The Efficiency of Vegetated Biofilters to Mitigate Highway Stormwater Runoff and the

Fate of these Contaminants within the Bed

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Abstract

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<u>The Efficiency of Vegetated Biofilters to Mitigate Highway Stormwater Runoff and the</u>

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The efficiency of vegetated biofilters to mitigate highway stormwater runoff was assessed utilizing two constructed biofilters and applying simulated stormwater runoff with high and low concentrations of metals at varying slopes. In this study the efficiency of vegetated biofilters was determined, the contaminant removal mechanisms and the soil fractions that retained the metals.

Results from these tests concluded that the vegetated biofilters were very efficient in mitigating highway stormwater runoff, with percent removals ranging from 92.5% - 99.0% for the high concentration tests and 31.3% - 91.2% for the low concentration tests. Metals were predominantly removed by adsorption to the suspended solids added to the influent, settling within the bed, and then further taken up by the leaves and roots. Chemical fractionation results indicated that the majority of the metals were concentrated in the Fe-Mn oxide and organic fractions of the soil, indicating that future remobilization of these metals was unlikely, because metals bound to these fractions are strongly retained.

Approved: _____

Guy Riefler

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Dedicated to my Grandma Nighswander: Whose love, wisdom, inspiration, and support helped guide me through the years – Forever missed and loved.

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1   Introduction

1.1   Background

On June 22, 1969, the Cuyahoga River burst into flames due to oil and other industrial wastes dumped into it. By the early 1970s, water pollution was a severe concern; not only because of the Cuyahoga River, but several of the U.S. waters were in a serious state. In 1971, Ralph Nader published a detailed report, *Water Wasteland*, which discussed how badly the nation's waters were polluted. From this report, it was found that 30 percent of water samples had concentrations of chemicals that exceeded the Public Health Service Limits, DDT was found in 584 of 590 fish samples, Indiana's Brandywine Creek was determine unfit for swimming due to high bacteria levels, and much more. This report opened up America's eyes, and made it clear that our own drinking water was not as safe as everyone thought (Adler et al., 1993).

The Clean Water Act or Federal Water Pollution Control Act of 1972 was set forth to address many visions and goals that prior federal water pollution laws were unable to properly enforce and manage. Congress passed the Clean Water Act and provided a definition which states that "the objective of this Act is to restore and maintain the chemical, physical and biological integrity of the Nation's waters" (Federal Water Pollution Control Act, 1972).

Another objective of the Clean Water Act was its focus on reducing effluent limits. Regulating effluent limits prevented large amounts of pollutants from initially discharging into nearby waters. This limit on effluent concentrations was brought forth in the 1972 amendments to the Federal Water Pollution Control Program (Prahaland et

al., 2007) under the National Pollutant Discharge Elimination System (NPDES). This new system "required permits for all point sources of pollution and [. . .] defined tough new requirements for these permits" (Adler et al., 1993, p. 8). NPDES also required industrial sources and publicly owned treatment works (POTWs) to incorporate pollution control technology. These tough new requirements were based on what the best available technology (BAT) could achieve. These technology-based controls were incorporated to "achieve across-the-board pollution reduction (and, wherever possible, elimination) and to create a level playing field for most dischargers" (Adler et al., 1993, p. 9).   The NPDES additionally mandated states to develop total maximum daily loads (TMDLs). These daily loads set the quantitative "maximum concentrations of pollutants that the water body could handle and still meet its designated use" (Prahaland et al., 2007, p. 89).

While all of these requirements appeared sufficient to clean up our Nation's waters dramatically, the NPDES initially only forbid discharges of pollutants by point sources. Point source pollution can be defined as "direct sources of water pollution from any number of discrete conveyances which discharge directly into water bodies as a matter of course" (Seidenberg, 2006, p. 703). While point sources account for a significant amount of water pollution, non-point sources "[. . .] may be responsible for as much as 50% of the nation's remaining water quality problems" (Copeland, 2006, p. 2). Despite this statistic, point sources are most commonly correlated with water pollution, which is why the Clean Water Act of 1972 had always focused on this particular source.

The Clean Water Act of 1972 was amended in 1987 which established the Non-point Source Management Program as part of Section 319. Non-point source pollution

"originates from many scattered small sources", such as "automobiles leaking small amounts of oil and grease" (Kubasek and Silverman, 2008, p.245), which particularly come from storm water runoff. Storm water runoff "impairs more water bodies, surface and ground, urban and rural, than any other pollution source in the country" (Adler et al., 1993, p. 171).

Stormwater runoff can be a point source pollutant when it comes from the operator of a municipal separate storm sewer system (MS4), which includes roads with drainage systems, municipal streets, catch basins, etc. These operators are required to obtain a NPDES permit under the Stormwater Phase II Final Rule. Stormwater discharged from MS4s is considered to be point source pollution, because it ends up in discrete conveyances. This research pertains to stormwater runoff that is considered a non-point pollutant, because highway runoff cannot be pinpointed to a specific location. Stormwater runoff that runs over highways is different from stormwater runoff that runs over municipal streets, because highways are not curbed, so there are no storm drains to collect the runoff. Instead, the stormwater runoff flows over the entire length of the highway, which is why it is literally non-point source pollution.

Highway stormwater runoff is one of the largest contributors to non-point source pollution because when it rains, pollutants on the impervious ground surface such as suspended solids, heavy metals, polycyclic aromatic hydrocarbons, and oil and grease get washed away with the storm water into nearby rivers or lakes (Hoffman et al., 1984). Heavy metal contaminants come from various car parts. Tire rubber contributes to zinc and cadmium contamination. This tire wear is increased when road conditions are poor

(Turer et al., 2000). Additional contaminants, such as copper, lead, and particulates, are released from break pad linings, extreme wear of the surface of the road, and combustion by-products (Lancaster et al., 2008).

Regulating non-point source pollution poses a problem because there is not one specific source to target - the pollution is coming from various scattered sources. Unlike the strict mandates required for point source pollution, Section 319 of the 1987 CWA Amendments "consists largely of grant incentives and encouragement of state projects rather than strict mandates" (Seidenberg, 2006, p. 702). In addition to these grant incentives instead of strict mandates, Section 319 does not require non-point source pollution to meet definite effluent limitations under best available technology standards. Instead, it regulates non-point storm water runoff by an individual or general permit system that utilizes best management practices (BMPs) (Seidenberg, 2006).

Best management practices use the most effective methods to control non-point source pollution. This type of management practice views the achievable pollutant control as the sum of all its parts rather than just focusing on individual practices. Specifically, a holistic management approach is taken that considers how effective each single practice is, the cost of each practice, and then the overall cost and effectiveness of the practice. Each individual practice may be combined with other practices in order to achieve a best management practice (US EPA, 2007).

Utilizing these management practices early on is the best way to mitigate highway runoff. Highway designs should consider the environmental and negative impacts that construction can have on local water bodies. With environmentally friendly designs and

proper post construction maintenance that incorporate best management practices, highway authorities have the ability to reduce the volume and concentration of stormwater runoff generated by traffic and highway repairs, which are the two main problems that need to be reduced (US EPA, 2007). In addition to pre-construction BMPs, post construction BMPs should also be implemented.

A variety of post construction BMPs are utilized that include detention/retention ponds, wetlands, infiltration, and filtering practices. Infiltration practices allow stormwater runoff to infiltrate into the soil after it temporarily sits for a few days. The three types of infiltration designs include basins, trenches, and permeable pavements. These designs are useful for treating runoff for the first flush of a storm. In order to prevent sediment clogging when utilizing these infiltration methods, a vegetated filter strip can be constructed right before the basin, trench, or permeable pavement as a pretreatment area (US EPA, Nov 2005).

1.2   Vegetated Biofilters

A vegetative filter strip is one of two types of vegetated biofilters, which also includes grassed swales. Vegetative filter strips consist of an area of land with dense vegetative cover that is specifically designed to collect overland sheet flow from stormwater runoff. They are used as a pretreatment area, because polluted runoff initially flows through them, before the runoff is discharged to other flow channels. Vegetated filter strips are designed to efficiently reduce "the discharge of sediments and associated pollutants, including hydrocarbons, metals, and nutrients, from highway runoff" (Han, Wu, and Allan, 2005, p. 1638). Vegetative filter strips can be found in numerous areas,

both natural and constructed, which include areas that are next to bodies of water and within parking lots.

The other type of vegetated biofilter is a vegetated swale. Based on several studies, these swales are an "effective, simple, and cost-effective method for non-point source runoff pollutant removal" (Stagge and Davis, 2006, p.5518). These vegetated swales function by initially infiltrating the first flush of storm water runoff that contains high concentrations of pollutants. Once the highest pollutant concentrations are infiltrated, the vegetated swale continues to reduce the pollutants within the runoff by attaching dissolved metals and sedimentation to exchange sites in the grass, soil, and roots, and filtering particulates and particulate-bound pollutants (Stagge and Davis, 2006, p. 5526). By the storm water runoff infiltrating and absorbing into the vegetated filter, the water that comes out of the effluent and into large bodies of water is much cleaner. Barrett et al. (1998) explains that highway medians that act as vegetated biofilters combine the characteristics of both vegetated filter strips and vegetated swales. Highway medians accept overland flow from stormwater runoff on the pavement, which mimics a vegetated filter strip. Once the concentrated runoff flows down the length of the median, it acts as a vegetated swale.

To date, the majority of highway stormwater runoff studies have been performed with grassy swales or strips already adjacent to highways (Li et al., 2008). A study conducted by Stagge and Davis (2006) monitored two full-scale grassed swales located on a four lane highway median in Maryland during 18 storm events. These grassed swales were constructed with the same cross-section designs which had side slopes of 3:1

(33%) and 4:1 (25%). The length of the first swale was 198 m with a channel slope of 1.6% and a pretreatment area of 15.2 m. The second swale had a length of 137 m and a channel slope of 1.2% without a pretreatment area. A flow rate of around 0.430 L/s was applied to the swales with the use of a weir, which corresponded to a rainfall intensity of 0.064 cm/hr. Samples were collected directly from the roadway which was considered the input and from the effluent which was the end of the swales. The influent and effluent samples were compared and the percent removal was determined for total suspended solids (TSS) and zinc, which is the most common heavy metal associated with highway stormwater runoff. Each of the two swales demonstrated significant removal of both TSS and zinc from the 18 storm events. The pretreatment area of the first swale did not contribute to higher percent removals, but gave similar results as the second swale. The normalized event mean concentrations (N-EMCs) were used to determine percent removals, which corresponds to the concentration that would occur if all of the highway stormwater that entered the swales was collected in one container, instead of separate samples. Based on the N-EMCs, TSS had a percent removal of 65-71% and zinc of 30-60%, which suggested that the grassed swales were successful in removing total suspended solids and zinc, because the influent and effluent mean values were significantly different.

In another study, Barrett (2005) examined grassed swales and compared them to other types of best management practices to mitigate highway stormwater runoff. They observed 42 separate storm events that fell over the grassed swales. Their results

indicated that the grassed swales were efficient, with TSS percent removals of 48%, zinc removal 54% and copper removal 24%.

Barrett performed other studies that assessed the efficiency of vegetated biofilters. Barrett et al. (1998b) monitored 34 storm events at two locations in Austin, Texas to determine the efficiency of the median, which acts as a grassed swale, to reduce the pollutant concentration and load in highway runoff. These two medians had different parameters which included slope and vegetative cover. The efficiency of these medians was determined by measuring the highway runoff before and after it entered the median. From 34 monitored storm events, 423 samples were collected with automatic samplers. The percent reductions in concentration associated with these 423 samples from the two sites are as follows: TSS (85-87%), zinc (75-91%), lead (17-41%), and iron (75-79%). The percent load reduction is as follows: TSS (87-89%), zinc (79-93%), lead (31-52%), and iron (79-83%). Barrett et al. determined that the percent load reduction was due to the reduction in pollutant concentration rather than infiltration of the medians. Overall, Barrett et al. (1998b) concluded that these grassy medians are efficient in reducing both pollutant concentration and load and should be considered a primary best management practice rather than a pretreatment device.

Barrett et al. (2004) conducted the Roadside Vegetated Treatment Sites Study, which was a 2-year project that utilized existing highway biofilters with natural vegetated slopes to remove various pollutants from highway stormwater runoff. Over the two-year period, eight locations across California were used as test sites. These eight test sites were designed with various parameters to determine which ones worked the best. Some

of these different parameters included slope, vegetation, climate, and vegetation coverage. The effect of buffer width on mitigating highway stormwater runoff was also assessed by placing concrete collection channels at various distances down the vegetated strip.

Based on this two-year study, these vegetated biofilters were successful in consistently reducing the amount of total metals and TSS, with percent reductions of 77-97% for TSS, 76-98% for copper, 83-99% for lead, and 87-99% for zinc throughout the eight test sites. In addition to reducing pollutant concentrations, the pollutant load was also reduced due to infiltration of runoff.

Barrett et al. (2004) also found that vegetative cover was strongly correlated with vegetated biofilter performance. If the vegetative cover fell below 80%, then the efficiency of the biofilter to remove pollutants from highway stormwater runoff decreased. At sites with vegetative cover greater than 80%, a buffer width of 4.2 meters for slopes less than 10% and a buffer width of 9.2 meters for slopes between 35% and 50% were necessary to see a decrease in pollutant concentrations. With vegetative cover less than 80%, it was necessary to have a 10 meter buffer width for slopes greater than 10% to effectively reduce pollutant concentrations. One last finding was that the accumulation rates of leachable metals was oddly low because each of these sites were subjected to high amounts of traffic on a daily basis for two years. Despite this heavy traffic, soil samples that were tested from the sites were well below what would classify them as a hazardous waste.

Li et al. (2008) studied the capacity of two Texas highway medians to mitigate highway stormwater runoff. For each highway, three sites were monitored for the first flush of stormwater runoff for a period of 16 months. Each of these sites had high average daily traffic values (> 30,000 vehicles per day), but had variations in their side slopes.

The results indicated that the vegetated median was effective in removing contaminants, with averaged percent removal efficiencies as follows: Highway A- TSS (68%), total copper (67%), and total lead (48%). Li et al. found a correlation between vegetation cover and TSS removal. If vegetation cover is 90% and above, TSS removal is much higher than if it is below 90%. Another direct correlation was between TSS and total metals.

A laboratory study was conducted that investigated vegetated strips and their ability to take up heavy metals from simulated stormwater runoff (FHA, 1996). They conducted their study indoors, because they could vary slope and flow without any outside factors affecting their results. The test plot had dimensions of 4.27 m x 1.22 m x 0.46 m (width x length x depth). The vegetation that was planted within the test plot was a mixture of seeds from the WSDOT (40% Red Fescue, 40% Perennial Rye, 10% Colonial Bentgrass, and 10% White Dutch Clover). After the bed was planted, it was placed on a frame that enabled it to slope from 0% to 50% (FHA, 1996).

Simulated stormwater runoff was distributed on the top of the bed by a slotted PVC pipe that was long enough to evenly distribute flow over the entire width of the plot. The simulated stormwater consisted of suspended solids, lead, cadmium, copper, and

zinc, with concentrations that mimicked actual highway stormwater runoff concentrations in Washington (FHA, 1996). Various types of storms were simulated with a total rainfall depth of 4.55 cm. Each conducted run had 3 parts: an initial saturation, first-flush, and a wash-out or flushing section. From these runs, heavy metal retention and migration, plant uptake of metals, metal sinks, and hydraulic characteristics (using Br tracer tests) were determined. The heavy metal migration results indicated that vegetated highway medians and shoulders are an effective best management practice for treating highway stormwater runoff. The percent retained values were as follows: lead (93%), cadmium (>99%), copper (>99%), and zinc (84%). The retention mechanism that retained the majority of the metals was adsorption onto the suspended solids. An additional mechanism was the adsorption of metals onto the plot soil, but this was difficult to quantify due to the initial high background concentrations. Based on the different slopes and flow rates, it was concluded that hydraulic detention times were most affected by a change in flow rather than slope (FHA, 1996).

The most recent vegetated biofilter study was conducted by the Civil Engineering Department at the University of Kansas, which also assessed the efficiency of vegetated highway embankments to mitigate highway stormwater runoff pollutants, such as heavy metals and suspended solids (KDOT, 2009). Specifically, this study determined the long term capability of vegetated biofilters and the annual mass pollutant load at three sites in eastern Kansas. This study was performed on site instead of in a laboratory, and samples were collected during 11 storm events at two different interstates. Runoff was only collected at two sites (R1 and R3), because the collecting apparatus was stolen at the

second site (R2). The two sites that did collect runoff used weir boxes made out of a PVC sheet and installed sediment traps to collect suspended solids. In addition to collecting runoff, soil samples were collected before and after the storm events at various soil depths, including 0.0 to 0.4 in, 2.0 to 2.4 in, and 3.9 to 4.3 in (KDOT, 2009).

In addition to on-site experiments, controlled field experiments were also conducted with artificial storm water simulating a 5-year 20-minute event. Three runoff applications were applied to the controlled vegetated strips: one with fluorescent microspheres and the other two without to determine how fast the water flows through the strip (KDOT, 2009).

For the on-site experiment, the average total metal concentration for both interstates was 40.0 μg/L for chromium, 14.0 μg/L for copper, 128 μg/L for lead, 152 μg/L for manganese, and 55 μg/L for zinc. For copper and zinc, the average percent of mean pollutant mass loading retained on soils for the two interstates ranged from 8.9% to 15.6% and 41.6% to 114% respectively. The microsphere results with various sizes determined that short vegetated biofilters (approx 4 feet) have the ability to remove particulates, with percent removals from 60% to 94%. The results also indicated that larger particles were removed more efficiently, and despite resuspension occurring, less than 10% of the particles were released from the biofilter. It was also found that a 1:6 slope (17%) was sufficient enough to reduce highway stormwater runoff. Analysis of the embankment soils indicated that the majority of pollutant adsorption occurred within the top 0-2 inches of the soil. Much like the other studies, KDOT concluded that vegetated embankments on highways, or vegetated biofilters, work efficiently to mitigate highway

stormwater runoff including heavy metals and suspended solids, and should be utilized as a best management practice for highways everywhere (KDOT, 2009).

Vegetated filter strips and swales that act as vegetated biofilters that mitigate highway stormwater runoff contaminants utilize a process called phytoremediation. Utilizing vegetated biofilters to phytoremediate polluted runoff is a cheap alternative to other methods, because it is natural and only requires photosynthesis for energy (Kramer, 2005).

1.3   Phytoremediation

Phytoremediation is defined as the use of plants, such as trees and grasses, to clean up inorganic and organic pollutants by various mechanisms, which include phytostabilization, phytoextraction, and rhizofiltration (Prasad, 2002). These plants can phytoremediate pollutants by removing, destroying, or sequestering the contaminants from their source, which consists of soil, water, or air (Prasad, 2002). Over the years, phytoremediation has become a very popular method to naturally and non-intrusively clean up contamination in both developed and developing countries (Prasad, 2002).   This emerging popularity is mainly due to how inexpensive this method is combined with the little government and state funding available for environmental cleanup, as well as the public acceptance (Smits, 2005). Phytoremediation is inexpensive, because it is solar-driven, and natural processes are used to remediate pollutants versus intrusive heavy machinery (Smits, 2005).

