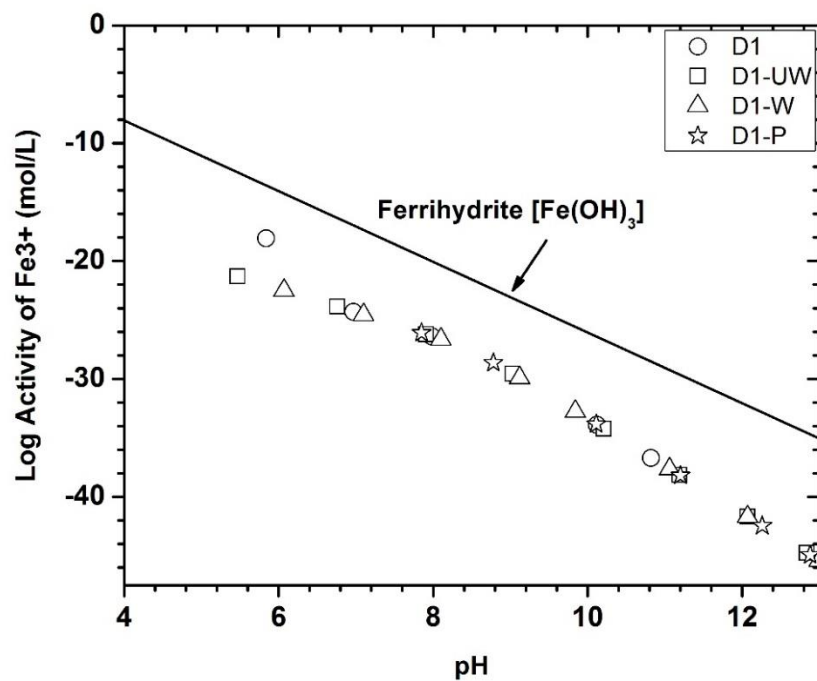


Figure 5.10 Log activities of Cu versus pH in leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

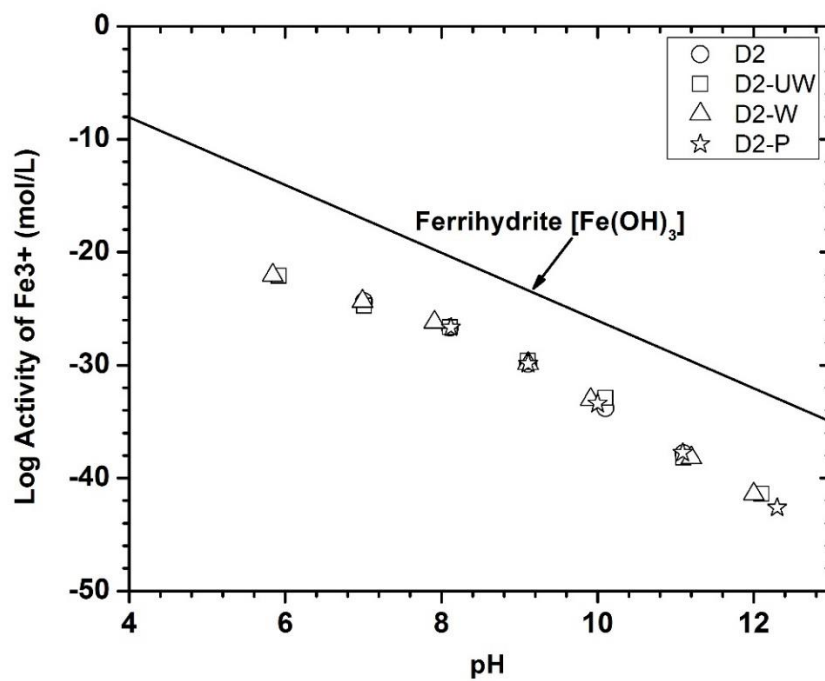
especially under alkaline conditions. Apul et al. (2005) also observed a similar pattern and showed undersaturation of Cu with respect to $\text{Cu}(\text{OH})_2$ at low pHs and attributed this behaviour to interactions of Cu with sorptive surfaces and other aqueous complexes. The leaching of Cu is well-predicted by surface complexation to Fe- and Al-(hydr) oxides in the pH range of 1-14. At $\text{pH} > 8$, tenorite (CuO) starts to precipitate and this causes Cu to oversaturate with respect to CuO (Dijkstra et al. 2006b). Based on saturation indices, $\text{Cu}(\text{OH})_2$ was determined to be the only solid species in the database that could have controlled the release of Cu. Payan et al. (2012) also performed geochemical analysis on the contaminated dredged sediments and indicated that the controlling phases for copper are $\text{Cu}(\text{OH})_2$ at pH 11-14, tenorite (CuO) at pH 9-13, and malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) at pH 10-14.

Fe^{3+} is the dominant oxidation state of Fe metals in the aqueous solutions of both the DM's and its blends with the quarry by-products, possibly due to long-term aging of these sediments in the stockpiles (Meers et al., 2006). The data in Figure 5.11 indicates that solubility of Fe is more likely controlled by $\text{Fe}(\text{OH})_3$ -amorphous and that Fe(III) is undersaturated with respect to ferrihydrite.

The concentrations of humic and fulvic acids are typically high in marine sediments and Iron (III) has a tendency of forming strong complexes with these two acids thus, the under saturation of Fe(III) with respect to the ferrihydrite may be because of the complex formation of iron(III) with humic and fulvic acids (Dijkstra et al., 2006). The role of leaching control by sorption of contaminants on mineral phases such as Fe and Mn oxides are potentially important and is much more pronounced in soil and sediment studies. Leaching control by sorption may be particularly relevant for aged materials.



(a)



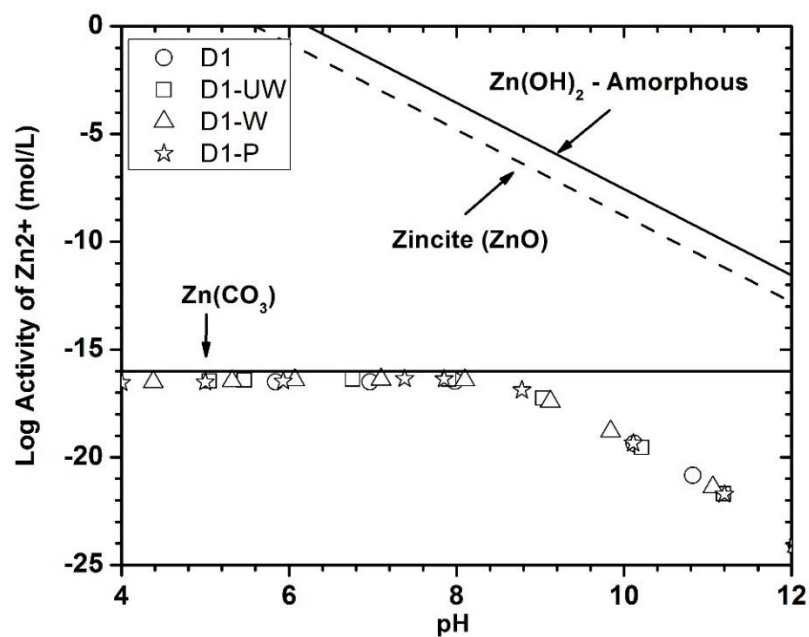
(b)