Currently, phytoremediation is one best management practice for cleaning up contamination due to highway stormwater runoff. This is mainly due in part to the large

areas of grass surrounding highways. Grass surrounding the highways can ". . . degrade, extract, contain, or immobilize contaminants" (Ruby and Appleton, 2009, p. 1) such as metals and oil that originate from various car parts. Phytoremediation is ideal for highway stormwater runoff pollutants, because it is best suited for cleaning up medium to low concentrations of contamination over a large area (EPA, 2010).

There are four different mechanisms by which plants phytoremediate contaminants in soil and water: phytostabilization, phytoextraction, phytovolatilization, and rhizofiltration (Prasad, 2002). Phytostabilization is used for contaminated sites, providing dense vegetative cover to prevent wind and water erosion (Prasad, 2002). Phytostabilization is typically used for metal contamination in soil, and specifically prevents contaminant migration that could occur from wind and water erosion or from the leaching of contaminants. Generally, plants suitable for phytostabilization have stable root systems, can tolerate various metal contaminants, and can immobilize these contaminants within their rhizosphere or root zone. Contaminants can become immobilized by binding to soil components. Vegetative cover can also phytostabilize the contaminants in the soil, preventing exposure of wind, water, humans, and animals, and therefore decreasing erosion. Phytostabilization is one of the easier forms of phytoremediation, because it typically utilizes plant communities already found on-site (Kramer, 2005).

Phytoextraction is the most effective phytoremediation technique, but also the most difficult and time consuming. Metal hyperaccumulator plants that are tolerant to pollutants are grown, where they have the ability to concentrate the contaminants in

above-ground tissue from the roots of the plant. These hyperaccumulator plants are preferred, but not necessary, because they can accumulate large concentrations of pollutants and still survive. The contaminants accumulating within the plants are from the soil water in the ground. Once these plants are fully grown, they are harvested, dried, and burned, or disposed in a hazardous waste landfill. This method is worthwhile if the biomass burned for energy can generate clean fumes. Similar to phytoextraction, phytovolatilization transfers contaminants from the subsurface but in a different way. Instead of accumulating pollutants in above-ground tissue, the plant takes up volatile contaminants, and then releases these compounds into the atmosphere (Kramer, 2005).

Rhizofiltration is the use of the plant's roots to ". . . absorb, concentrate, and/or precipitate hazardous compounds, particularly heavy metals or radionuclides, from aqueous solution" (Prasad, 2002, p. 690). During rhizofiltration, several different mechanisms occur within the roots, which include surface absorption, biosorption, intracellular uptake, deposition in vacuoles, translocation to the shoot, and the use of plant exudates to precipitate the metal from solution (Prasad, 2002). Rhizofiltration is primarily effective for large volumes of water containing dilute concentrations of contaminants.

Phytostabilization is a significant mechanism within the vegetated biofilter, because the present vegetative cover allows the TSS to settle within the biofilter and avert it from quickly flowing over the biofilter surface. Because the vegetative cover allows the TSS to settle, metals can directly adsorb to the soil surface, preventing the adsorbed metals from entering the surface runoff. Phytoextraction is also a prominent mechanism

within the biofilter since large volumes of highway stormwater runoff infiltrate into the bed. In particular, the dissolved metals from the runoff could be extracted by the roots and concentrated in the above-ground grass.

1.4   Chemical Fractionation

Since 1979, sequential extraction procedures have been utilized to speciate trace metals associated with soils. The first and most widely used and modified sequential extraction procedure originated from Tessier et al. (1979). Before this time, total metal concentrations were the main focus when analyzing sediment samples. However, when considering only the total metal concentrations within the soil, all forms of each metal are assumed to impact the environment in the same way. Clearly, this is not the case (Tessier et al., 1979). What actually determines the mobility and bioavailability, and thus environmental impact of the metals, is the particular chemical species or form (Olajire et al., 2003). Currently, sequential extraction procedures are more commonly employed, which can selectively extract metals from separate soil fractions based on the chosen extracting reagents. Separating the metals into their source soil fractions provides further information on the bioavailability of the metals, as well as their mobility and transport within the environment (Tessier et al., 1979). How bioavailable the metals are will ultimately determine how easily plants can take them up as a means of phytoremediation and how easily the metals can be mobilized in the future (Olajire et al., 2003).

The five fractions of metal partitioning selected by Tessier et al. were fractions that commonly exist in soil and were most likely to trap metals. These fractions are: exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to

organic matter, and residual. The exchangeable fraction deals with metals that are adsorbed on the soil surface, and can most easily be sorbed and desorbed (Zerbe et al., 1999). The sorption-desorption process can be affected by changes in the ionic composition of water. The carbonate fraction deals with metals that are associated with sediment carbonates. This particular fraction is susceptible to pH changes in the water. Iron and manganese oxides are considered the reducible phase (Olajire et al., 2003) and exist as nodules within soil and can also coat soil. These oxides attract metals and scavenge them; however, under anoxic conditions they are considered thermodynamically unstable. Metals can be bound to different types of organic matter in soil, and under oxidizing conditions the organic matter can be degraded, thus releasing the soluble metals into the environment. The first four fractions are considered the non-residual portion of the soil, while the fifth fraction is the residual portion. This fraction comprises the metals that can be held within the crystalline structure of the soil and should not be released under natural environmental conditions (Tessier et al., 1979).

In addition to being useful for the chemical speciation of metals in aquatic soils, a sequential extraction procedure can also be used to speciate the metals in soils contaminated with highway stormwater runoff (Turer and Maynard, 2003). Highway roadside soils have been found to be a significant, but unsuspected source of metal contamination in nearby streams (Turer and Maynard, 2003). These anthropogenic metals mainly come from the various wear of vehicles, engine exhaust, and highway maintenance, such as Pb and Ni from gasoline, Zn from tires, and Cu from brake linings (Preciado and Li, 2006). Turer and Maynard (2003) found that even though sequential

extraction procedures are typically used to determine the partitioning of metals in soil fractions, few highway roadside studies have included this procedure in their analysis. In two of the studies that did employ a sequential extraction procedure for highway roadside soils, the Tessier et al. (1979) extraction scheme was used, where it was found that Pb and Zn were mostly related to the iron and manganese oxide fraction of the soil, secondly to the carbonate fraction, and finally to the organic fraction (Turer and Maynard, 2003). For their study, Turer and Maynard (2003) utilized the first three steps (exchangeable-0.5 M potassium nitrate, absorbed-ultrapure water, and organically bound-0.5 M sodium hydroxide fractions) of the sequential extraction procedure from Sposito et al. (1982), which was derived from the Tessier et al. (1979) extraction procedure (2003). The results from this procedure showed that from the three fractions, the concentrations of Pb, Zn, Cu, Ni, and Ba were low. Because these concentrations were low in the exchangeable fraction, mobilization of these metals will also be low.

Another study that evaluated the metal speciation and bioavailability of metals in highway roadside soil was Preciado and Li (2006). Collected soil samples were analyzed using the sequential extraction procedure as described by Li (2003), which included the following six fractions: water soluble, exchangeable, carbonate bound, Fe-Mn oxides, organic matter, and residual. Results from this study concluded that Pb and Cu were the most easily remobilized metals, while Fe was primarily related to the Fe-Mn oxides and residual fractions and Zn was primarily related to the Fe-Mn oxides and organic fractions (Preciado and Li, 2006).

For the purposes of this research, the sequential extraction procedure as used by Olajire et al. (2003) and derived from Tessier et al. (1979) was employed on vegetated biofilter soil samples. In their research, soil samples from an industrial area of Southern Nigeria were analyzed using a sequential extraction procedure. A six step sequential extraction procedure was utilized and the following fractions could be obtained: water soluble, exchangeable, carbonate-bound, Fe-Mn oxides-bound, organic bound, and residual (Olajire et al., 2003). These six fractions are in order of decreasing solubility of metals, meaning that as the solubility decreases, the bioavailability of the metals also decreases, when the assumption is made that bioavailability is related to solubility. Therefore, metals associated with the water soluble fraction will be the most bioavailable and most easily remobilized, while metals associated with the residual fraction will be the least bioavailable and least easily remobilized. The evaluated metals were Pb, Cd, Cu, Ni, and Zn, which were all metals evaluated in this vegetated biofilter research (Olajire et al., 2003).

Results from the sequential extraction procedure indicated that Cd was present in exchangeable (30%), carbonate (14%), and residual fractions, with most of the Cd in the residual fraction (47%) (Olajire et al., 2003). Combining the exchangeable and carbonate fractions, over 40% of Cd was bioavailable, since these fractions represent a higher solubility of metals. Pb was mostly in the nonresidual fractions (75% average), with the exchangeable and carbonate fractions combined averaging 50.3%, meaning that the bioavailability of Pb was very high and readily available for plant uptake. Cu was mostly present in the nonresidual fractions, and Ni was mostly present in the residual fractions

(50% average). Zn was present in both the nonresidual and residual fractions. Overall, it was found that Pb was the most bioavailable for plant uptake, because it was mostly associated with the exchangeable and carbonate fractions, followed by Zn, Cu, Ni, and Cd was the least bioavailable (Olajire et al., 2003).

1.5   Objectives

This research will focus on the overall efficiency of vegetated biofilters to mitigate highway stormwater runoff, the basic reactions taking place, and the fate of the contaminants within the bed, which include metals and suspended solids. The efficiency of vegetated biofilters is essential to determine how effective the biofilter will be to keep contaminants out of nearby bodies of water. Determining the fate of the runoff contaminants is important to understand the future mobility and chemical fractionation of the contamination as stormwater runoff continues to flow over the biofilter from various rain events.

The first section of this thesis work will answer the research question: What is the efficiency of vegetated biofilters at various slopes and simulated stormwater runoff concentrations? This efficiency will be determined by comparing the initial influent contaminant concentration with the effluent contaminant concentration.

The second section will answer the research question: How are the contaminants removed within the biofilter? This question is complex, because many different removal mechanisms may occur while the stormwater flows over and interacts with the bed. For example, the contaminants may be removed by adsorption to the bed, uptake into plants, or attachment to particles that settle within the bed.

The third section will answer the research question: Once the metals are removed from the water, where will they be concentrated – or what is their fate within the bed? The grass, soil, and roots might each play a part in the removal of the contaminants, and determining which media predominates will help to further establish the future mobility of the contaminants. For example, if the contaminants concentrate in the grass, then they could easily become remobilized from routine cutting.

The fourth section will further investigate metals that accumulate in the soil and will answer the research questions: How are the metals bound to the soil? Which metals are most likely to become remobilized if predominantly accumulated in the soil?

The first and second research questions which focus on the mechanistic interactions of the bed will be answered by conducting experiments on various vegetated biofilters that mimic actual highway biofilters. From these tests, the efficiency of the biofilters will be determined by comparing the influent/effluent data. The second research question can be more specifically understood by answering the following questions: Do the metals adsorb to the suspended solids in the stormwater before reaching the bed? What fraction of the TSS added to the simulated stormwater as the influent gets captured by the bed? Determining the specific physical mechanisms will help to clarify how the contaminants are removed and can be done so by tracking suspended solids particles and comparing the total and dissolved metals data. The metal concentrations from the influent, bed, and effluent will give a better understanding of the fate of the simulated stormwater constituents as well as the efficiency of the bed.

The fate and future mobility of the highway stormwater runoff contaminants are described by research questions three and four. The fate and future mobility of the runoff contaminants also ties into research questions one and two, because the mechanistic interactions of the stormwater constituents will ultimately determine their fate within the bed. The grass, soil, and roots within the bed have a certain affinity for metals and will adsorb different masses of each. Core samples will be taken throughout the bed after stormwater treatment, then separated and digested to determine heavy metal concentrations in the grass leaves, soil, and roots.

The chemical fractionation of the metals will determine the mobility of the metals and how they interact with the bed. The individual speciation of these heavy metals is important, because it tells how each element separately affects the fate of the contaminants within the bed and the chances each will become remobilized. To determine this chemical speciation, a selective sequential extraction procedure will be used. This procedure will give the different fractions that have partitioned from particulate heavy metals. This procedure gives five different fractions of each metal which include water soluble (F1), exchangeable cations (F2), metals bound to carbonates (F3), metals bound to Fe-Mn oxides (F4), and metals bound to organic matter (F5)

2   Materials and Methods

2.1   Vegetated Biofilter Construction and Testing

Vegetated biofilters were constructed for testing purposes, where simulated stormwater runoff was applied to each bed at various slopes and flow rates to simulate storm events. Each biofilter was 4 ft (1.23 m) by 14 ft (3.86 m) and contained a perforated pipe drainline along the center bottom. On top of the drainline, a 4-inch layer of gravel and stones was added with one foot of screened A-6 soil on top. The A-6 soil was obtained from the Nelsonville bypass project in ODOT District 10. The grass planted in each of the beds was a standard ODOT grass seed mix which included the annual rye grass (10%), creeping red fescue (34%), and hard fescue (56%). Target coverage of the beds was at least 80%, as per ODOT instructions, and each of the beds met this target percentage. Figure 2.1 displays the first constructed vegetated biofilter in its stand, ready for testing. Even though three vegetated biofilters were constructed for testing, only two will be discussed.

Figure 2.1: Constructed vegetated biofilter in stand

Table 2.1 displays the 5th percentile, mean, and 95th percentile concentrations of highway stormwater runoff from various studies, and the artificial stormwater runoff concentrations that were used for testing. The artificial (simulated) stormwater runoff concentrations were fixed based on the detection limits of the inductively coupled plasma-optical emission spectrometer (ICP-OES). Low concentrations were 5 times the analytical detection limit, medium concentrations were 5 times the low level, and high concentrations were 5 times the medium level. The simulated stormwater was pumped onto the bed from a continuously stirred drum through a perforated tube and onto the influent drip plate before hitting the bed (see Figure 2.2 and Figure 2.3). The simulated stormwater flowed down the length of the bed, where some of the runoff infiltrated the bed and was collected in the underdrain (see Figure 2.4), and some exited as surface runoff (see Figure 2.5).

Table 2.1: Concentrations of Metals and Other Contaminants in Roadway Runoff Taken From Literature Along with Concentrations Adopted in this Project for Artificial Runoff at Low, Medium, and High Concentrations

Constituent		unit	Literature			DL	Artificial runoff		
			5%	Mean	95%		Low	Med	High
Total metals	Cd	(µg/L)	0.05	2	6	4	20	100	500
	Cr	(µg/L)	1	6	17	5	25	125	625
	Cu	(µg/L)	3	55	179	7	35	175	875
	Fe	(µg/L)	249	7719	16500	3	250	7700	16500
	Ni	(µg/L)	2	9	30	19	95	475	2375
	Pb	(µg/L)	1	271	1133	43	215	1075	5375
	Zn	(µg/L)	7	425	1660	4	10	425	1700
	TSS	(mg/L)	9	207	737	-	9	207	737

Figure 2.2: Application of simulated stormwater runoff to bed

Figure 2.3: Influent drip plate

Figure 2.4: Collection of underdrain samples from bed

Figure 2.5: Surface runoff from bed

Each vegetated biofilter was tested at an 8:1 slope (7.13°) with a medium flow rate, a 4:1 slope (14.0°) with a medium flow rate, a 2:1 slope (26.6 °) with a medium flow rate, and a 2:1 slope (26.6 °) with a high flow rate. For the first biofilter, the medium flow simulations used an initial flow rate of 2.17 gpm for 15 min followed by a flow rate of 0.43 gpm for 45 min to represent a 1 hour 2 year storm. A high concentration of

simulated stormwater was applied to the bed for the first 15 min (first flush of the storm), followed by a medium concentration of simulated stormwater for the remaining 45 min (see Table 2.1). The high flow simulation used an initial flow rate of 5.43 gpm for 6 min followed by a flow rate of 1.18 gpm for 24 min to represent a 30 minute 10 year storm. A high concentration of simulated stormwater was applied to the bed for the first 6 min (first flush of the storm) as the influent, followed by a medium concentration of simulated stormwater for the remaining 24 min (see Table 2.1).

For the second biofilter analyzed here, the medium flow simulation used an initial flow rate of 3.99 gpm for 15 min followed by a flow rate of 1.11 gpm for 45 min to represent a 1 hour 10 year storm. The high flow simulation used an initial flow rate of 5.54 gpm for 6 min followed by a flow rate of 1.20 gpm for 24 min to represent a 30 minute 10 year storm. The first flush portion of the medium and high flow simulations used a low concentration of simulated stormwater as the influent, followed by tap water for the remainder of the tests (see Table 3.14).

For each of these tests, total metals, dissolved metals, and TSS samples were collected at the influent, surface, and underdrain areas of the biofilter. The influent samples represented the simulated stormwater as it was pumped onto the bed, but before it hit the bed. The surface samples represented the simulated stormwater that flowed over the surface of the bed, and the underdrain samples represented the simulated stormwater that infiltrated into the bed.

2.2   Total and Dissolved Metals Analysis

Total metal samples were collected directly into 15 mL plastic vials, while the dissolved metal samples were filtered (0.45 μm) into 15 mL plastic vials. These samples were then acid preserved with 200 mL of 20% nitric acid and placed into coolers with ice.

Total metal samples were digested utilizing the EPA Method 200.7 (Clesceri et al., 1998). All glassware used was soaked in a 0.1 N nitric acid bath overnight and rinsed with ultrapure water. Ten mL of each sample were pipetted into a 50 mL beaker along with 200 μL 1:1 HNO_3 and 100 μL 1:1 HCl. The beakers were placed onto a hot plate at a temperature around 85 °C to prevent sample losses from boiling. Two-inch watch glasses were set on top of the beakers with a small opening, which allowed the sample to evaporate, but also prevented particles from settling into the beakers (see Figure 2.6). The volume of each sample was reduced to 2 mL and refluxed for 30 min by covering the entire top of the beaker with the two-inch watch glass. After 30 min, the beakers were taken off of the hot plate and cooled. The samples were then transferred to a 10-mL volumetric flask and made to volume with ultrapure water. The samples were sent to the Chemistry Department to be analyzed for metal concentrations by an inductively coupled plasma optical emission spectrometer (Varian). Dissolved metal samples were directly sent to the Chemistry Department after being filtered and acid preserved.

Figure 2.6: Digestion of total metals samples

2.3 Total Suspended Solids Analysis

Total suspended solids samples were taken in duplicate from the influent, surface
and underdrain areas of each vegetated biofilter. These samples were collected directly
into 125 mL plastic Nalgene bottles and placed into coolers with ice and analyzed by
Standard Method #2540 D (Clesceri et al., 1998).

In order to begin the total suspended solids procedure, aluminum dishes with glass
microfibre filters (Whatman # 934-AH RTU4) were weighed for each total suspended
solids sample. Each glass fiber filter was carefully placed onto a vacuum filtration
apparatus and wet with ultrapure water to set it. The volume of each sample was marked
on the container, and each sample was poured onto the filter under vacuum. Each total
suspended solids bottle was thoroughly rinsed with ultrapure water to ensure full removal
of any remaining particles. Each filter was then washed with three successive 10 mL
volumes of ultrapure water, and vacuum was maintained for three minutes after
washings. The filters were then carefully taken off of the filtration apparatus and placed

back into the aluminum dish (see Figure 2.7). The aluminum dishes were then placed

into an oven overnight with a temperature of 104 °C. The following day, the aluminum

dishes with filters were taken out of the oven and placed in a dessicator until weighed.

The following calculation was used to determine the concentration of total suspended

solids in each sample:

$$mg\ total\ suspended\ solids/L = \frac{(A-B)\ X\ 1000}{sample\ volume, mL}$$

where:
  A = weight of aluminum dish, filter, and residue, mg.
  B = weight of aluminum dish and filter, mg.

Figure 2.7: Filtration apparatus used for TSS analysis

2.4   Grass, Soil, and Roots Digestion

Twenty core samples were collected from each bed to determine the total metal

accumulation within the grass, soil, and roots (see Figure 2.8 and Figure 2.9). For each

core sample, the top 2 in of soil was used. Core samples were placed into plastic bags

and stored at 5 °C until separated. Each core sample was separated into grass, soil, and

roots. Roots were gently washed with ultrapure water to remove residual soil. The grass

and roots were oven dried and cut into small pieces, and the soil was oven dried and

ground with a glass mortar (see Figure 2.10). One gram of each grass, soil, and root

sample was utilized for digestion.

Figure 2.8: Collecting a core sample from a bed

Figure 2.9: Core sample after it was collected

EPA Method 3050B was used for the determination of metals in grass, soil, and roots (US EPA, 1998). Figure 2.11 depicts a few of the grass, soil, and root samples being digested by this method. All glassware used was soaked in a 0.1 N nitric acid bath overnight and rinsed with ultrapure water. For each grass, soil, and roots sample, one gram was added to a 250 mL wide-mouthed Erlenmeyer flask. Ten mL of 1:1 nitric acid was added to each flask, mixed, and covered with a two-inch watch glass. The samples were refluxed for 10 to 15 min at a temperature that would not allow the sample to boil. The samples were then cooled, 5 mL concentrated nitric acid was added, placed back on the hot plate, and refluxed for 30 min. After 30 min, the watch glasses were removed and the samples were evaporated to approximately 5 mL, which took around 2 hr. The samples were taken off the hot plate and cooled, and then 2 mL water and 3 mL 30% hydrogen peroxide were added to each flask, covered with a watch glass, and placed back on the hot plate to start the peroxide reaction. The samples were heated until effervescence subsided and were then taken off the hot plate to cool. Once cooled, the samples were placed back on the hot plate, and if effervescence continued, 1 mL aliquots of 30% hydrogen peroxide (not to exceed 10 mL) were added to the samples until effervescence was minimal or the general sample appearance was unchanged. The watch glasses were removed from the flasks, and the sample was evaporated to approximately 5 mL. The samples were then cooled, and 10 mL concentrated hydrochloric acid was added to each flask, covered, and placed on the hot plate to be refluxed for 15 min. The samples were cooled, and the digestates were filtered with a 0.45 μm syringe filter and collected into a 100 mL volumetric flask and made to volume with ultrapure water. The

samples were then sent to the Chemistry Department to be analyzed for metal

concentrations by an ICP-OES (Varian).

Figure 2.10: Grass, roots, and soil separated and dried from core samples

Figure 2.11: Grass, root, and soil samples being digested by EPA Method 3050B

2.5   Sequential Extraction Procedure

A modified version of the Tessier et al. sequential extraction procedure (Olajire et al., 2003) was utilized to determine the distribution and chemical fractionation of heavy metals in the following five soil fractions: water soluble, exchangeable, carbonate-bound, Fe-Mn Oxides-bound, and organic-bound.

Two core samples were collected from bed one where the simulated stormwater from the influent hit the bed, which represents the highest concentrations of metals along the bed. These two core samples were then separated, where only the top inch of soil was used for analysis. The separated soil was then air dried, ground with a glass mortar, and sieved with a 2 mm sieve.

Triplicates were conducted on each of the samples, giving a total of nine soil samples to extract utilizing the sequential extraction procedure given by Olajire et al, 2003. In addition to the triplicates conducted on the two influent soil samples, three blank samples were extracted using clean soil. One gram of each soil sample was weighed into a 50-mL centrifuge tube. Once all of the soil samples were weighed and placed into the appropriately labeled centrifuge tubes, the sequential extraction procedure from Olajire et al. (2003) was started.

Prior to use, all glassware for the reagents were soaked in a 0.1 N nitric acid bath for 48 hr and rinsed with ultrapure water. For the water soluble fraction, the soil samples were extracted with 15 mL ultrapure water for 2 hr. After 2 hr, the samples were centrifuged at 14,400 X g for 30 min. The supernatant was then removed with a pipette, filtered with a 0.2 μm filter (Whatman Puradisc nylon membrane), and analyzed for

metal concentrations. The samples were then shaken (New Brunswick Scientific, Edison, NJ) for 30 min with 8 mL ultrapure water, centrifuged again, and then the wash solution was discarded.

Using the soil residue from the water soluble fraction, the process was repeated again using 8 mL of 1 M magnesium chloride for 5 hr to determine the exchangeable fraction. The solution was adjusted to a pH of 7.0 with a 1:1 solution of nitric acid.

Using the soil residue from the exchangeable fraction, the process was repeated again with   8 mL of 1 M sodium acetate (pH 5.0 with acetic acid) for 5 hr to determine the carbonate-bound fraction.

Using the soil residue from the carbonate-bound fraction, the process was repeated again with 20 mL of 0.04 M hydroxylamine hydrochloride (Ricca Chemical Company, Arlington, Texas) in 25% (V/V) acetic acid (Acros Organics, New Jersey) at 96 °C with occasional agitation for 6 hr to determine the Fe-Mn oxides-bound fraction.

Using the soil residue from the Fe-Mn oxides-bound fraction, the samples were extracted with 3 mL of 0.02 M nitric acid (Fisher Scientific, Fairlawn, New Jersey) and 5 mL of 30% hydrogen peroxide (Fisher Scientific, Fairlawn, New Jersey) (adjusted to pH 2.0 with nitric acid). The mixture was then heated to 85 °C for two hours with occasional agitation. Next, another 3 mL of 30% hydrogen peroxide was added and heated to 85 °C for 3 hr, with occasional agitation. The samples were cooled, and 5 mL of 3.2 M ammonium acetate (Fisher Scientific, Fairlawn, New Jersey) in 20% (V/V) nitric acid was added. After adding the ammonium acetate, the samples were diluted to 20 mL and continuously agitated for 30 min. After 30 min, the samples were centrifuged at 14,400

X g for 30 min. The supernatant was then removed with a pipette, filtered with a 0.2 μm filter (Whatman Puradisc nylon membrane), and analyzed for metal concentrations. The samples were then shaken (New Brunswick Scientific, Edison, NJ) for 30 min with 8 mL ultrapure water, centrifuged again, and then the wash solution was discarded.

2.6   Statistical Analysis

Statistical significance of samples was determined using a two-tailed t test to see if the two means were different from each other using an alpha of 0.05. The mean of the background samples, where no contamination was present, was compared with the mean of the collected samples after the four tests were completed on each bed. T values were calculated based on mean and standard deviations, and could then be compared to tcrit values. If the tcrit value was lower than the tcalc value, then the two means were statistically different, and there was a statistically significant amount of accumulation within the bed.

2.7   Removal Efficiency

When determining the removal efficiencies of the vegetated biofilters, event mean concentrations were calculated, which represented the total contaminant mass in the storm event divided by the total water volume. For each contaminant, nondetects were evaluated at half the detection limit. Percent removals could then be determined from the influent and effluent event mean concentrations, which provided more consistent results than comparison of the measured concentrations.

3   Results and Discussion

3.1   High Concentration Experiments

In this series of tests, a high concentration of contaminants, as described in Table 3.1 was delivered to the test biofilter during an initial first flush period, followed by a longer tailing period with a medium concentration of contaminants at a lower flow rate. Baseline samples were collected prior to each of the four tests for bed 1 and bed 3, and average baseline concentrations are displayed in Table 3.2. A total of four tests were conducted which included the following: 1) an 8:1 slope (7.13°) with a medium flow rate, 2) a 4:1 slope (14.0°) with a medium flow rate, 3) a 2:1 slope (26.6 °) with a medium flow rate, and 4) a 2:1 slope (26.6 °) with a high flow rate. The medium flow simulations used an initial flow rate of 2.17 gpm for 15 min followed by a flow rate of 0.43 gpm for 45 min. The high flow simulation used an initial flow rate of 5.43 gpm for 6 min followed by a flow rate of 1.18 gpm for 29 min. All tests were performed on the same test plot, designated bed 1. After completion of the performance tests, a series of resuspension tests were performed at all slopes with tap water to investigate the release of contaminants laid down from previous tests.

Table 3.1: High and Medium Simulated Stormwater Concentrations

	High Concentration (µg/L)	Medium Concentration (µg/L)
Cd	500	100
Cr	625	125
Cu	875	175
Fe	16500	7700
Ni	2375	475
Pb	5375	1075
Zn	1700	425
	High Concentration (mg/L)	**Medium Concentration (mg/L)**
TSS	737	207

Table 3.2: Average Concentrations in Baseline Tests

	Bed 1 Surface	Bed 1 Underdrain	Bed 3 Surface	Bed 3 Underdrain
Dissolved Cd (µg/L)	2.7	3.0	< 2	< 8
Dissolved Cr (µg/L)	< 7	< 7	< 9	< 9
Dissolved Cu (µg/L)	14.3	11.3	< 12	< 7
Dissolved Fe (µg/L)	< 6	13.3	< 8	81.0
Dissolved Ni (µg/L)	< 17	< 17	< 18	< 7
Dissolved Pb (µg/L)	< 55	< 55	< 77	< 71
Dissolved Zn (µg/L)	< 5	< 5	< 7	< 5
Total Cd (µg/L)	< 3	1.7	< 8	< 8
Total Cr (µg/L)	< 7	< 7	< 6	< 6
Total Cu (µg/L)	15.3	15.0	< 12	< 12
Total Fe (µg/L)	139	779	82	332
Total Ni (µg/L)	< 17	< 17	< 18	< 18
Total Pb (µg/L)	< 55	< 55	< 77	< 77
Total Zn (µg/L)	27.0	36.7	25.9	31.9
TSS (mg/L)	14.4	55.4	1.8	10.2

3.1.1   Suspended Solids Results

Figure 3.1 through Figure 3.4 depict the suspended solids concentrations for the

four high concentration tests. The solid lines represent the average concentration of the

samples collected for the first flush of the test, followed by the average concentration of

the samples collected for the tail end of the test. Sieved soil (<0.841 mm) was mixed

with the two influent drums at target concentrations of 737 mg/L for the initial high

concentration flow and 207 mg/L for the subsequent medium concentration flow. Actual

concentrations measured in the influent flow as it sprayed onto the distributor plate varied

greatly from the target concentration on more than one occasion, which is possibly due to

particles settling in the influent mixing container. Specifically, particulate concentrations

appeared to decrease over time during the initial high concentration flow. This decrease

could be caused by the pumps drawing water from the bottom portions of the tanks, as

the particles settled in the influent mixing container. The other low concentration test

used lower simulated runoff concentrations, so this settling was not a problem.
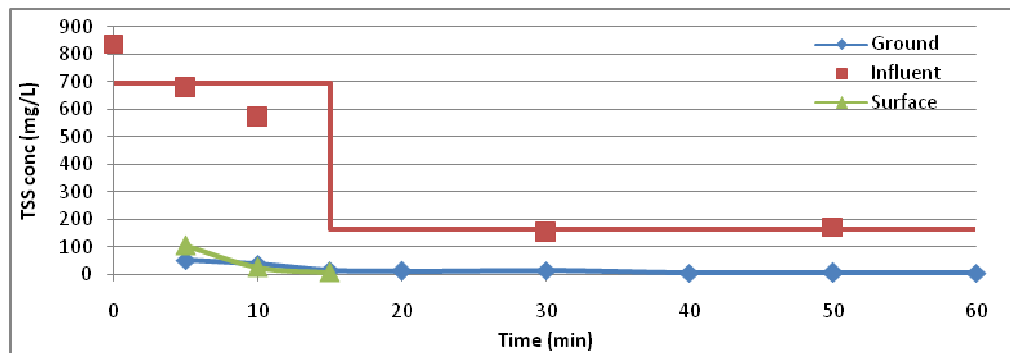
Figure 3.1: Concentration of suspended solids in 8:1 slope, medium flow rate
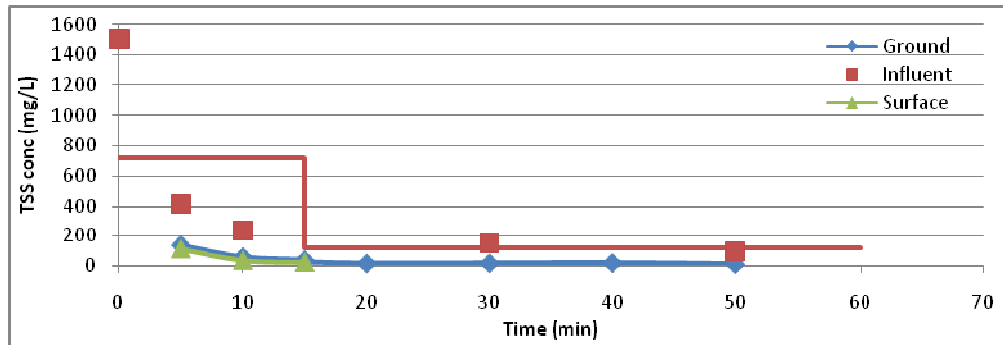
Figure 3.2: Concentration of suspended solids in 4:1 slope, medium flow rate
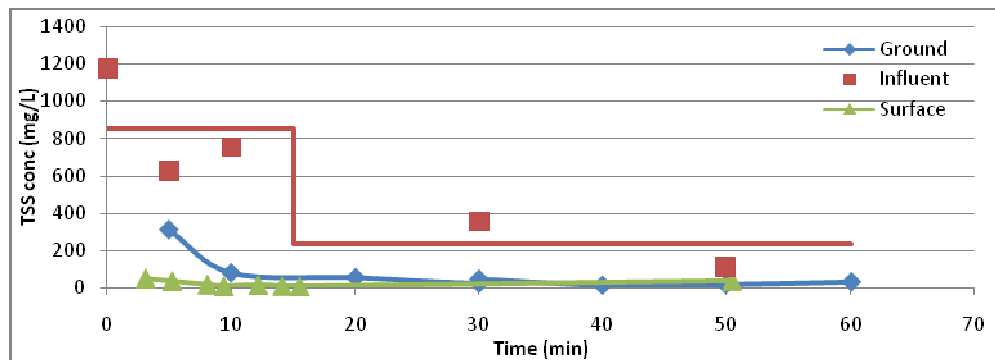
Figure 3.3: Concentration of suspended solids in 2:1 slope, medium flow rate
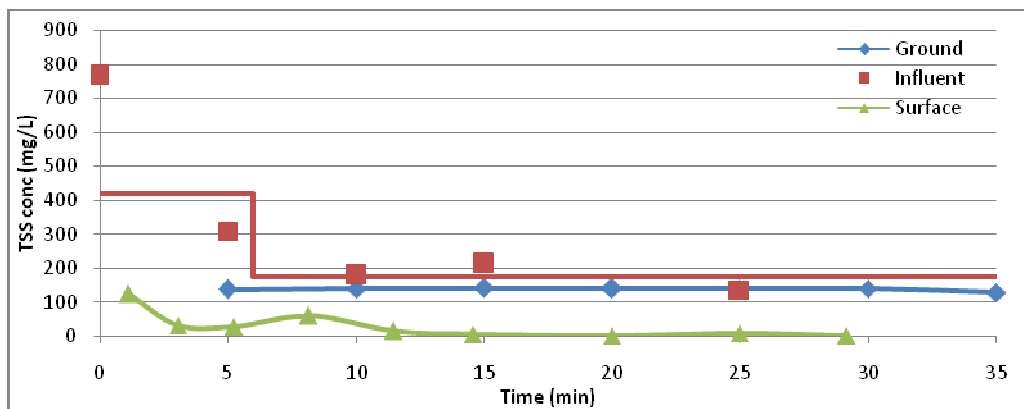
Figure 3.4: Concentration of suspended solids in 2:1 slope, high flow rate

Despite the settling of suspended solids in the influent, most average

concentrations were reasonably close to the target values. For the high concentration

tests with a medium flow, influent concentrations averaged 695 mg/L, 721 mg/L, and 851 mg/L for the first three tests. The average of these values was within a 15% margin of the target concentration of 737 mg/L. For the high concentration test with a high flow, the average influent concentration was 419 mg/L, which was significantly below the target concentration of 737 mg/L. Suspended solids concentrations decreased during the lower flow rate for the tailing 45 min for the first three tests and for the tailing 24 min for the last test. Concentrations averaged 163 mg/L, 122 mg/L, 232 mg/L, and 175 mg/L, respectively for the four tests, where the average of these numbers was within a 20% margin of the target value of 207 mg/L for three of the tests.

For the first three medium flow tests, surface runoff was only generated during the first 15 min of the test during the high concentration and initial high flow. Once the concentration and flow decreased for the tailing 45 min, all the water delivered to the bed infiltrated, and no surface samples could be collected. Overall, the suspended sediment concentrations were low in the surface runoff and decreased over time, with average concentrations of 47.0 mg/L for the 8:1 slope, 57.9 mg/L for the 4:1 slope, and 22.2 mg/L for the 2:1 slope with medium flow. The high flow run generated surface runoff throughout the entire test. Suspended sediment concentrations were also low for this test, with an average initial concentration of 62.4 mg/L for the first 6 min and an average tailing concentration of 16.4 mg/L for the last 24 min. These values should be compared with baseline suspended solids concentrations that averaged 14.4 mg/L and represent the lower limit of TSS concentrations that can be achieved in runoff concentrations even with clean influent flowing over the grassy slope. All effluent concentrations were on the

same order of magnitude as these minimum concentrations, and two were very close.

When accumulated over the entire storm, the percent removals of the event mean

concentrations were 91.9% for the 8:1 test, 88.0% for the 4:1 test, 96.6% for the 2:1

medium flow rate test, and 87.8% for the 2:1 high flow rate test. Based on these percent

removals, the change in slope of the bed did not significantly affect the percent removals

of the suspended solids.

In addition to collecting surface samples, groundwater samples were also

collected from the underdrain. For all four tests, significant amounts of the simulated

runoff from the influent infiltrated into the bed and exited out the underdrain. Suspended

sediment concentrations in the underdrain were very low for the first three medium flow

tests averaging 18.2 mg/L for the 8:1, 38.5 mg/L for the 4:1, and 72.0 mg/L for the 2:1.