Figure 5.11 Log activities of Fe versus pH in leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

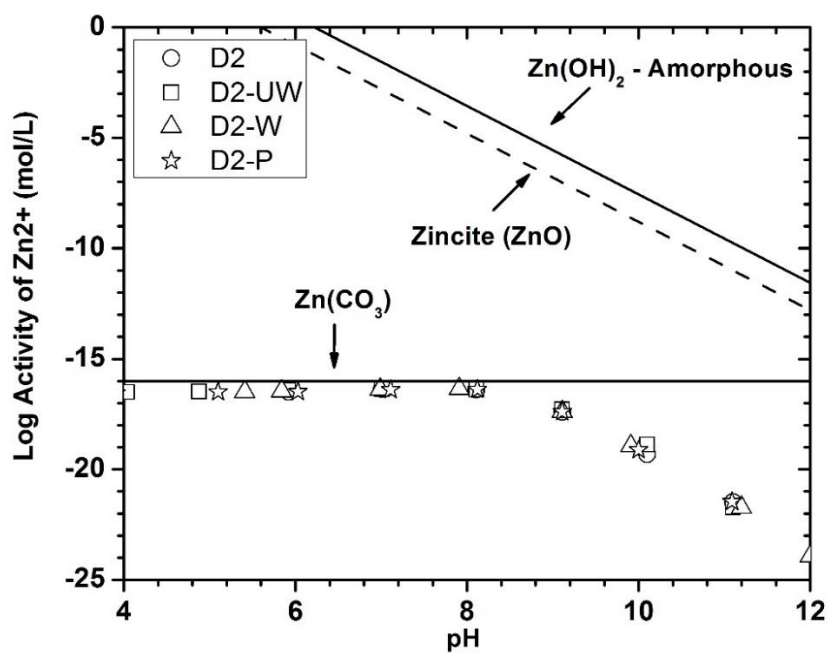
aging of wastes by weathering changes the mineralogy and increases the abundance of sorbing mineral phases (Zevenbergen et al., 1994).

Solubility of Zn is mainly controlled by precipitation and dissolution reactions in the soil matrix (Murarka et al. 1992). Smithsonite (ZnCO_3) is identified as the controlling solids for Zn^{2+} in the pH range of 5-9 (Figure 5.12). At $\text{pH} > 9$, undersaturation of Zn from the leachates is present for both DMs and the blends. Geochemical analysis performed by Cappuyns and Swennen (2007) on dredged sediments showed that the controlling phase for Zn is smithsonite (ZnCO_3) at pH 5-9, hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) at pH 9-13, and at zincite (ZnO) and $\text{Zn}(\text{OH})_2$ at pH 10-13. Payan et al. (2012) tested dredged sediments and showed that ZnCO_3 may govern the leaching of Zn in the pH range of 5-13 i.e. Zn may precipitate as ZnCO_3 . The distribution of zinc species in the freshly deposited DM has been determined by Isaure (2002) using spectroscopic techniques. It followed that zinc was primarily present as sphalerite (ZnS) and to a lesser extent as willemite (Zn_2SiO_4), Zn-containing ferric oxides, zincite (ZnO), and Zn-containing phyllosilicates. Cappuyns et al. (2014) showed that at $\text{pH} > 10$, the solubility of Zn might be governed by willemite (Zn_2SiO_4). At basic pH, Zn can also exist in the solution mainly in the forms of ZnSiO_3 , ZnOH^+ , $\text{Zn}(\text{OH})_2(\text{aq})$, $\text{Zn}(\text{OH})^{3-}$, and $\text{Zn}(\text{OH})_4^{2-}$ (Yan et al. 2008).

Ni(II) was the dominant oxidation state of the Nickel metal that was leached from both the DM and the blends. Previous studies also reported Ni(II) as the dominant nickel species in the dredged sediments (Fathollahzadeh et al., 2015; Payan et al., 2012). Figure 5.13 illustrates that Ni is undersaturated with respect to $\text{Ni}(\text{OH})_2$ for both the DM (D1 and D2) and its blends with pond fines (D1-P and D2-P) for $\text{pH} < 7$. At $\text{pH} > 8$, Ni is undersaturated with respect to NiCO_3 for D1 and D2 and its blends with quarry-by-product. Tahervand and Jalali (2016) observed that Ni solutions were undersaturated with respect to $\text{Ni}(\text{OH})_2$ (am) at all equilibrium pHs, and that at $\text{pH} > 7$, free



(a)



(b)

Figure 5.12 Log activities of Zn versus pH in leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