For all three tests, suspended sediment concentrations decreased over time. The 2:1 test

was different from the other tests, because concentrations started out high with a

suspended sediment value of 311 mg/L in the underdrain and exhibited a much higher

average suspended sediment concentration of 139 mg/L. This concentration was similar

to the average influent concentration of 175 mg/L at a 2:1 slope and high flow rate for the

tailing portion of the test. Baseline underdrain suspended solids concentrations averaged

55.4 mg/L for the 2:1 slope, which was higher than the 8:1 and the 4:1 medium flow rate

tests. As the slope increased to 2:1, a higher concentration of suspended solids was

detected in the underdrain.

3.1.2 Total Metals Results

Total metals were determined by ICP-OES analysis following acid digestion. These samples were not filtered prior to digestion, and results represent the combined total of metals dissolved in the water and sorbed to suspended solids. Table 3.1 displays the high and medium target concentrations of simulated stormwater runoff. For the medium flow rate test with an 8:1 slope, total metal concentrations are displayed in Figure 3.5 through Figure 3.11. Measured influent concentrations of each metal were somewhat lower in both the high and medium concentrations than the target concentrations. For example, the high target concentration for cadmium was 500 µg/L, and the average measured concentration was 409 µg/L. The medium target concentration was 100 µg/L and the average measured concentration was 83 µg/L. Nevertheless, all metals except Pb were within a 20% margin of the target values. Pb concentrations were 75% of the target values. Despite this decrease, the influent concentrations remained constant over time for every metal.

Collected surface runoff was only generated for the first 15 min during the initial higher flow rate of the 8:1 medium flow test. Surface runoff concentrations were very low for each metal, and removal of metals from the surface runoff was excellent. Cr and Pb were not detected in all surface runoff samples with limits of 7 µg/L and 55 µg/L, respectively. Cd and Cu were detected at concentrations below 30 µg/L, Ni and Zn below 100 µg/L, and Fe between 100 and 1,000 µg/L. In the surface baseline samples, Cd, Cr, Ni, and Pb were not detected with limits of 2 µg/L, 7 µg/L, 17 µg/L, and 30 µg/L, respectively. Cu, Fe, and Zn were detected in the baseline samples at average

concentrations of 15 µg/L, 139 µg/L, and 27 µg/L, respectively. These concentrations were similar to the experimental surface concentrations, so a large portion of these metals in the surface runoff likely originated from the original grassy slope itself and not the influent. Percent removals of the event mean concentration for Cd, Cr, Cu, Fe, Ni, Pb, and Zn were as follows: 86.0%, 99.1%, 93.2%, 97.7%, 96.2%, 99.1%, and 94.3%. In the 8:1 slope test, Cr and Pb had the highest percent removals out of all the metals.

Underdrain samples had even lower metal concentrations for each metal. Cr and Pb were not detected, with limits of 7 µg/L and 55 µg/L, and Ni was only detected twice near the detection limit of 17 µg/L. Cd remained below 5 µg/L , Cu below 30 µg/L , Zn below 65 µg/L , and Fe below 1,000 µg/L . Each individual metal concentration remained reasonably consistent over time, except Cu and Fe, which had the highest concentrations in the initial sample. In the underdrain baseline samples, Cr, Ni, and Pb were also not detected, with the same detection limits. Cd was detected at 3 µg/L in the first collected underdrain sample, but was not detected in the other two samples with a detection limit of 2 µg/L. Cu and Zn were detected at average concentrations of 15 µg/L and 37 µg/L, respectively, but Fe was higher in the first underdrain baseline sample at 1370 µg/L and an average of 484 µg/L in the other two samples. This higher Fe concentration correlates with the higher underdrain baseline concentration in the suspended solids at 120 mg/L, which shows that the soil contains a high concentration of Fe. So, compared with baseline samples, none of the total metals concentrations in the underdrain from the high concentration tests exceeded those expected from clean water leaching through the clean soil.
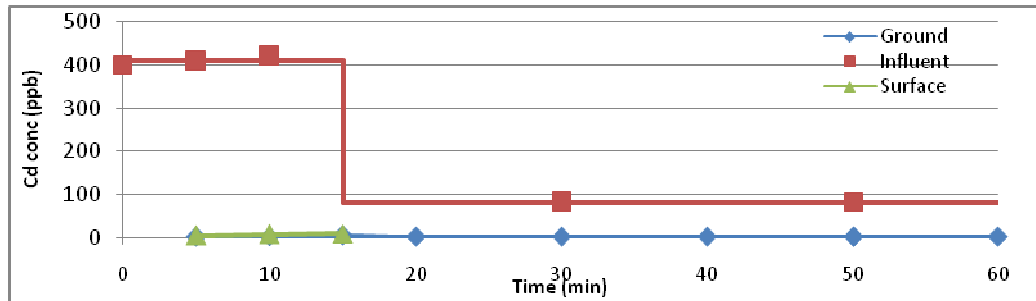
Figure 3.5: Total concentration of cadmium in 8:1 slope, medium flow rate
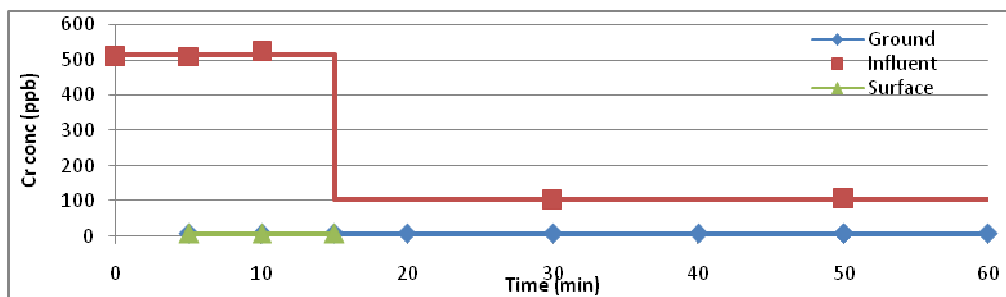
Figure 3.6: Total concentration of chromium in 8:1 slope, medium flow rate
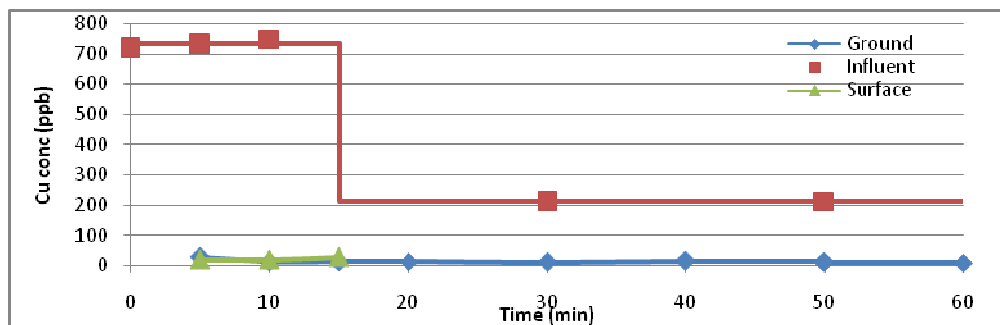
Figure 3.7: Total concentration of copper in 8:1 slope, medium flow rate
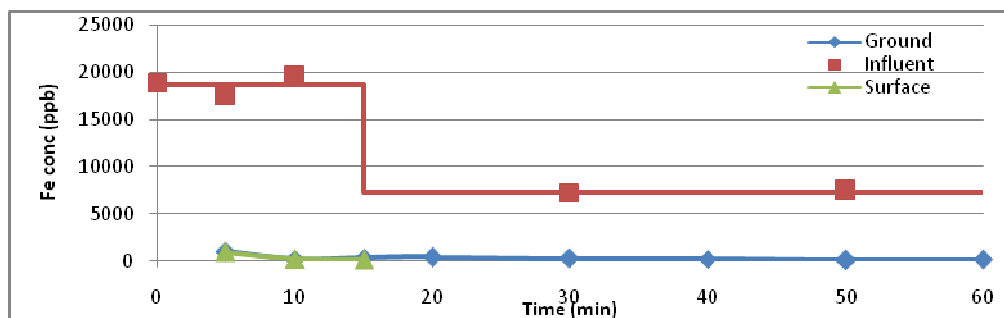
Figure 3.8: Total concentration of iron in 8:1 slope, medium flow rate
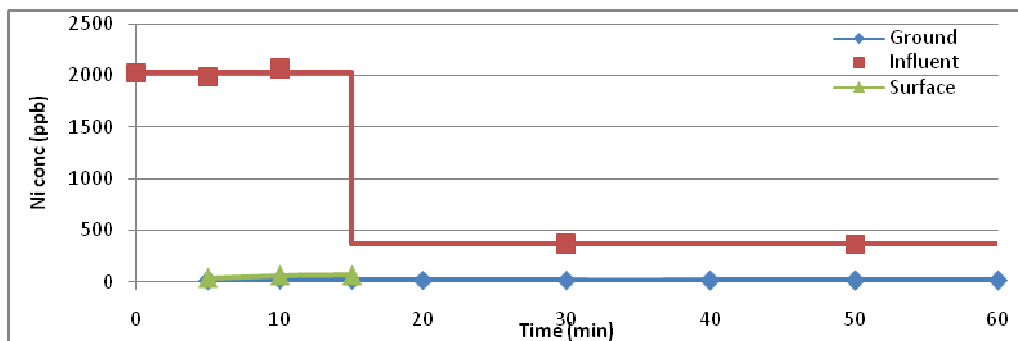
Figure 3.9: Total concentration of nickel in 8:1 slope, medium flow rate
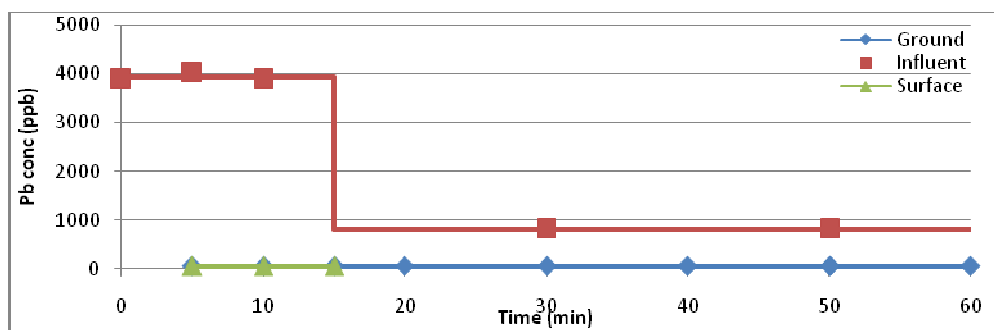
Figure 3.10: Total concentration of lead in 8:1 slope, medium flow rate

Figure 3.11: Total concentration of zinc in 8:1 slope, medium flow rate

For the medium flow rate test with a 4:1 slope, total metal concentrations are displayed in Figure 3.12 through Figure 3.18. When compared with the 8:1 slope test, the influent metal concentrations vary slightly. Instead of being consistent for the initial high concentration, there is a slight decrease over time for every metal except Zn, which

remained consistent throughout. The tailing portion of the test had consistent concentrations for each metal. Similar to the 8:1 slope test, several of the metals had lower average concentrations than the target values, but all were within a 20% margin except Pb which was 72% of the target value.

The surface and underdrain samples exhibited similar trends to the 8:1 slope test with low metals concentrations and excellent removals of metals from the surface runoff. In the surface runoff, Cr and Pb were not detected with limits of 7 μg/L and 55 μg/L respectively. Concentrations for Cd, Cu, Fe, Ni, and Zn remained low and consistent, except Ni which increased over time from 39 μg/L to 135 μg/L. The baseline surface sample concentrations were not detected for Cd, Cr, Ni, and Pb, and Cu concentrations detected in surface baseline were higher than those detected in the surface performance test. A large portion of the metal detected in surface runoff for Fe and Zn in the performance tests could be explained by significant concentrations in the surface baseline. Percent removals of the event mean concentration for Cd, Cr, Cu, Fe, Ni, Pb, and Zn were as follows: 97.1%, 99.0%, 97.4%, 98.2%, 94.6%, 99.0%, and 95.6%. As with the 8:1 slope, Cr and Pb had the highest percent removals out of all the metals. Overall, it seems as if the slight increase in slope did not have much of an effect on metal removals.

The underdrain samples also contained consistently low metal concentrations, with Fe, Zn, and Ni decreasing over time. Zn had a large spike in concentration at 50 min, much unlike any of the other metals. Cr and Pb were not detected throughout the entire test in the underdrain samples, while Cd and Ni were initially detectable near

detection limits in the first 15 min with the high concentration flow, but then became

undetectable with limits of 2 μg/L and 17 μg/L when the medium concentration was

pumped onto the bed. In the baseline samples, Cd, Cr, Ni, and Pb were also not detected.

Cu and Fe were detected in baseline samples at the same concentrations that were

detected in underdrain samples from the performance test. Ni and Zn were higher than

baseline in two samples each.

Figure 3.12: Total concentration of cadmium in 4:1 slope, medium flow rate
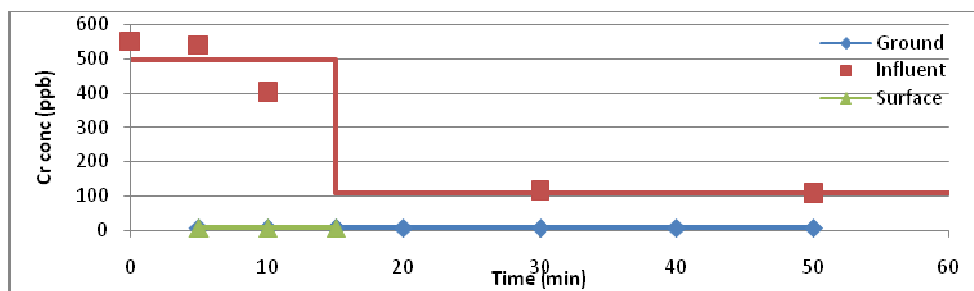
Figure 3.13: Total concentration of chromium in 4:1 slope, medium flow rate
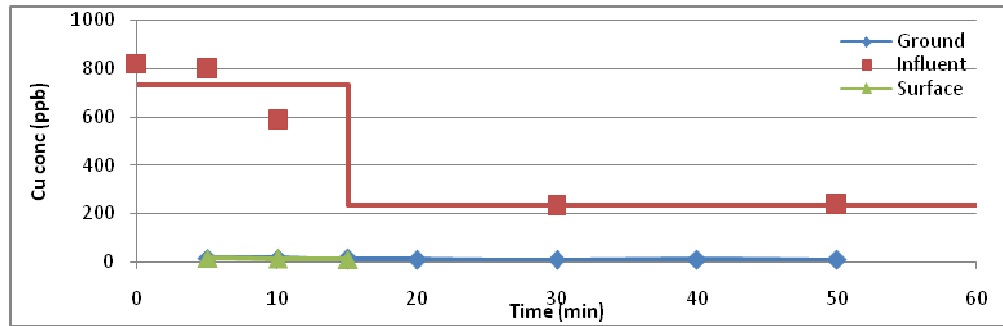
Figure 3.14: Total concentration of copper in 4:1 slope, medium flow rate
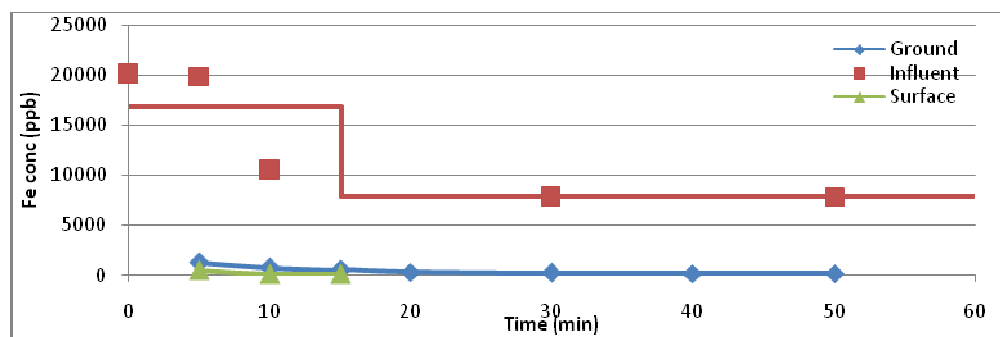
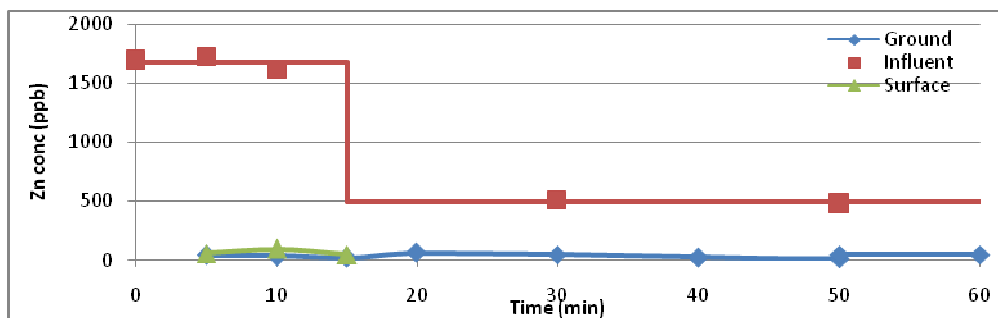**Figure 3.15: Total concentration of iron in 4:1 slope, medium flow rate**
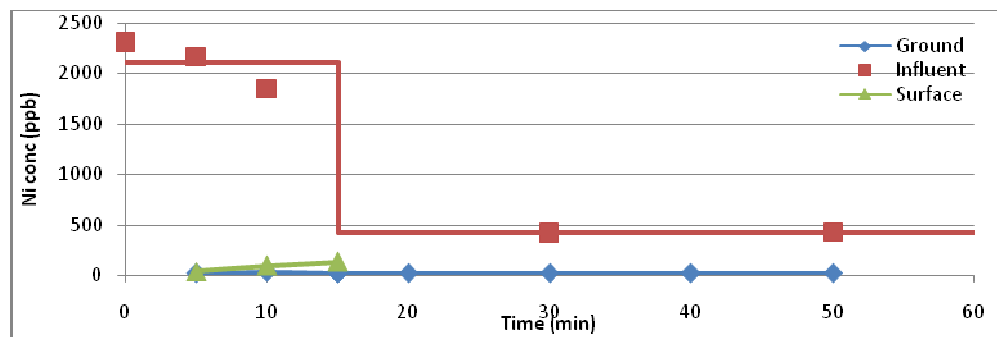
Figure 3.16: Total concentration of nickel in 4:1 slope, medium flow rate
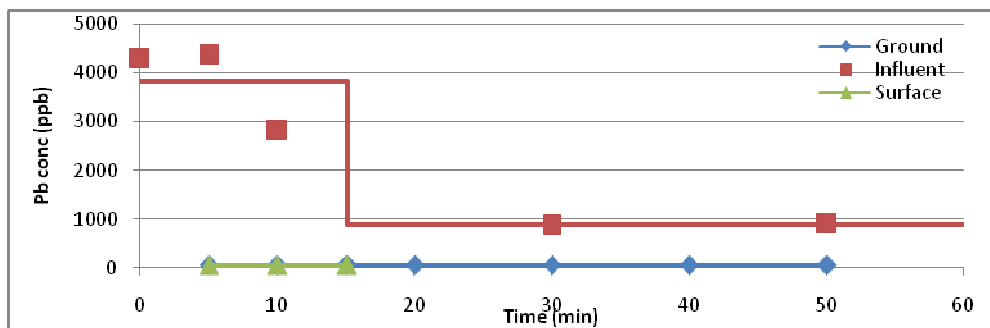
Figure 3.17: Total concentration of lead in 4:1 slope, medium flow rate

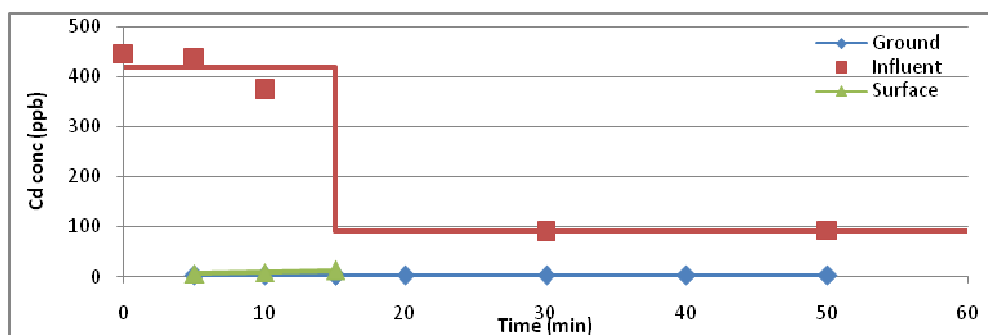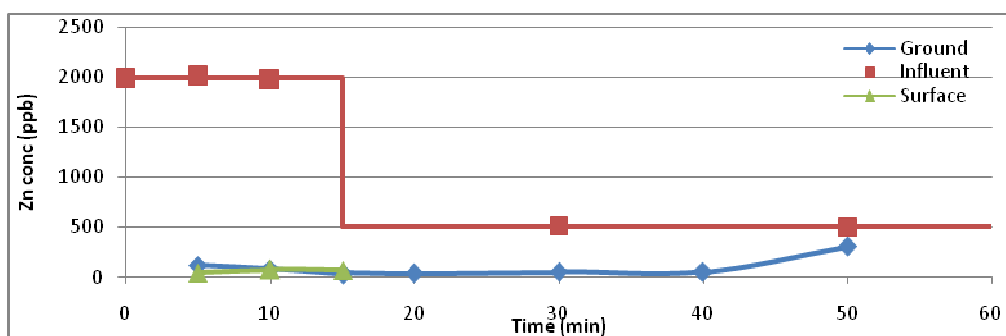**Figure 3.18: Total concentration of zinc in 4:1 slope, medium flow rate**

Figure 3.19 through Figure 3.25 portray the 2:1 slope test with a medium flow. The influent samples exhibited similar trends as the 8:1 slope test for Cd, Cr, Cu, and Zn, because these influent concentrations were slightly lower than their target concentrations, but within a 15% margin except for Ni and Pb, which were only 58% and 70% of the target values. This was due to a low 5 min sample concentration for both metals. The tailing end of the test had the same consistently low metal concentrations as the other two tests.

Even with the 2:1 slope, surface runoff virtually ceased to be generated after the initial 15 min high flow period. Water was dripping into the surface trough throughout the tailing portion of the storm, but at such a slow rate that only one set of sampling

bottles could be collected. One significant trend for each metal within the surface

samples was at 5 min into the test. At this point, each metal was detected at its highest

concentration, even Pb. Cr was not detected in the surface runoff for the 4:1 slope but

was detected with the 2:1 slope. This difference could be from the simulated stormwater

runoff having less time to infiltrate into the bed at the higher slope. The only metal that

was not detected in the surface runoff after the 5 min sample was Pb with a detection

limit of 48 μg/L. During the tail end of the surface runoff, concentrations were low and

consistent over time. Cd and Cr had surface concentrations only slightly above the

baseline detection limits, while Ni had significantly higher concentrations than the

baseline. For the metals that were detected in both the performance test and the baseline

test, Cu was only slightly above the baseline concentrations, while Fe and Zn were well

above baseline concentrations. Overall, the surface runoff concentrations were low, and

still resulted in excellent percent removals of event mean concentration for Cd, Cr, Cu,

Fe, Ni, Pb, and Zn as follows: 96.7%, 96.6%, 95.7%, 90.1%, 94.9%, 97.1%, and 92.4%.

As with the first two slopes, Cr and Pb exhibit the some of the highest percent removals,

with Cd high as well. These percentage removals are slightly lower than the 4:1 test.

The underdrain samples had consistently low concentrations for every metal over

time except Fe and Zn. Fe had a spike in concentration at 10 min during the initial high

flow with a concentration of 1800 μg/L versus the average concentration of 840 μg/L.

Zn had a slight increase in concentration at the tail end of the flow during 30 and 40 min

from 76 μg/L to 150 μg/L with an average of 105 μg/L. Cd and Pb were not detected

throughout the run, with limits of 5 μg/L and 48 μg/L respectively. Cr and Ni were

detected for up to 20 min, and then were not detected after 20 min with limits of 2 µg/L and 13 µg/L respectively. Baseline concentrations were significantly lower for Cr and Ni for the first 20 min of the run, and for Fe and Zn for the entire run. Cd and Pb were also not detected in the baseline samples. In short, underdrain concentrations of Cd, Cu, Fe and Pb in the performance test were no different than baseline concentrations, while Cr, Ni, and Zn concentrations in the performance test were above baseline concentrations.

Figure 3.19: Total concentration of cadmium in 2:1 slope, medium flow rate
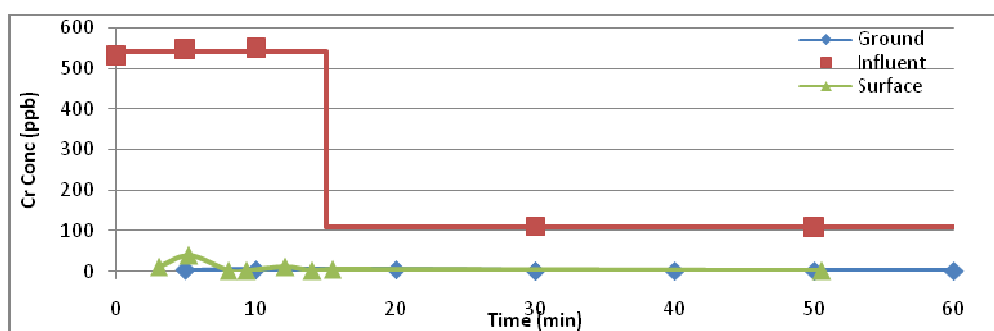
Figure 3.20: Total concentration of chromium in 2:1 slope, medium flow rate

Figure 3.21: Total concentration of copper in 2:1 slope, medium flow rate

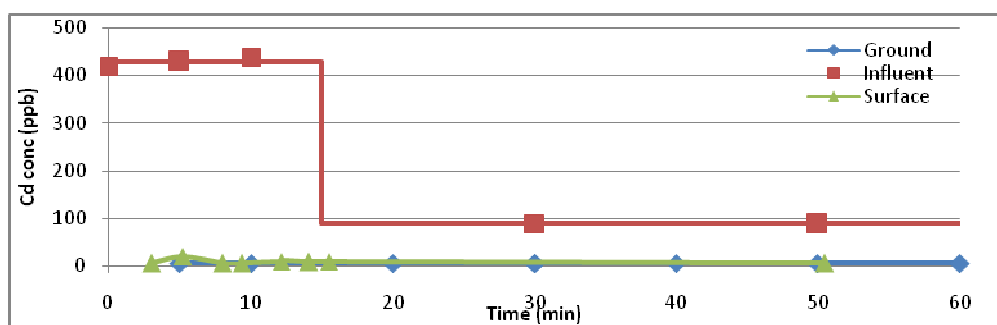**Figure 3.22: Total concentration of iron in 2:1 slope, medium flow rate**

Figure 3.23:   Total concentration of nickel in 2:1 slope, medium flow rate

Figure 3.24: Total concentration of lead in 2:1 slope, medium flow rate

Figure 3.25: Total concentration of zinc in 2:1 slope, medium flow rate

Figure 3.26 through Figure 3.32 portray the fourth high concentration test, which consisted of a 2:1 slope at a high flow rate. For the high flow simulation, an initial flow rate of 5.43 gpm was maintained for 6 min and then followed by a flow rate of 1.18 gpm for 29 min. The initial influent flow had lower concentrations than the target values listed in Table 3.1 but within a 20% margin, except for Zn which had an initial average concentration 190% of the target value due to a single, very high detection. For the first 5 min, the influent concentration slightly decreased for every metal, but stayed consistent throughout, except Zn, which had a large decrease from 0 to 5 min, which started off at 4790 µg/L and decreased to 1672 µg/L. The tail end for the influent flow was consistent for every metal as it was for the other three tests.

Surface runoff was generated throughout the entire test, and metal concentrations were highest during the first 5 min of the test, and then decreased at the tail end for the remainder of the run. The only metal that did not display this trend was Pb because it was not detected throughout the run with a detection limit of 58 μg/L. Cr was also not detected after the first 5 min at a limit of 6 μg/L. Surface baseline concentrations were lower for Cd, Fe, Ni, and Zn. For the first 5 min, Cr was above the undetected baseline concentration of 7 μg/L. Cu concentrations were similar in both the baseline and experimental surface samples. Overall, the surface runoff concentrations were low, and gave average percent removals for Cd, Cr, Cu, Fe, Ni, Pb, and Zn as follows: 91.7%, 98.2%, 96.5%, 96.9%, 86.1%, 98.9%, and 94.3%. As with the other three slopes, Cr and Pb had the highest percent removals.

The underdrain samples differed from the 2:1 medium flow test, because different metals were detected. For the 2:1 medium flow test, Cd, Cr, Ni, and Pb were not detected, while for the 2:1 high flow test, Cr, Cu, and Pb were not detected, with detection limits 6 μg/L, 8 μg/L, and 58 μg/L. This was the only test, where Cu was not detected in several samples. Cu was detected at concentrations of between 9 μg/L and 16 μg/L in four samples. Every metal except Pb had a higher concentration in the beginning of the run, and then the concentrations decreased during the tail end of the test. The underdrain baseline concentrations were lower for Cd, Fe, Ni, and Zn, but the baseline Cu concentrations were higher than the experimental underdrain Cu concentrations. Cr and Pb were not detected in both the experimental and the baseline

underdrain samples. Overall, the concentrations were low compared to the influent

samples.

Figure 3.26: Total concentration of cadmium in 2:1 slope, high flow rate
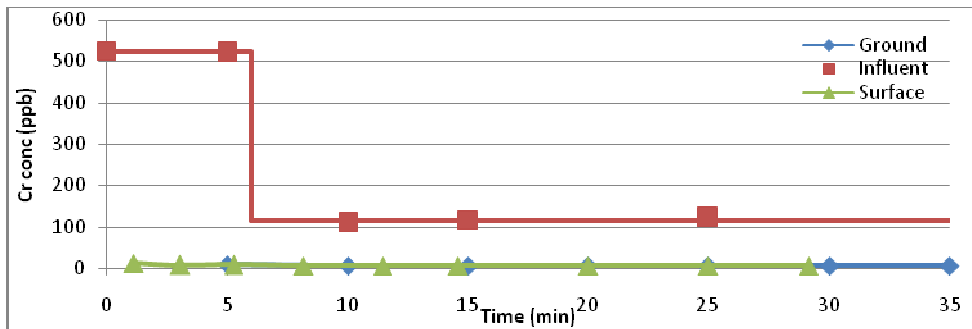
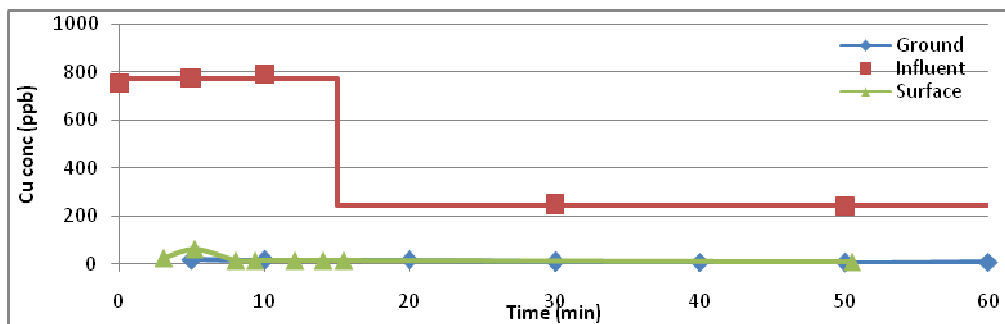**Figure 3.27: Total concentration of chromium in 2:1 slope, high flow rate**
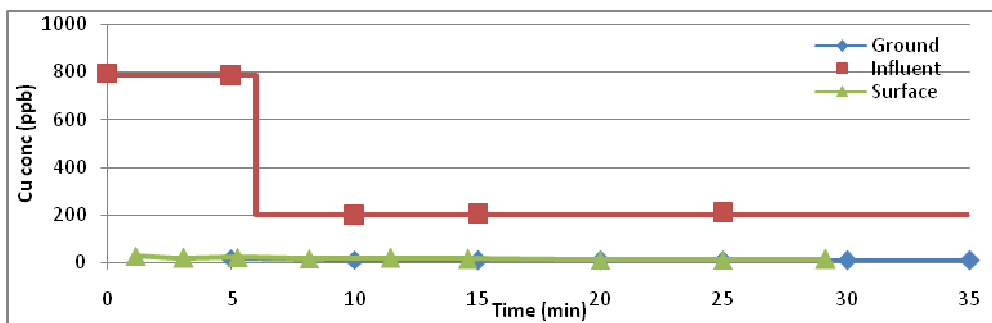
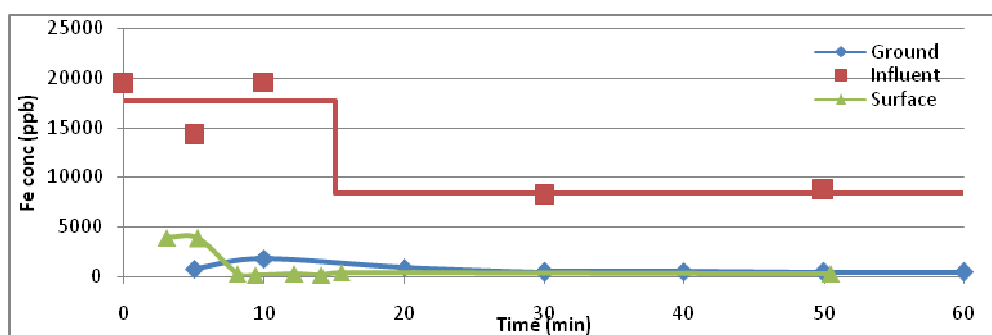**Figure 3.28: Total concentration of copper in 2:1 slope, high flow rate**
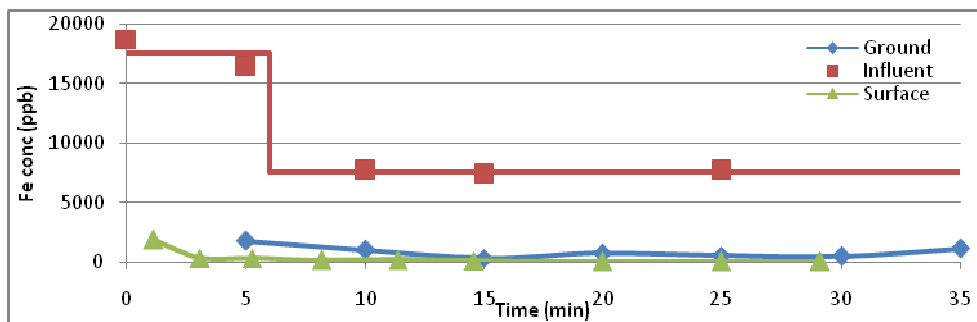
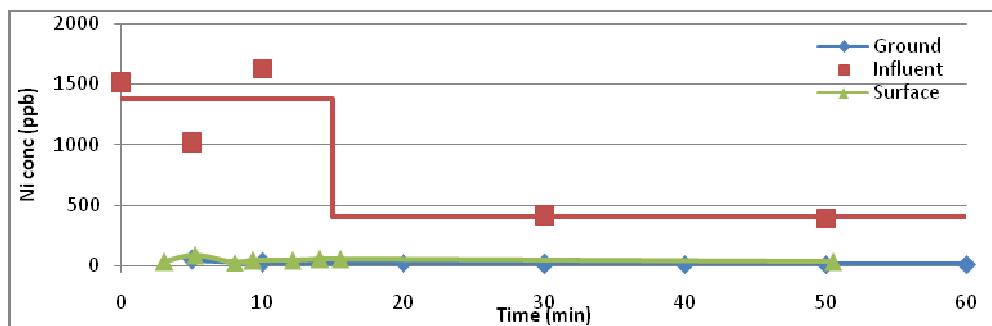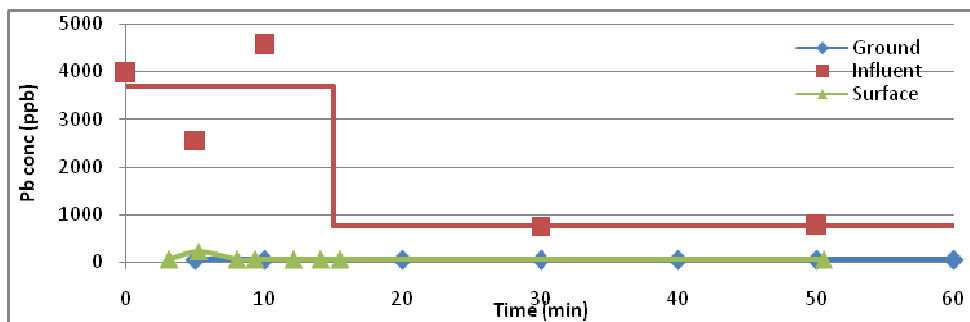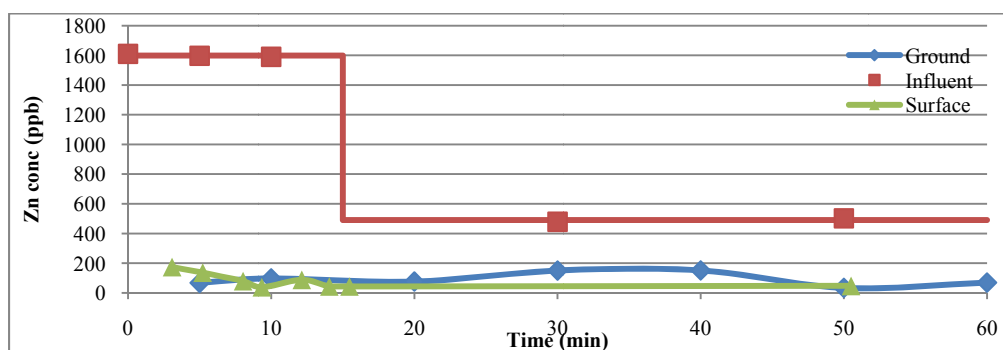**Figure 3.29: Total concentration of iron in 2:1 slope, high flow rate**
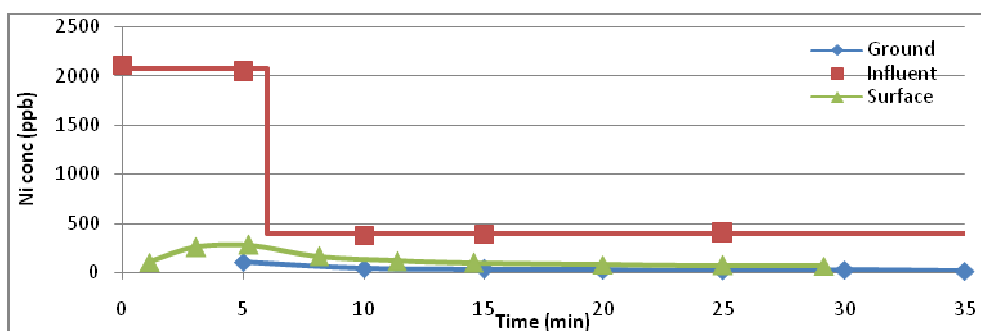
Figure 3.30: Total concentration of nickel in 2:1 slope, high flow rate