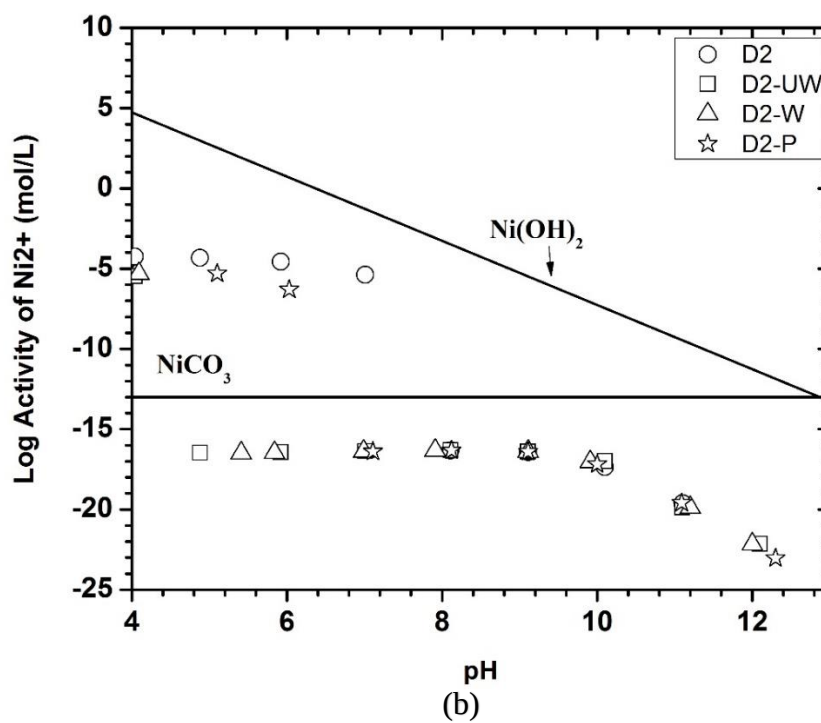
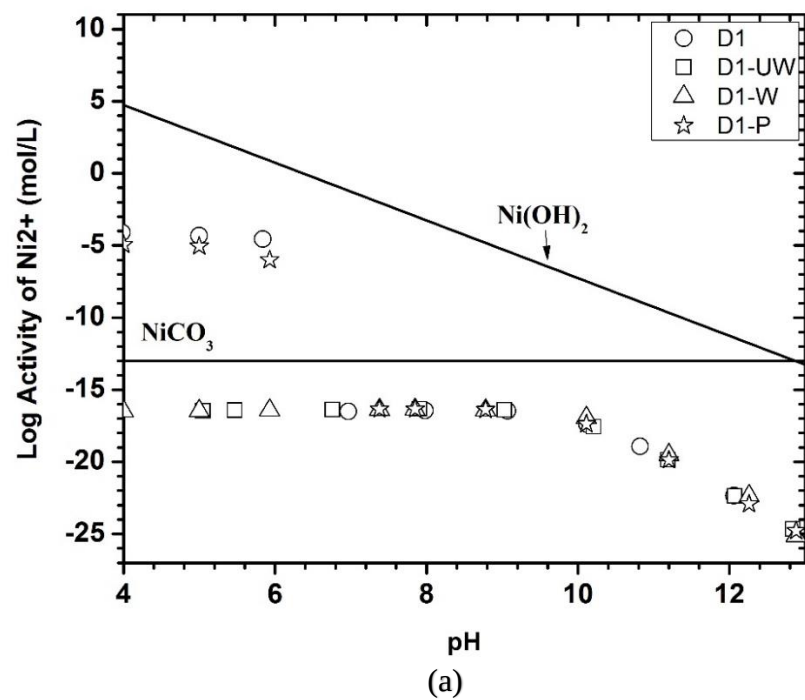


Figure 5.13 Log activities of Ni versus pH in leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

Ni were the major species in soil solution. The under saturation of Ni with respect to $\text{Ni}(\text{OH})_2$ may be because of surface adsorption reaction at a pH range of 4-8 (Yan et al., 2008).

5.3 Conclusions

Sequential column leach test metal concentrations of pure and treated dredged materials were input to a numerical model, named UMDSurf, to simulate the effect of natural formation and distance on surface water contaminations. A series of geochemical analyses conducted using Visual MINTEQ allowed to predict the chemical species in leachates from sediments at different pH values. The following conclusions can be made:

- 1) The results of UMDSurf showed that the metal concentrations decreased to levels below the EPA WQLs after travelling through the natural formation and even before reaching to surface waters. The aqueous concentrations of Zn and Cu that were initially above the WQLs conformed to the regulatory limits upon reaching the surface waters. The decrease in the metal concentrations was more clearly pronounced in the case of the CL-ML formation than the CL formation due to its near-neutral pH and the greater metal retardation capability.
- 2) The results from UMDSurf also confirmed that the concentrations of metals in surface waters decreased even further as the horizontal distance away from the natural formation increased.
- 3) The results of the geochemical analysis identified dissolution-precipitation reactions as the mechanisms controlling aqueous concentrations of Al, As, Cu, Ni, Fe, and Zn that leached from DM and its blends with quarry by-products with hydroxide and carbonate solids.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary and Conclusions

A battery of geoenvironmental tests were performed on pure Chesapeake Bay dredged material (DM) and blends of dredged material and quarry by-products to investigate the geotechnical and environmental stability of these materials in a highway embankment setting. The environmental tests included batch leach tests (pH_{stat} and TCLP) and sequential column leach tests (SCLT). UMDSurf was used to define the transport of contaminants in surface waters. Geochemical analysis via VisualMINTEQ was conducted to investigate the speciation of metals in aqueous solutions. The overall conclusions are summarized below.

- 1) The maximum dry unit weight of the blends of dredged material and quarry by-products ranged from 112.5 pcf to 113.5 pcf (17.67 kN/m^3 to 17.82 kN/m^3), which was higher than the maximum dry unit weight of pure DM (95.4 pcf/ 14.98 kN/m^3). The blends satisfied the Maryland SHA compaction unit weight limit of 100 pcf (15.7 kN/m^3) for soils in highway embankment construction.
- 2) Addition of quarry-by-products to DM increased the overall shear strength. The effective angle of friction increased from 30° to 47° upon amending the dredged material with the quarry by-products. Since both the blends and DM were cohesionless, the increase in shear strength manifested itself in an increase in friction angle only.
- 3) Leaching of As during the pH_{stat} leaching tests followed an amphoteric pattern for pure DM and a cationic pattern for the blends; its concentration was above the EPA WQL at extremely low and high pHs. The addition of quarry by-product to DM was able to immobilize As at these extremely high and low pHs and keep the As leaching below detection limit at $\text{pH} \sim 6.5\text{--}9$. Similarly, Al, Cu, Fe, Ni and Zn concentrations leached from the blends were below the EPA WQL at near-neutral pHs. The variations in

dredged material pHs were small (pH=8.18 for D1 versus pH=7.2 for D2) thus, no discernable difference was observed between the concentrations of metals leached from these two DMs.

- 4) DMs and their blends with the quarry by-products showed elevated concentrations of Cu and Zn in the SCLTs, however, the concentrations dropped to below the detection limits after several pore volumes. The peak SCLT concentrations of the metals leaching from DMs decreased by 14-60% upon stabilizing the materials with the quarry by-products, and the concentrations further decreased by 50-100% once the leachate past through the embankment soil.
- 5) The concentration of the metals leached from the DM and the blends were below the EPA water quality limits (WQLs) at the entrance location of surface water, based on the results of a numerical analysis to simulate contaminant transport in aqueous environment adjacent to the embankment. A significant reduction in the concentrations was evident due to existence of a natural formation located between the DM or treated DM and the body of surface water. At 50 m in the surface water, the metal concentrations were further reduced by ~50%, and dropped to non-measurable levels (i.e., below the detection limits) at 300-900 m into the surface water for the CL formation and 130-400 m for the CL-ML formation.
- 6) The results of the geochemical analysis identified dissolution-precipitation reactions as the mechanisms controlling aqueous concentrations of Al, Cu, Fe, Ni and Zn that leached from DM and DM-quarry by-product blends, except for As, since no geochemical reactions controlling the release of As could be identified due to a leaching pattern for As leaching that was not solubility-controlled. As can leach out, most probably as less toxic pentavalent arsenic (As(V), under acidic and basic conditions.