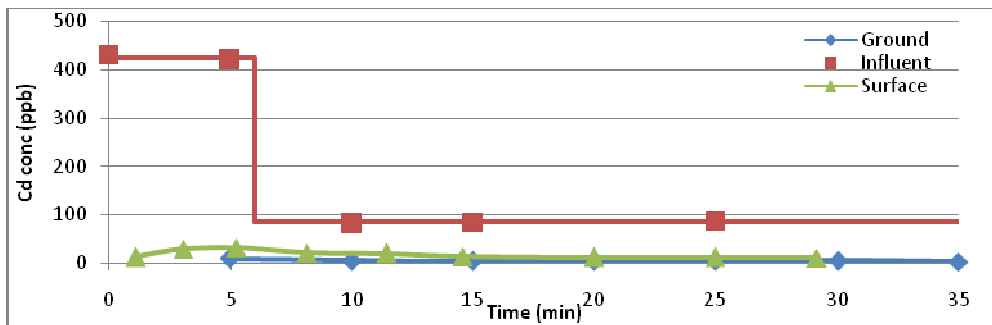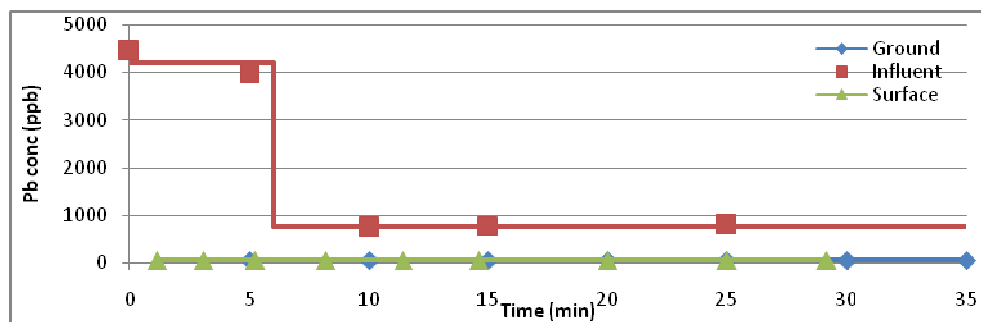**Figure 3.31: Total concentration of lead in 2:1 slope, high flow rate**
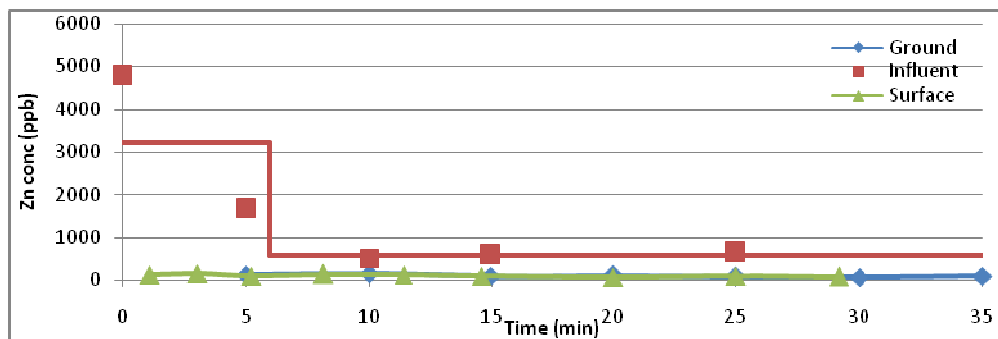
Figure 3.32: Total concentration of zinc in 2:1 slope, high flow rate

3.1.3 Dissolved Metals Results

Dissolved metal samples were collected on-site by filtering the samples with a 0.45 μm syringe filter. These samples were preserved with acid and analyzed by ICP-OES. Figure 3.33 through Figure 3.38 display several of the dissolved metals for the 8:1 medium flow test and the 4:1 medium flow test. Each test displayed similar trends for every dissolved metal. For each test, Cr, Cu, and Pb were not detected for influent, surface, and underdrain samples, with detection limits of 7 μg/L, 9 μg/L, and 55 μg/L for both tests. Cd, Ni, and Zn also displayed similar results with initial erratic influent concentrations, most likely due to varying amounts of suspended solids being delivered. The tail end influent samples were much lower than the initial surface samples. The underdrain and surface samples for Cd and Zn were all not detected, or very close to the detection limits of 2 μg/L and 5 μg/L, which means that most of the metals did not dissolve and were particulate bound. Ni was detected in surface runoff, with an average concentration of 46.7 μg/L for the 8:1 test and 96.7 μg/L for the 4:1 test, although these values were far below dissolved influent concentrations of 1,100-1,600 μg/L. The only

dissolved metals detected in baseline samples were Cd at 3 μg/L, Cu at 14 μg/L, and Fe at 14 μg/L.
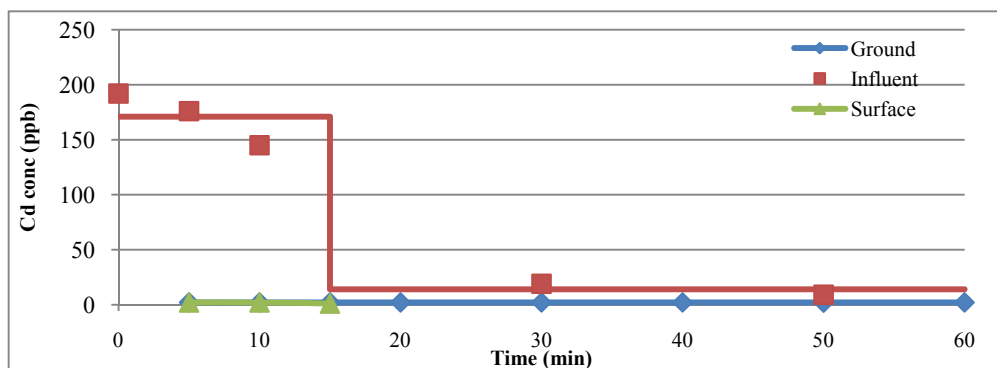
Figure 3.33 Dissolved concentration of cadmium in 8:1 slope, medium flow rate
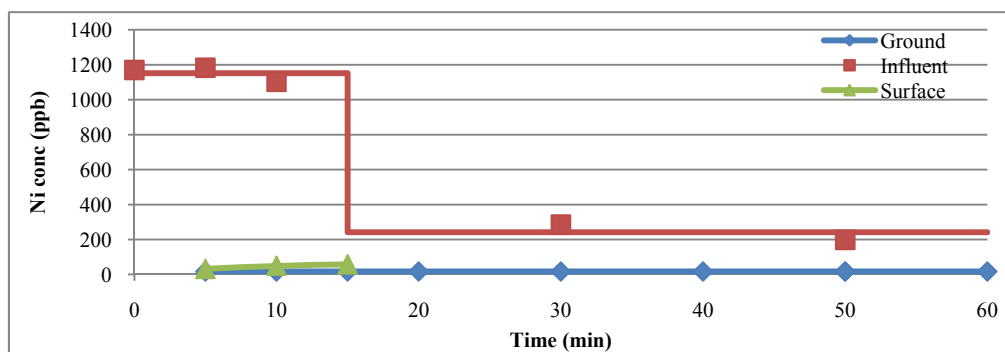
Figure 3.34 Dissolved concentration of nickel in 8:1 slope, medium flow rate
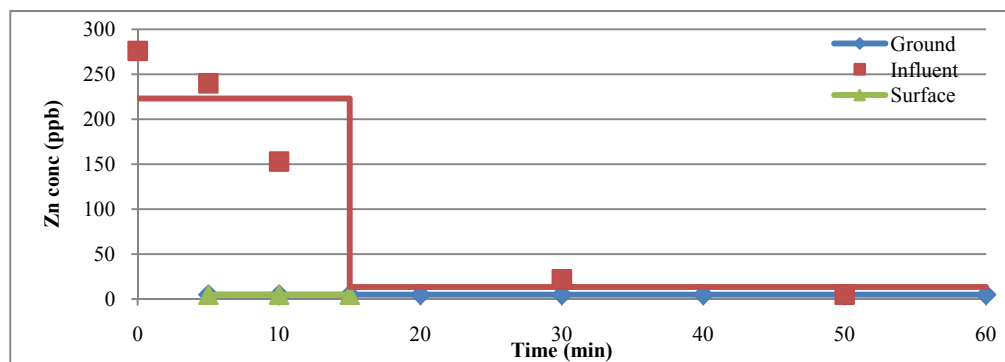
Figure 3.35 Dissolved concentration of zinc in 8:1 slope, medium flow rate
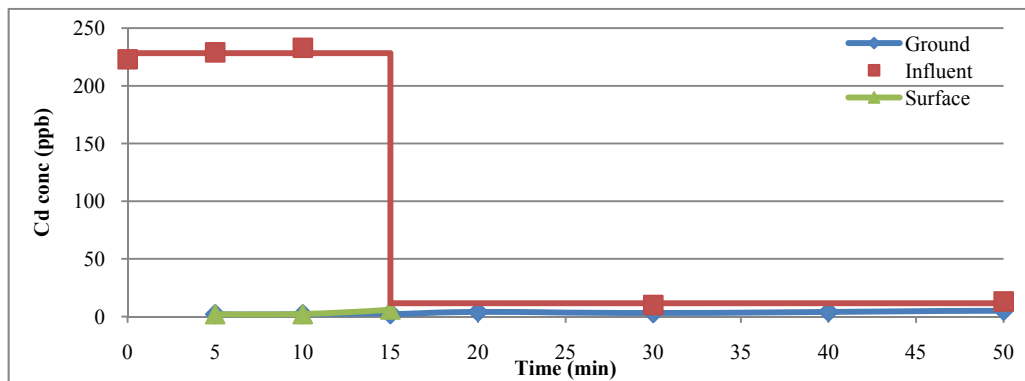
Figure 3.36 Dissolved concentration of cadmium in 4:1 slope, medium flow rate
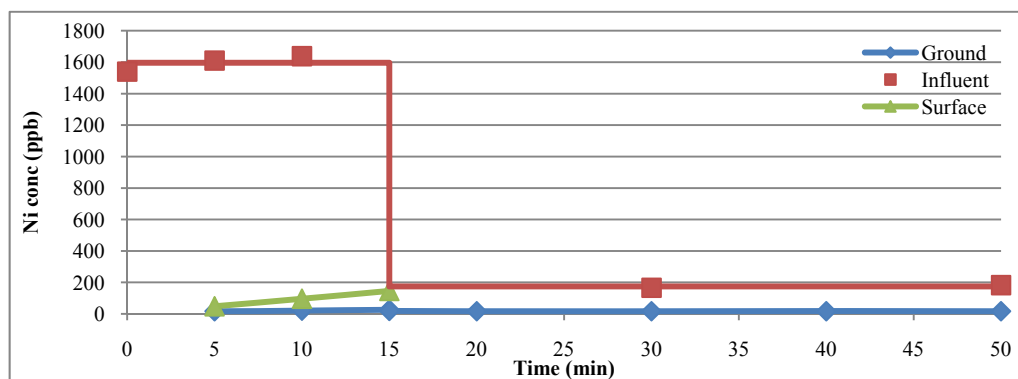
Figure 3.37 Dissolved concentration of nickel in 4:1 slope, medium flow rate
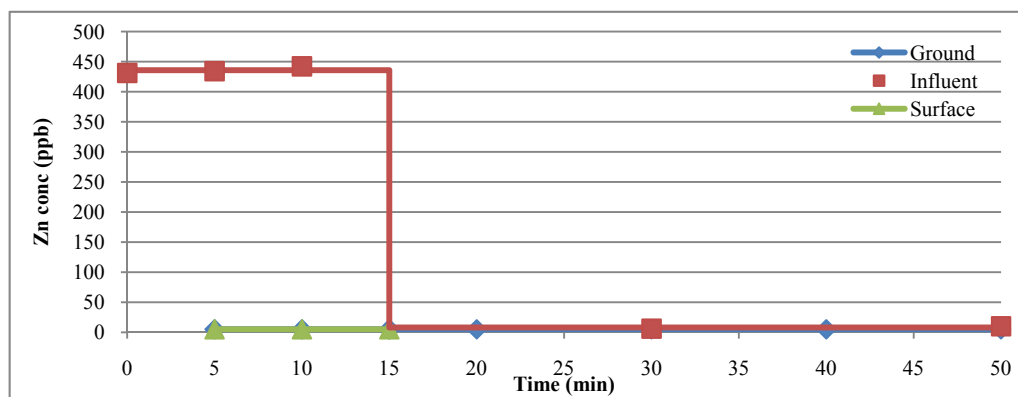
Figure 3.38 Dissolved concentration of zinc in 4:1 slope, medium flow rate

Figure 3.39 through Figure 3.45 display the dissolved metals results for the 2:1

medium and high flow tests. For the 2:1 medium flow test, Cr and Pb were not detected

in the influent, surface, and underdrain samples with detection limits of 2 µg/L and 48 µg/L respectively. Cd and Zn were both detected in the influent with slightly lower concentrations in the tail end flow, but were not detected or detected near limits in surface and underdrain samples at limits of 5 µg/L and 3 µg/L. Dissolved Cu was detected in all samples between 4 µg/L and 17 µg/L, similar to baseline concentrations. Ni was detected at the highest concentrations in the influent, up to 717 µg/L, and at low concentrations in the surface runoff at or near detection limits of 13 µg/L in the underdrain. Fe was unusual among the metals and was near the detection limit of 6 µg/L in the surface runoff, but above influent concentrations in the underdrain indicating leaching out of the soil.
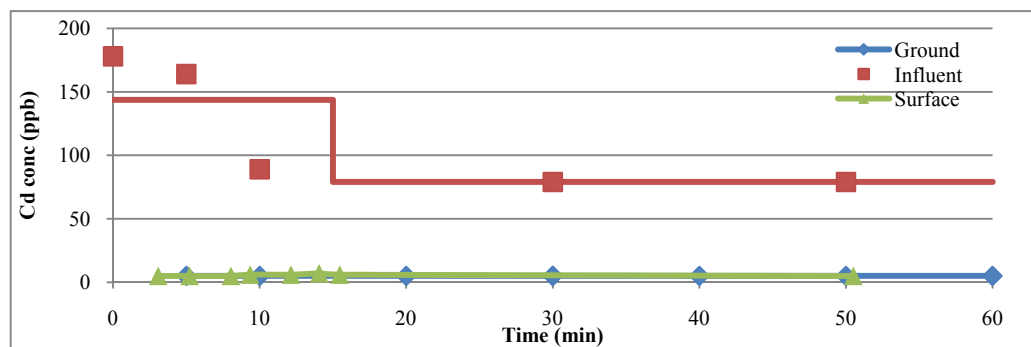
Figure 3.39 Dissolved concentration of cadmium in 2:1 slope, medium flow rate
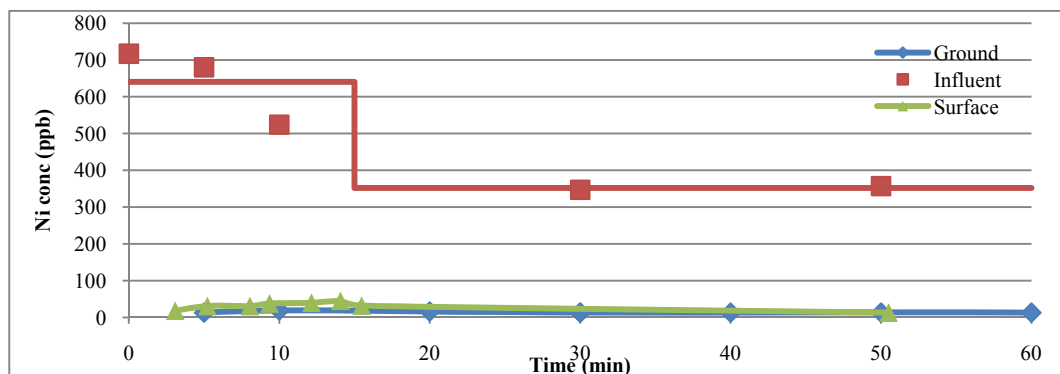
Figure 3.40 Dissolved concentration of nickel in 2:1 slope, medium flow rate
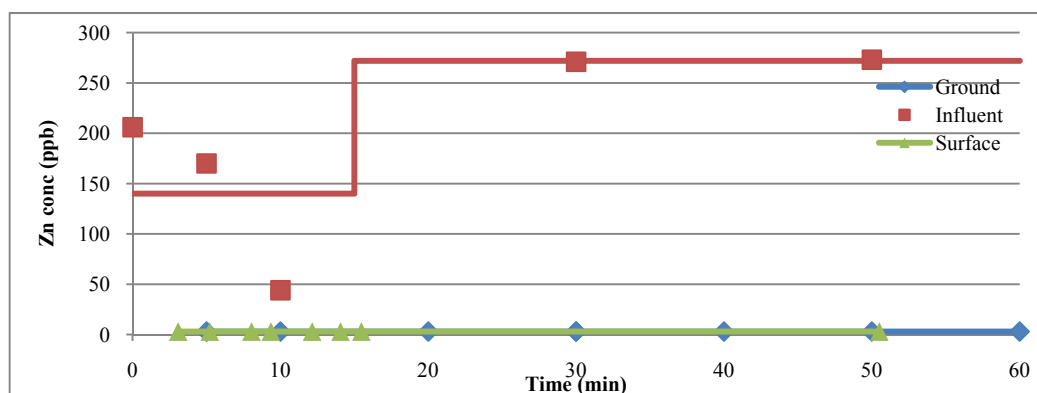
Figure 3.41 Dissolved concentration of zinc in 2:1 slope, medium flow rate