Hydroxide minerals control the leaching of Al, Cu and Fe; whereas, leaching of Ni and Zn were controlled by carbonate minerals.

6.2 Recommendations for Future Work

The quarry by-product amended DM can be used for various beneficial purposes depending on the measured geotechnical properties. Field pilot tests should be carried out to simulate typical field highway construction scenarios and performance of blends should be studied with the change in rainfall patterns. The significant increase in the effective angle of friction of the blends of DM-quarry-products is likely to result in a higher factor of safety for slopes constructed with these blends. Limit equilibrium method or finite element method should be used for the slope stability analysis, assuming the worst condition on the blend, before using it as a highway embankment material.

Lysimeters should be used to collect leachates as part of future field tests since characteristics of the environment (e.g., pH, climatic stresses) where leaching takes place affect the rate and extent to which inorganic components are released from the DM and blends. Spiking of influent solution for SCLT should be done with various metals likely to exist in highway runoff (e.g., Fe, Ni) if there is any interest in simulating typical field storm water runoffs.

The dredged material used in this study was a 10-year-old material. Various geotechnical and geochemical tests should be performed on the fresh dredged materials procured from the Bay to better characterize the variability in mechanical and environmental properties. If the dredged material is stored for larger period then, its recommended that regular mechanical and environmental tests should be perform. To model the variability of index and engineering properties of the dredged materials in stockpiles, a geostatistical analysis can be beneficial.

It should be noted that only one set of quarry by-products and one type of dredged material collected from a particular stockpile (Stockpile A) were utilized in this study and, in its current study, the results of the geotechnical and environmental tests are only applicable to these materials. To generalize the behavior, a series of tests need to be conducted with materials with varying pHs, geotechnical parameters, organic matter, dissolved organic carbon content, carbonate content, and total metal content.

APPENDICES

APPENDIX A: BATCH LEACH TEST ON DREDGED MATERIAL AND BLENDS

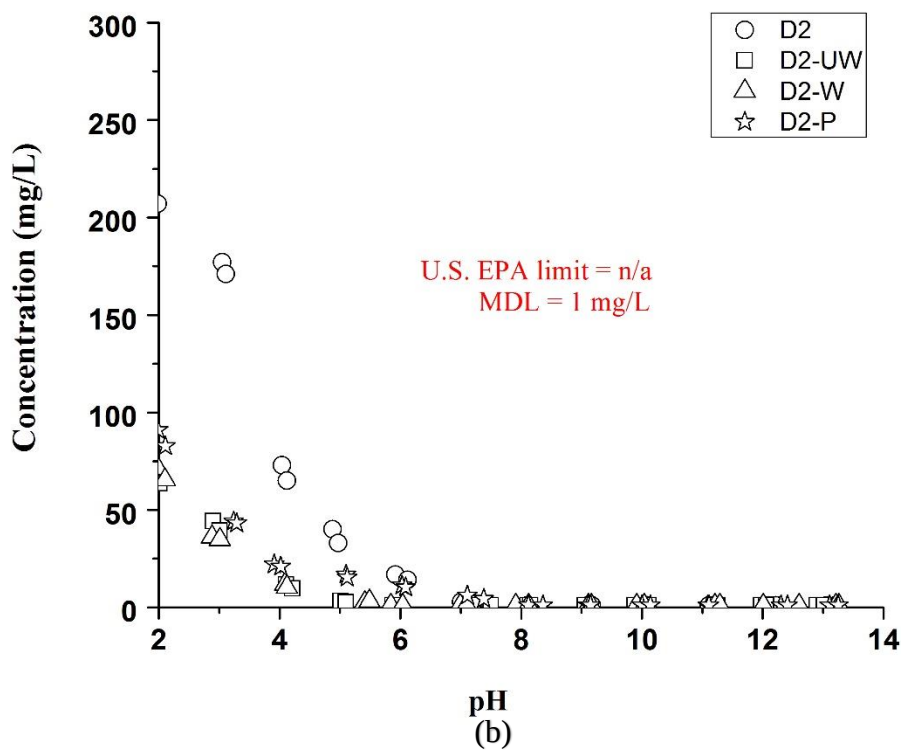
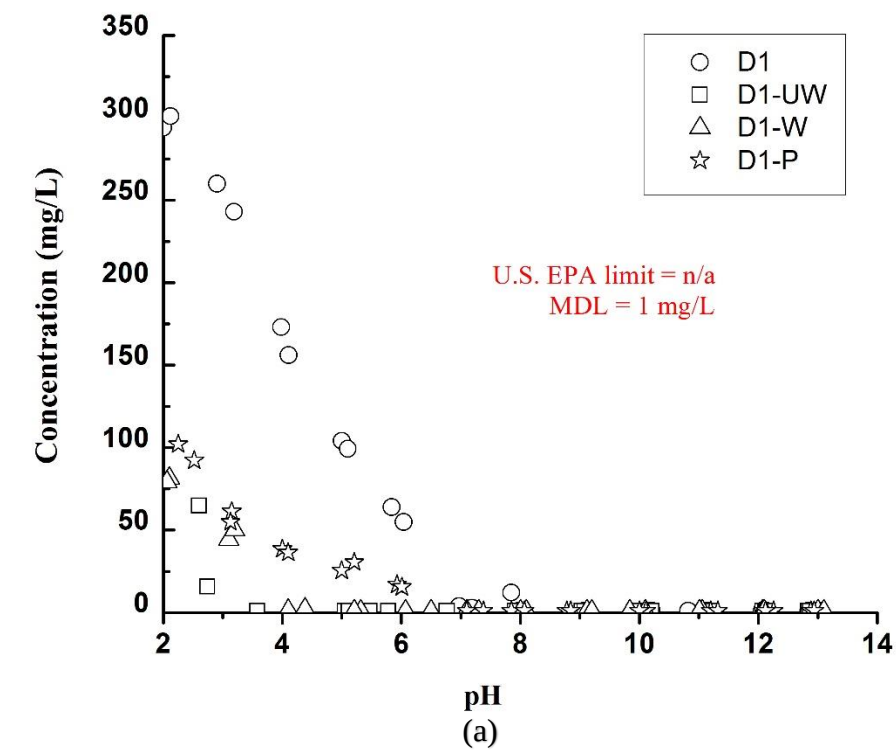


Figure A.1. Concentrations of Mn as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

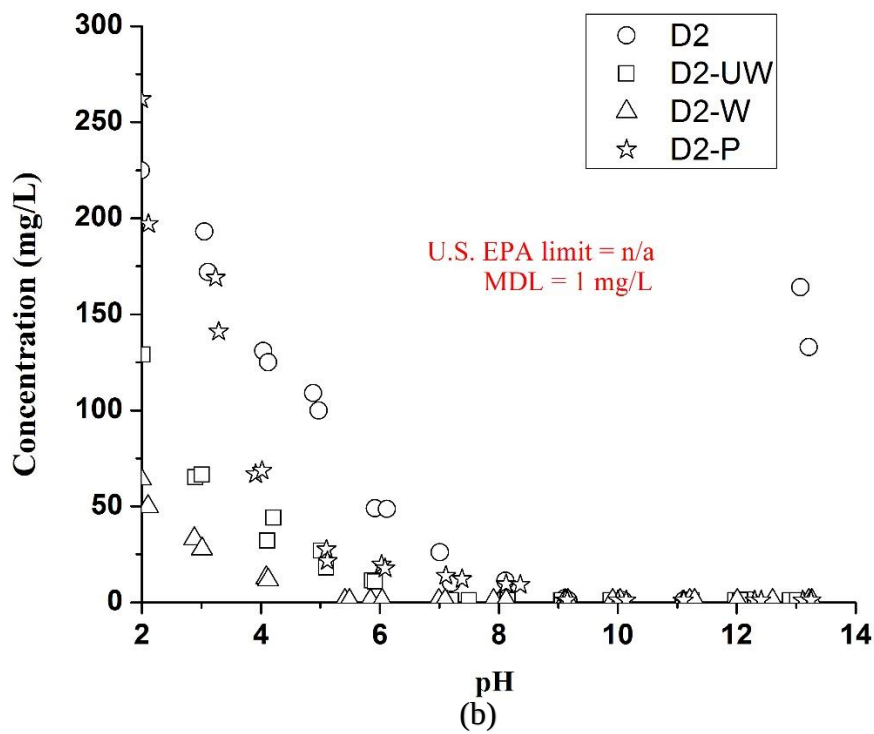
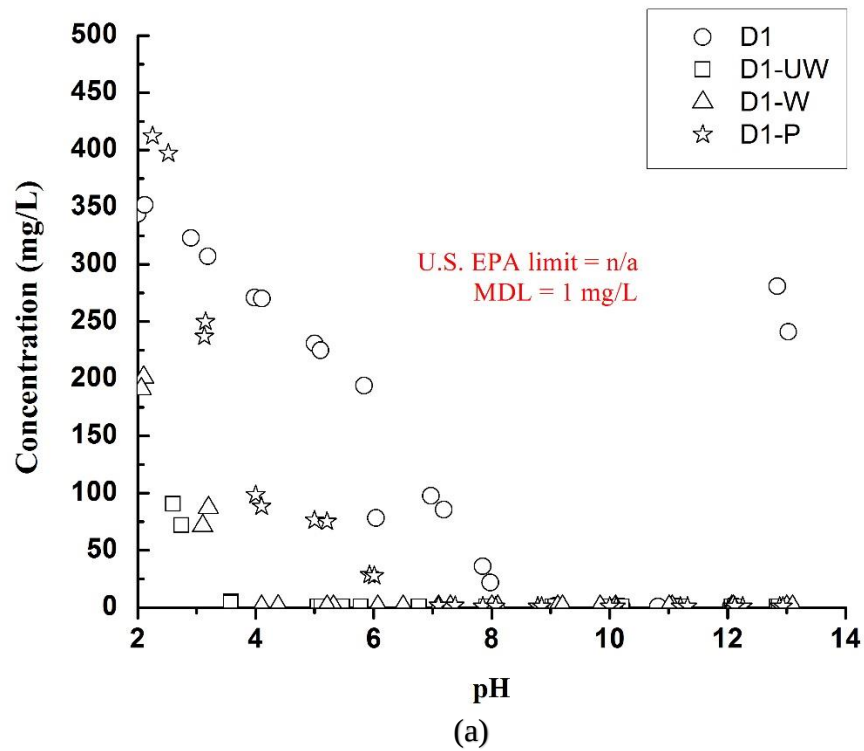


Figure A.2. Concentrations of Mg as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

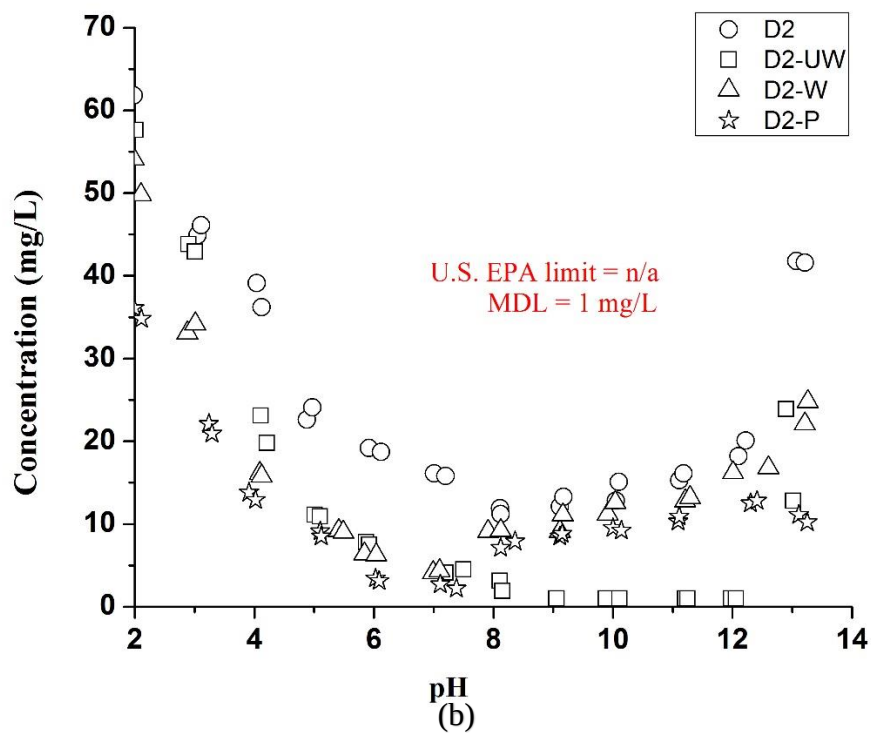
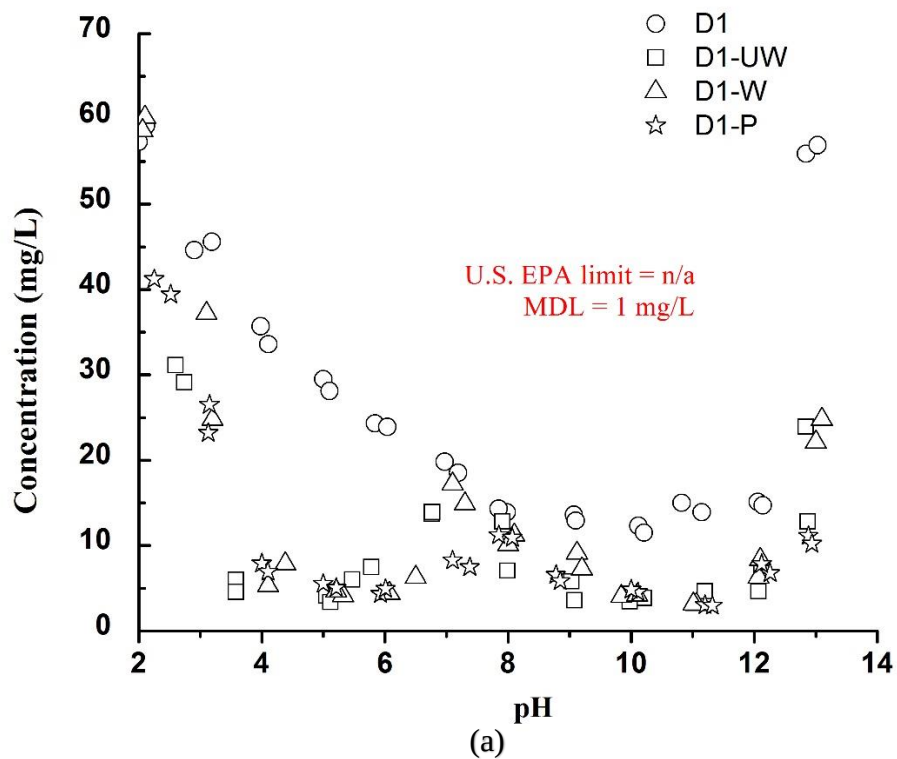