The 2:1 high flow test metals results were similar to the 2:1 medium flow results, as displayed in Figure 3.42 to Figure 3.45. Cr, Cu, and Pb were not detected or near limits for the influent, surface, and underdrain samples with detection limits of 6 µg/L, 8 µg/L, and 58 µg/L respectively, except for the 5 min influent sample. This sample had uncharacteristically high levels of all dissolved metals indicating a problem with the sample, possibly failure of the filter to remove all particles. Cd and Zn were both detected in the influent with slightly lower concentrations in the tail end flow, and were detected at much lower concentrations in surface runoff, but were not detected or detected near limits in underdrain samples at limits of 3 µg/L and 4 µg/L. Ni was detected at highest

concentrations in influent, up to 1910 μg/L, and at low concentrations in the surface

runoff and underdrain. Fe was unusual among the metals and was near the detection limit

of 6 μg/L in the surface runoff, but above influent concentrations in the underdrain

indicating leaching out of the soil.
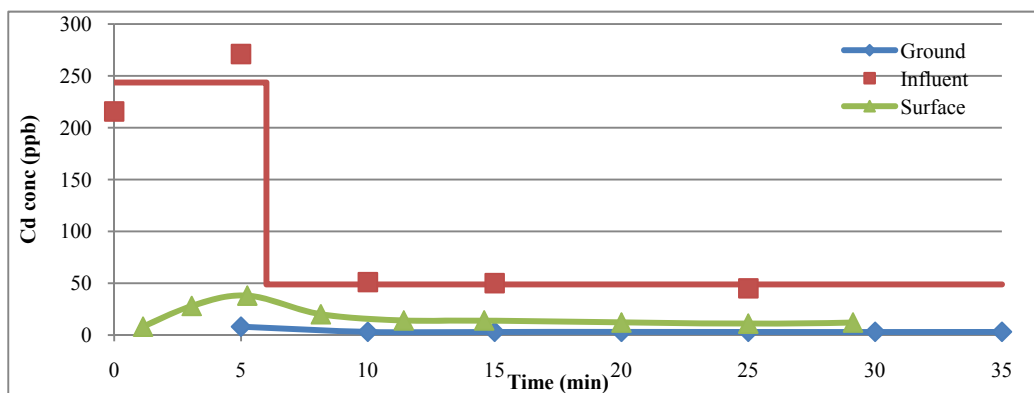
Figure 3.42 Dissolved concentration of cadmium in 2:1 slope, high flow rate
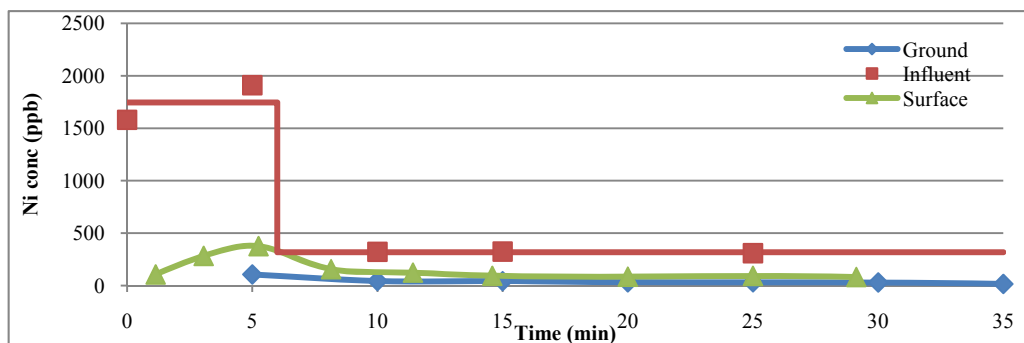
Figure 3.43 Dissolved concentration of nickel in 2:1 slope, high flow rate
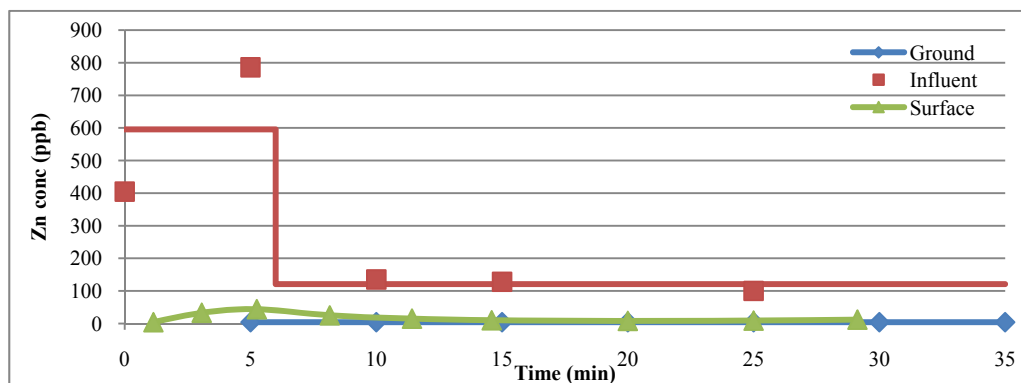
Figure 3.44 Dissolved concentration of zinc in 2:1 slope, high flow rate
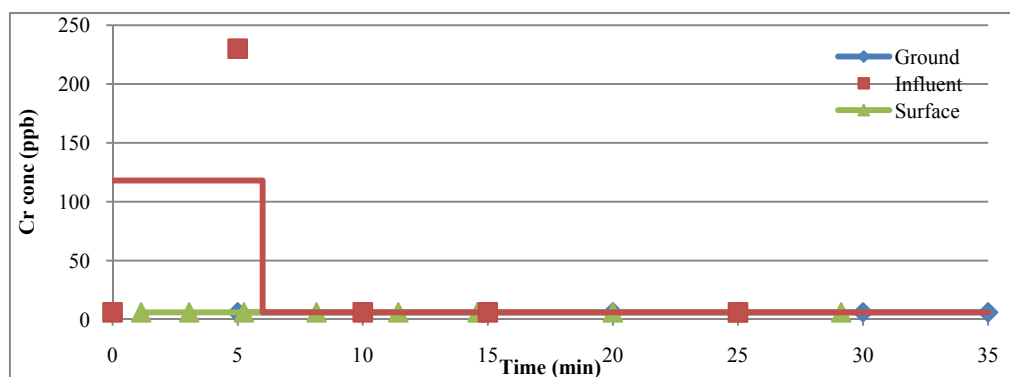
Figure 3.45 Dissolved concentration of chromium in 2:1 slope, high flow rate

3.1.4   Resuspension Results

After the four tests were completed on the bed, resuspension tests were conducted to determine the amount of tagged suspended solids that could become remobilized. Four resuspension tests were conducted that represented each slope and flow rate used for the initial testing. For the initial 8:1 slope performance test, target concentrations of La tagged suspended solids were added to the influent; 737 mg/L for the first flush portion of the test and 207 mg/L for the tail end of the test. Subsequent tests did not use tagged the suspended solids in the influent. As displayed in Figure 3.46, the first three collected influent samples exhibited tagged suspended solids concentrations near the target

concentration for the first flush, with an average tagged suspended solids concentration of

810 mg/L, and an average La concentration of 48,767 µg/L. The last two collected

influent samples exhibited tagged suspended solids concentrations very close to the target

concentration for the tail end of the test, with an average tagged suspended solids

concentration of 208 mg/L, and an average La concentration of 12,550 µg/L.
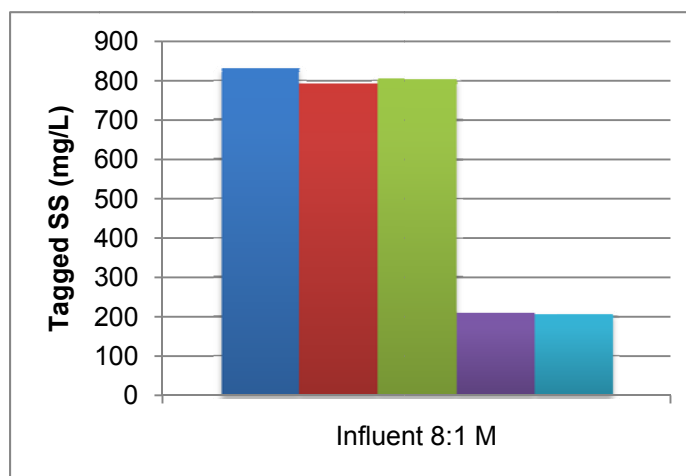
**Figure 3.46 Influent tagged suspended solids concentration in 8:1 slope, medium
flow rate**

Figure 3.47 displays the tagged suspended solids concentrations in the surface

runoff samples for each test on bed 1, four performance tests and four resuspension tests.

As seen from this figure, the tagged suspended solids concentrations were highest for the

8:1 medium flow test, with an average tagged suspended solids concentration of 4 mg/L

and an average La concentration of 226 µg/L. It was during this test that the tagged

suspended sediment was being released in the influent. These surface runoff

concentrations were well below the average influent tagged suspended solids

concentration of 810 mg/L and average La concentration of 48,767 μg/L. The fraction of La tagged soil in samples greatly decreased from around 1.2 in the influent to 0.2 in the surface samples. This low surface runoff concentration showed that the majority of the added suspended solids were settling within the bed, and a very small amount flowed over the bed without settling. The majority of the total suspended sediment in the runoff (average of 47 mg/L for this run, see Figure 3.1) eroded from the bed itself and did not originate from the influent water. Additional evidence of this was the baseline TSS concentrations in surface runoff which averaged 14.4 mg/L with only tap water as influent.

The other three performance tests resulted in very low concentrations of tagged suspended solids in surface runoff, averaging 0.29 mg/L for the 4:1 medium flow test, 0.24 mg/L for the 2:1 medium flow test, and 0.06 mg/L for the 2:1 high flow test. In the 4:1 medium flow test, La was detected, with an average concentration of 17 μg/L. In the 2:1 medium flow test, La was only detected for the first 8 min, and then was not detected for the remainder of the test, with a limit of 8 μg/L. In the 2:1 high flow test, La was not detected throughout the entire test.
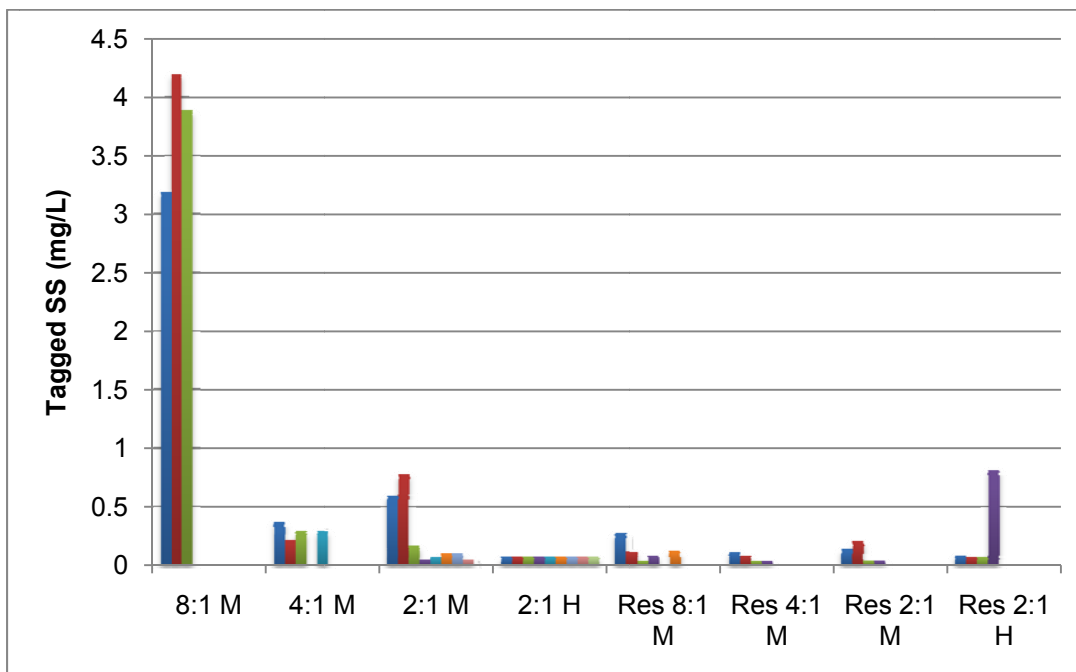
Figure 3.47 Tagged suspended solids concentrations for experimental and resuspension tests

Each of the resuspension tests also had very low concentrations of tagged suspended solids, with average concentrations of 0.12 mg/L for the 8:1 medium flow test, 0.07 mg/L for the 4:1 medium flow test, 0.10 mg/L for the 2:1 medium flow test, and 0.26 mg/L for the 2:1 high flow test, which were all lower concentrations than the initial tests, except for the 2:1 high flow test. La concentrations remained low for each test, except a spike in surface La concentration for the 2:1 high flow test with a concentration of 49 µg/L, which was around the same concentration of the 2:1 medium flow spike for the performance tests, with a surface La concentration of 47 µg/L. Based on this data, it appears that the tagged suspended solids initially added to the 8:1 medium flow influent did not become resuspended, except when the slope and flow rate were higher, but even then these concentrations were approximately 1000 times lower than the average 8:1

medium flow influent La concentration. During these eight consecutive storms, resuspension of particulate matter was negligible.

3.1.5   Efficiency of Vegetated Biofilter to Mitigate Highway Stormwater Runoff

Figure 3.48 displays the average percent removals of the event mean concentration for each total metal and total suspended solids of the performance tests for bed 1. Event mean concentrations are defined as the total contaminant mass in the storm event divided by the total water volume. Event mean concentrations were calculated, and then percent removals were determined, because the event mean concentrations provide more consistent results than comparison of measured concentrations. It can be seen from this figure that percent removals were consistently high over every metal and for the total suspended solids from each slope. The lowest average percent removal came from the total suspended solids at 87.8% for the 2:1 (high) slope. Cr and Pb had the highest percent removals over all four slopes. For the high concentration set of tests, a change in slope did not appear to affect percent removals within the bed. These consistently high percent removals proved the vegetated biofilter to be very efficient in mitigating simulated highway stormwater runoff.
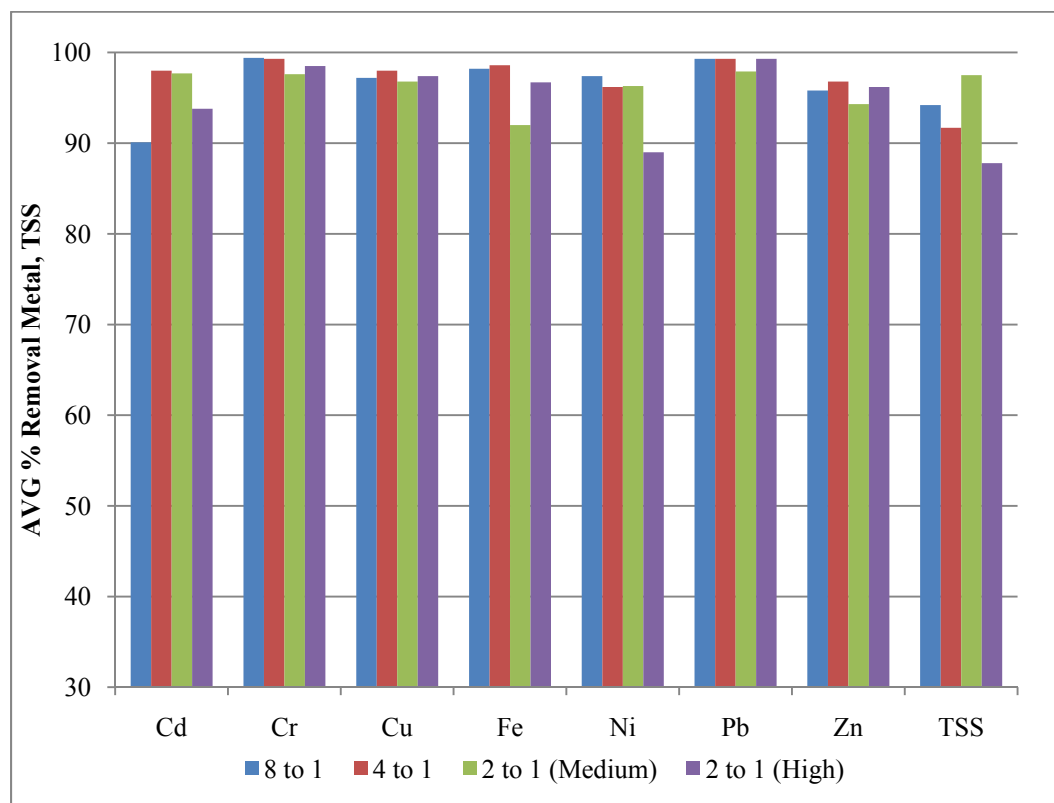
Figure 3.48: Average percent removal of event mean concentration for total metals and total suspended solids for bed 1

3.1.5.1 Comparison with Other Vegetated Biofilter Studies

When comparing the average percent removals in Figure 3.48 with the percent removals in other vegetated biofilter studies previously mentioned, it appears that the percent removals for this biofilter study were much higher than other studies. For example, Stagge and Davis (2006) reported TSS percent removals between 65-71% and zinc percent removals between 30-60% using event mean concentrations. The vegetated biofilter slopes used for this study were similar to ours, at 3:1 (33%) and 4:1 (25%); however the length was much longer, at 198 m and 137 m compared to our biofilters each with a length of 3.85 m. Stagge and Davis (2006) used a flow rate of 0.430 L/s to apply the stormwater runoff, which was much higher than our flow rate of 0.137 L/s for bed 1.

Our results gave an average TSS percent removal of 92.8% and an average zinc removal of 95.8%, which may seem much higher than what Stagge and Davis (2006) reported, but a higher flow rate was applied to their biofilters, and could have made the percent removals lower.

In another study by Barrett (2005), it was reported that the vegetated biofilter gave an average TSS percent removal of 48%, zinc removal of 54%, and copper removal of 24%. We observed a TSS percent removal of 93%, average zinc removal of 96%, and average copper removal of 97%. However, Barrett (2005) did not compute event mean concentrations, which could have skewed their percent removals and made them lower.

In addition to these two studies, Li et al. (2008) also reported average EMC percent removals that were lower than the values reported for this study as follows: TSS (68%), copper (67%), and lead (48%). These values could have been lower because actual storm events were sampled over a 16-month period, therefore rain intensity and concentration of highway stormwater runoff contaminants could not be controlled. Li et al. (2008) also found a correlation between vegetation cover and TSS percent removal, and concluded that if vegetation cover is over 90% then TSS percent removals will be higher; however, our vegetation cover was at least 80% and our TSS percent removals were still high.