Figure A.3. Concentrations of K as a function of pH in the leachates of (a) D1 and (b) D2 and the blends prepared with the quarry by-product.

APPENDIX B: SEQUENTIAL COLUMN LEACH TEST RESULTS

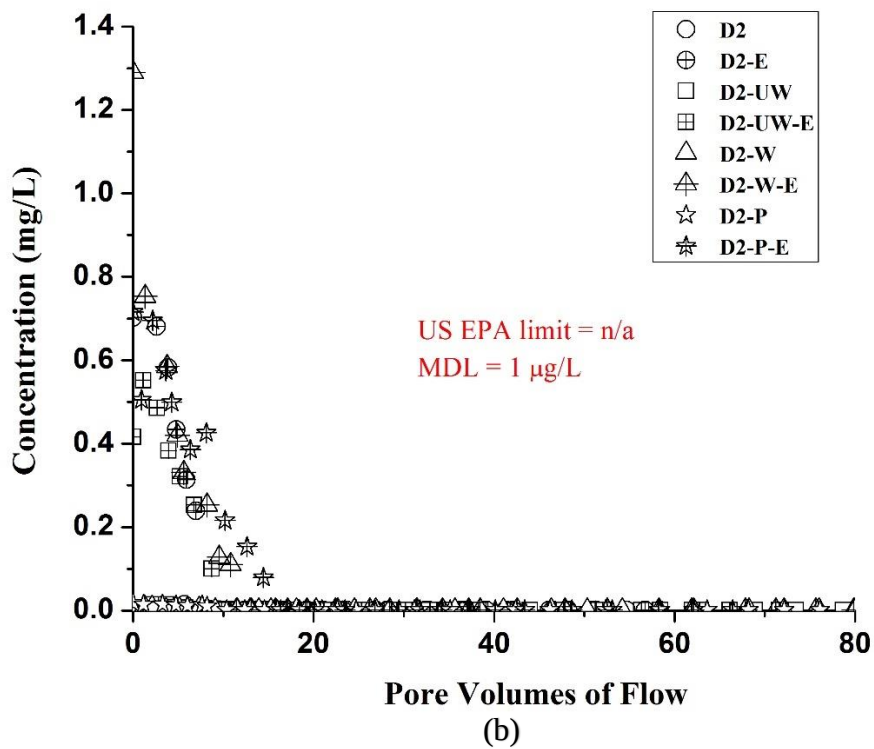
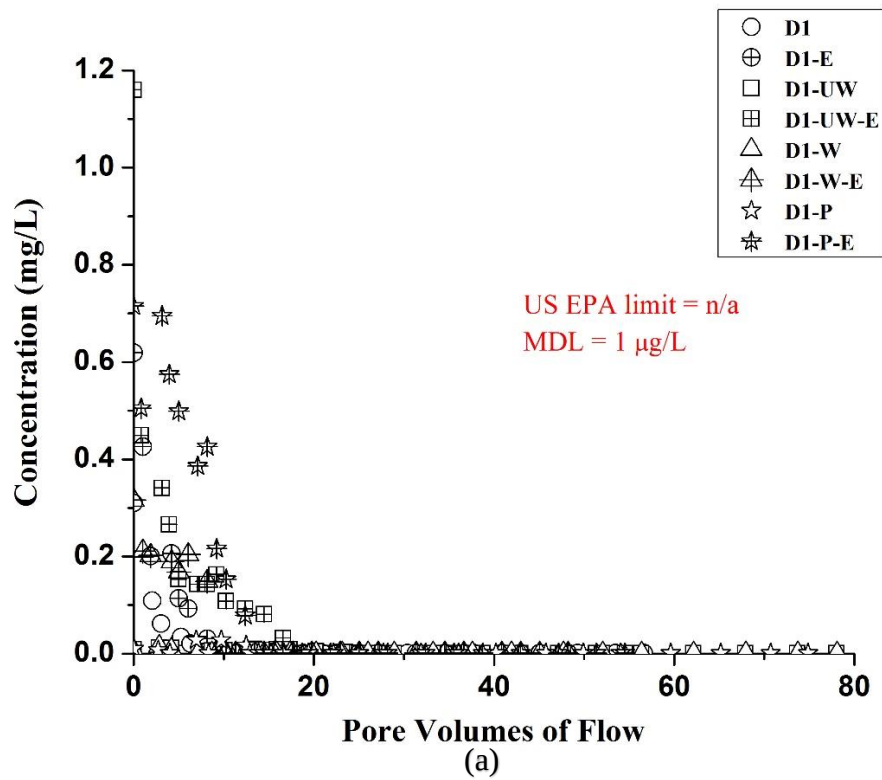


Figure B.1. SCLT elution curve for Ba for (a) D1 and (b) D2 and its blends with quarry by-products

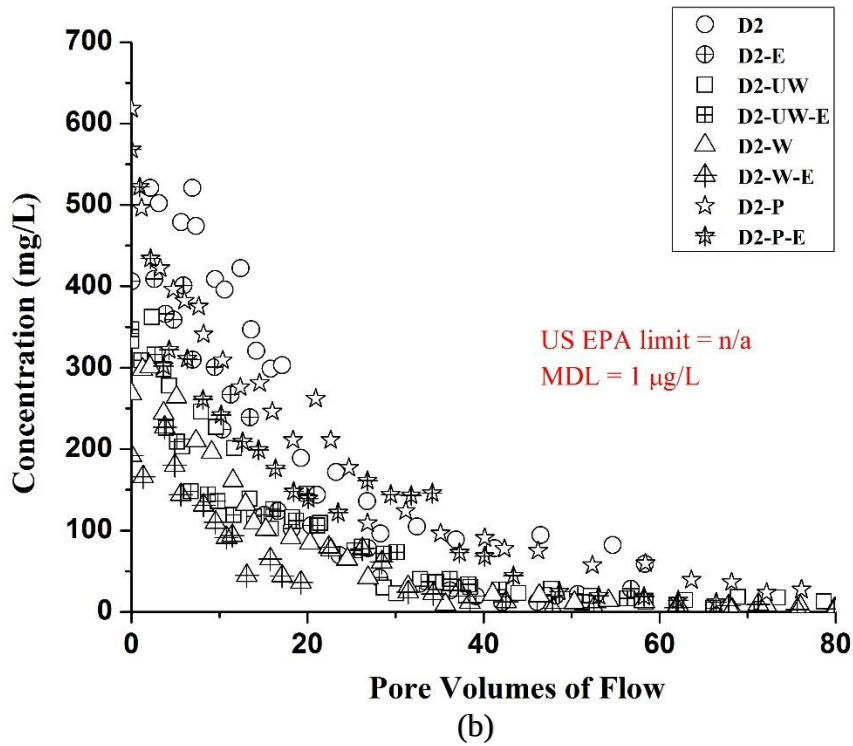
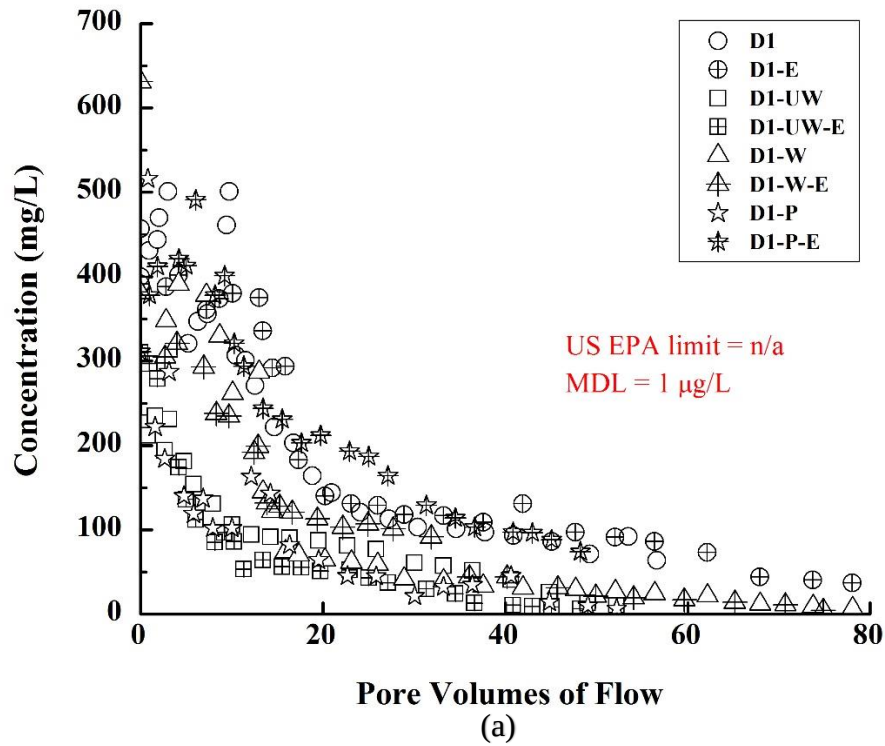


Figure B.2. SCLT elution curve for Ca for (a) D1 and (b) D2 and its blends with quarry by-products

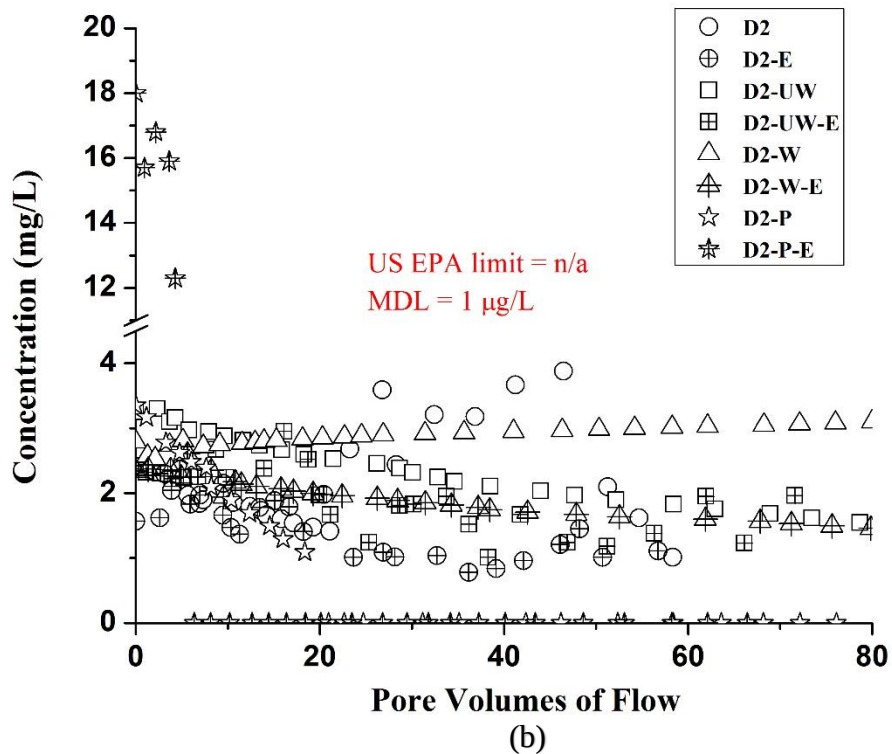
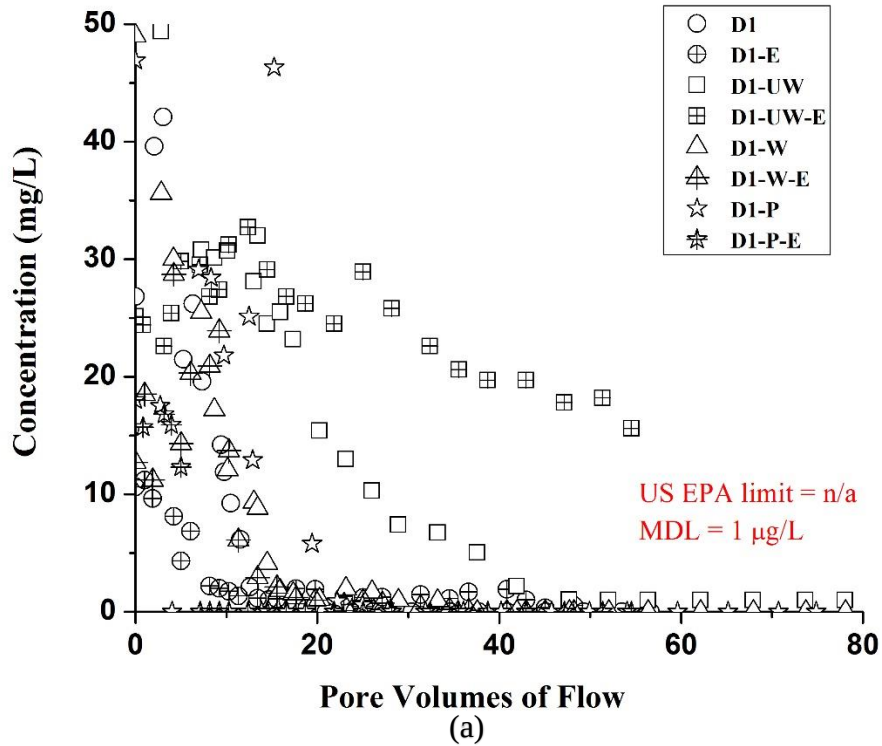


Figure B.3. SCLT elution curve for K for (a) D1 and (b) D2 and its blends with quarry by-products

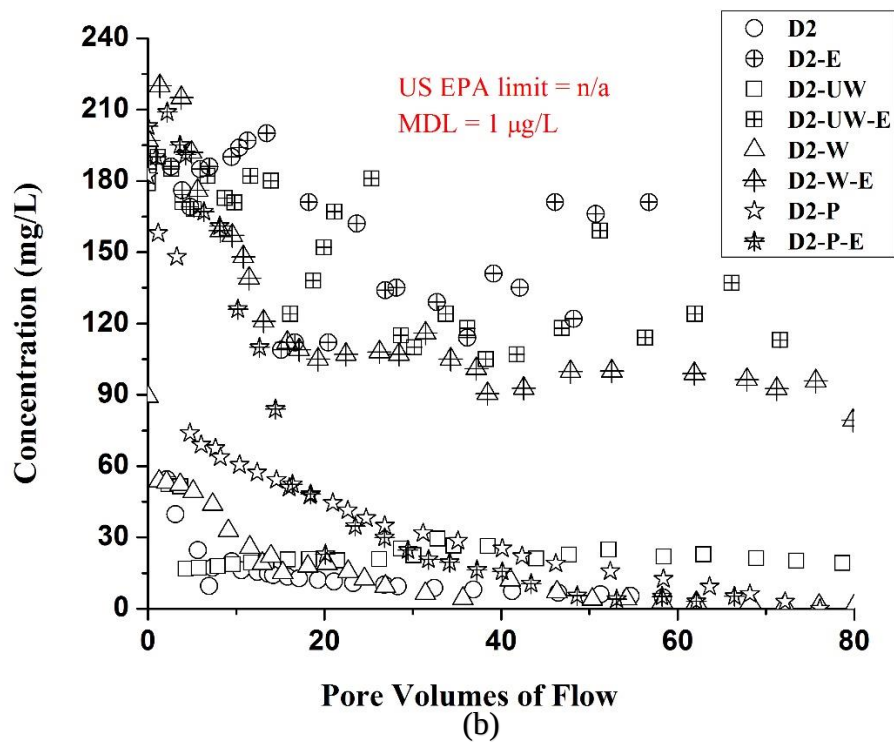
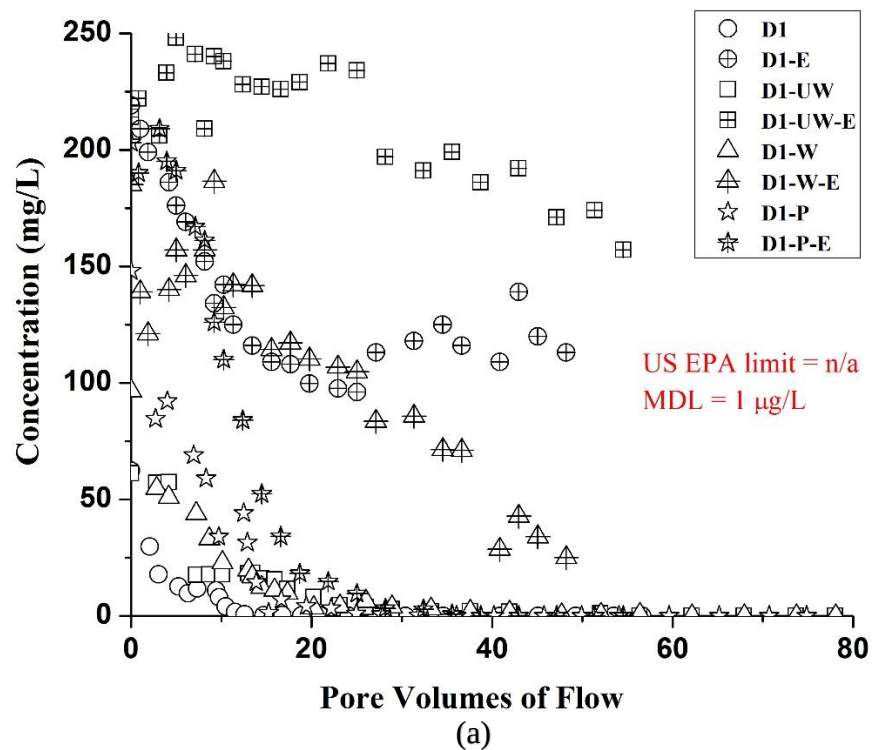


Figure B.4. SCLT elution curve for Mg for (a) D1 and (b) D2 and its blends with quarry by-products

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