One study that reported percent removals similar to our results was the Federal Highway Administration in Washington (FHA, 1996). Average percent removals were as follows: lead (93%), cadmium (>99%), copper (>99%), and zinc (84%). This study was most comparable to our study, because it was conducted in a laboratory setting,

where they could control the slope and flow rate; however their width and length were different than ours at 1.22 m by 4.27 m, while ours were 1.23 m by 3.86 m. Flow rates were almost identical, where this study used flow rates that ranged from 0.13 L/s to 0.025 L/s and we used flow rates that ranged from 0.13 L/s to 0.027 L/s. Added simulated stormwater concentrations were mostly lower at 250 mg/L, 75 µg/L, 199 µg/L, 2425 µg/L, and 2055 µg/L for TSS, Cd, Cu, Pb, and Zn respectively. Our high Zn concentration of 1700 µg/L for bed 1 was more similar to theirs of 2055 µg/L. Since most of their study parameters were similar to ours, it is easy to see why our percent removals were much alike.

Overall, these additional studies further validated how efficient the vegetated biofilters in this study were with removing high concentrations of simulated stormwater runoff. In addition to determining if the vegetated biofilters were efficient in removing the simulated stormwater runoff, it was also important to establish the specific removal mechanisms within the bed.

3.1.6 Metal Accumulation in Grass, Soil, and Roots

Five soil cores were initially collected from the bed from random locations to determine the baseline metals concentrations. After completion of all performance and resuspension tests, twenty cores were collected throughout the bed, four replicates at five different locations down the length of the bed. As described previously, the cores were separated into grass, root, and soil fractions, and each fraction was digested and analyzed for metals concentrations. The metals added to the influent included Cd, Cr, Cu, Fe, Ni, Pb, and Zn. Figure 3.49 to Figure 3.55 display the concentrations in mg of metal/kg of

dry matter within the grass, soil, and roots down the length of the bed. Because four core samples were collected at each distance along the bed, average values were plotted and error bars at each point on the graph represent one standard deviation. The solid horizontal lines on each graph represent the average baseline concentrations of the grass, soil, and roots before any tests were conducted.

All of the metals except Fe show similar results, with the highest concentrations detected in root tissue, next highest in grass tissue, and low concentrations detected in soil. In terms of the spatial distribution of the metals, concentrations decreased along the length of the bed with highest concentrations detected at a distance of 4.4 ft from the beginning of the bed. Influent water dripped onto the bed at the 2.2 ft location. Grass and root concentrations varied considerably among the duplicate samples, so even though average concentrations were often above background levels, in many cases the differences were not statistically significant ($\alpha=0.05$ for all tests). Average soil concentrations, though much lower than average grass and root concentrations, had smaller standard deviations and in some cases were significantly higher than background concentrations, even though it is not apparent in the figures. The one exception to all of these trends was Fe which had high background concentrations in all media, and all levels detected after testing were not significantly different from those background concentrations.

Cd was the only metal that had a statistically significant amount of accumulation throughout the bed in the grass, soil, and root media (see Figure 3.49). Highest concentrations were found in the roots and grass. Even though concentrations in soil

were only slightly above background concentrations, because the variability was low, the differences were statistically significant (see Figure 3.49). Pb was also detected at elevated concentrations throughout the bed in the roots and soil (see Figure 3.54). Pb was found above background in grass at the 2.2, 4.4, and 6.6 ft distances, but beyond that concentrations were not significantly different than background. Cu similarly had elevated concentrations in roots throughout the bed and in soil at the 2.2, 4.4, and 6.6 ft locations (see Figure 3.51). All concentrations of Cu in grass were indistinguishable from background. Ni had elevated concentrations in the roots throughout the bed, but was only found at a significant level above background in the grass at the 2.2 ft location (see Figure 3.53). Ni was not above background in soil. Cr was only above background concentrations in the roots at the 2.2 and 4.4 ft locations and in the grass at the 2.2 ft location (see Figure 3.50). Cr was not above background in soil. Zn was only above background concentrations in the roots at the 2.2 and 4.4 ft locations, and was not above background in any of the soil or grass samples (see Figure 3.55). This was in part due to high background Zn concentrations, which may be due to the presence of Zn in tap water used to water the bed (see Table 3.3). Fe being a common element was present at high levels in background samples and consequently not detected at concentrations above background in any samples (see Figure 3.52). In addition, average concentrations of Fe did not decrease along the length of the bed like all the other metals.

Table 3.3 Average Tap Water Concentrations

	Cd	Cr	Cu	Fe	Ni	Pb	Zn
On Site Average Tap Water Concentrations (ppb)	<5	<5	<9	84	<18	<43	16
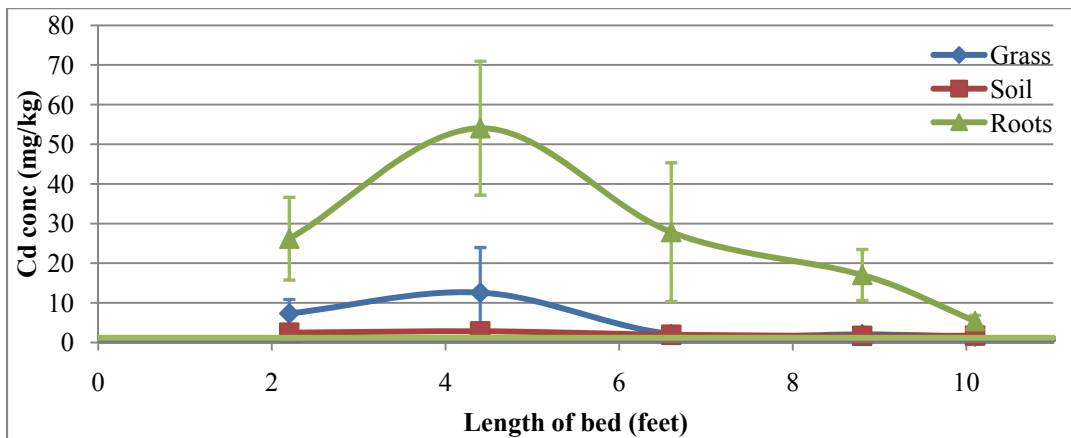
Figure 3.49: Concentration of Cd throughout Length of Bed
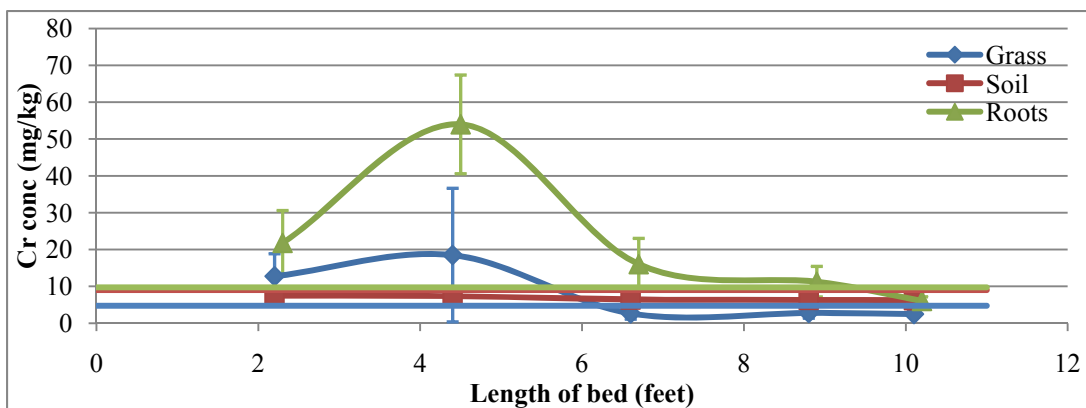
Figure 3.50: Concentration of Cr throughout Length of Bed
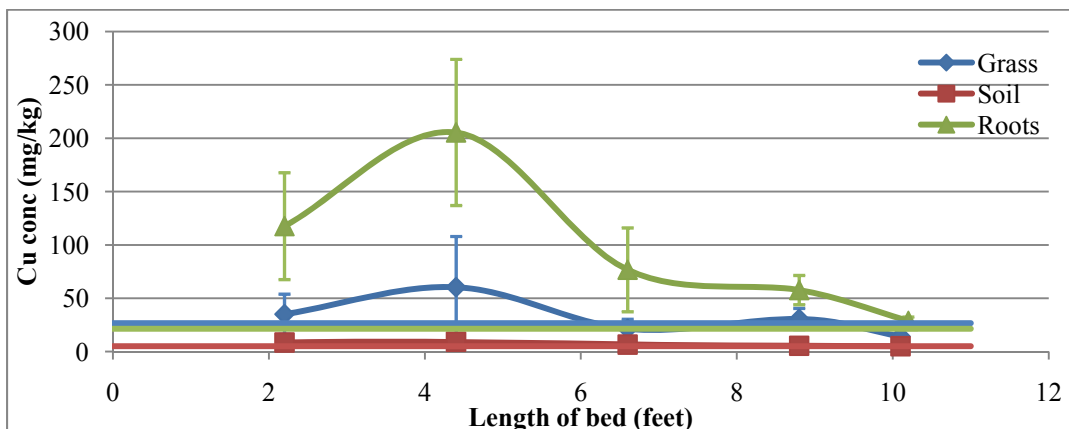
Figure 3.51: Concentration of Cu throughout Length of Bed
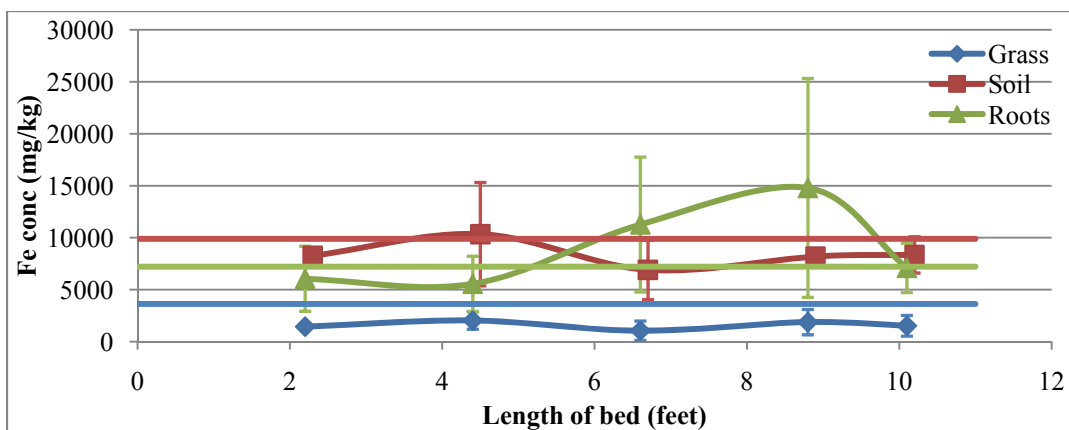
Figure 3.52: Concentration of Fe throughout Length of Bed
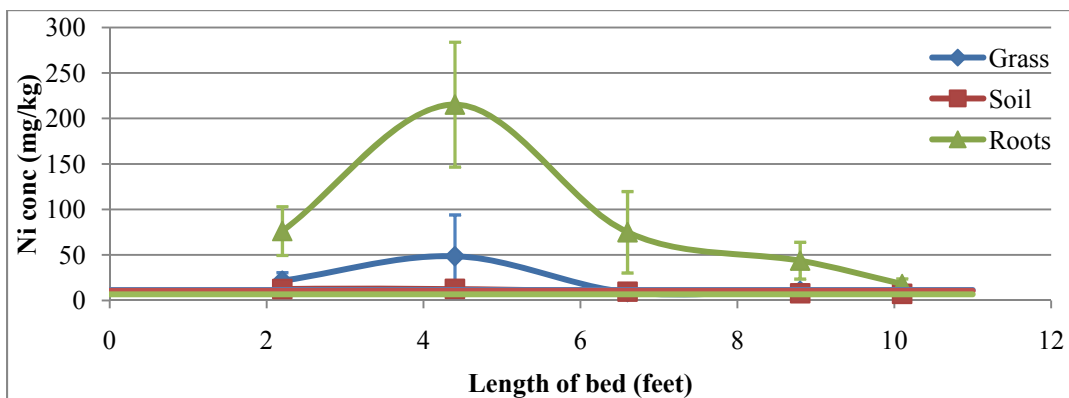
Figure 3.53: Concentration of Ni throughout Length of Bed
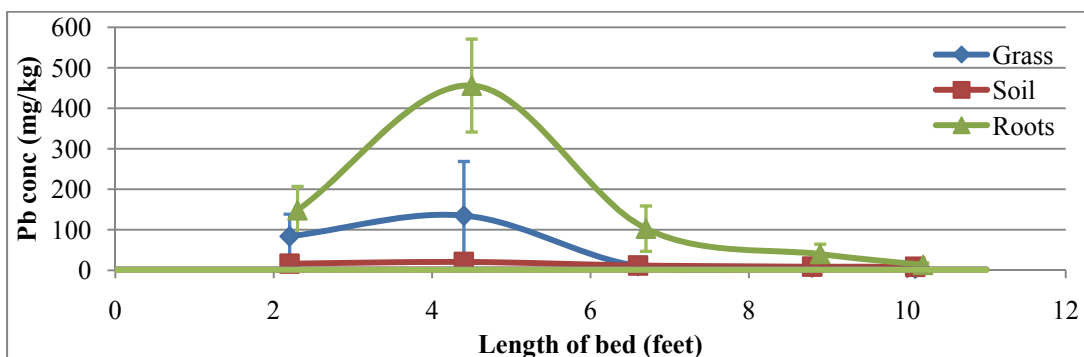
Figure 3.54: Concentration of Pb throughout Length of Bed
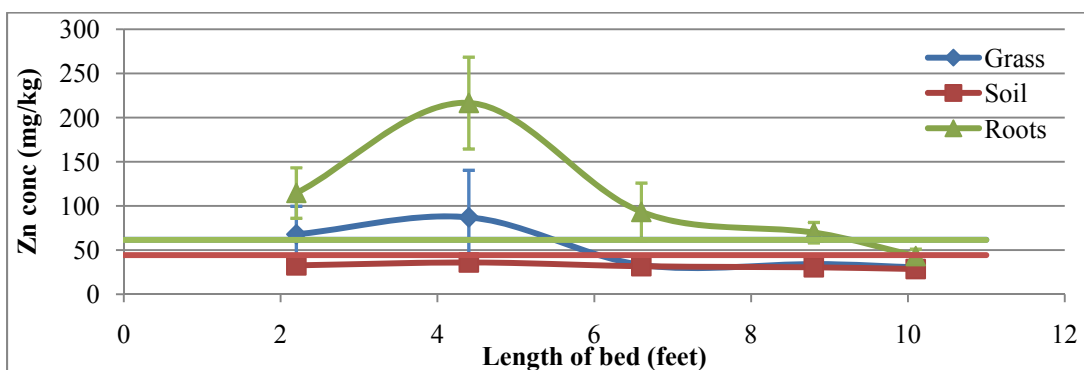
Figure 3.55: Concentration of Zn throughout Length of Bed

In the roots, every metal except Fe showed a statistically significant amount of accumulation along the length of the bed. Cd, Cu, Ni, and Pb accumulated significantly down the entire length of the bed. Cr and Zn only accumulated significantly at the 2.2 and 4.4 ft locations. Highest concentrations for all metals were found in the roots. Pb accumulated to the highest concentration of all the metals in the roots at 456 mg/kg, but Pb was also at the highest concentration in the influent water. As a fraction of the concentration in the roots to the concentration in the influent, Cu accumulated in the roots in the greatest proportion at 0.23, while the remaining metals accumulated in the proportion of 0.08 to 0.13.

In the grass, Cd, Cr, Ni, and Pb accumulated significantly in the tissues, but only in the upper portions of the bed for most of these, at concentrations much higher than seen in the soil. There are two explanations for the higher concentrations in vegetation than in the soil. It appears metals were taken up into the plant and concentrated in the tissues as an active mechanism. However, this is exaggerated by reporting concentrations in terms of dry mass. Because vegetation has a much higher moisture content than soil, metals are greater concentrated in vegetation than soil during drying compared with the native conditions. On average the moisture content of the root, grass, and soil samples from Bed 1 were 83.1%, 64.4%, and 10.5%. This was used to convert concentrations of mg/kg dry mass to mg/kg wet mass for the highest concentrations found in the bed (see Table 3.4). After correcting for this distortion, root concentrations were still significantly higher than soil concentrations for Cd, Cr, Cu, Ni, and Pb, but not for Zn. Because of high standard deviations in the grass concentrations, there was no significant difference for any of the metals concentrations between the grass and the roots and between the grass and the soil. Therefore, it is apparent that the vegetation preferentially took up the metals Cd, Cr, Cu, Ni, and Pb and concentrated them in their roots. Metals also accumulated in the tiller portion of the grass, although not at higher concentrations than seen in the soil.

Table 3.4: Maximum Core Concentrations in Bed 1 per Wet Mass

mg/kg dry mass						
	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
roots	54.1	54.0	205.4	215.2	456.2	216.6
grass	12.6	18.5	60.4	48.7	135.0	87.1
soil	2.8	7.4	9.3	12.7	20.7	35.9
mg/kg wet mass						
	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
root	9.2	9.1	34.8	36.4	77.2	36.7
grass	4.5	6.6	21.5	17.3	48.0	31.0
soil	2.5	6.6	8.3	11.3	18.5	32.1

In the soil, Cd, Cu, and Pb accumulated significantly at maximum concentrations

of 2.8, 9.3, and 20.7 mg/kg, but still an order of magnitude lower than concentrations

observed in vegetation. Again, Pb was found at the highest concentration, but it was also

at the highest concentration in the influent. As a fraction of the concentration in the soil

to the concentration in the influent, Cu accumulated in the greatest proportion at 0.011, as

it did in the roots, while Cd and Pb accumulated in the proportions of 0.0057 and 0.0038,

respectively. The low concentrations of metals in the soil compared to the vegetation

give the impression that the vegetation captured the majority of the metals. However,

concentrations are based on mass of contaminant per mass of media, and the total mass of

soil in the test bed greatly exceeds the mass of vegetation. A mass balance was

performed to determine the total mass of grass, roots, and soil in the bed. Extrapolating

the relative mass of soil, roots, and grass from the cores over the extent of the bed, and

assuming that the metals did not penetrate any deeper than the 2 in depth cores, the mass

of contaminants collected by each media fraction was computed (see Table 3.5). Metals

displaying a mass of zero in the table represent where their background metal

concentrations were higher than the concentrations in the media, therefore there was no

observable metal accumulation in this media. The majority of the metal mass was

concentrated in the roots of the grass for all metals except Pb for which a clear majority

of the mass accumulated in the soil.

Table 3.5: Estimated Mass of Metal Accumulated in Different Media over the Entire Bed

	Total in Top 2" of Bed (kg dry mass)	Cd (g)	Cr (g)	Cu (g)	Ni (g)	Pb (g)	Zn (g)
Grass	46.3	0.21	0.15	0.35	0.44	2.17	0
Roots	29.1	0.80	0.41	2.38	2.58	4.91	1.55
Soil	692	0.77	0	1.40	0	8.30	0

3.1.7 Analysis of Total Suspended Solids and Adsorbed Metals

Table 3.6 displays the average dissolved and adsorbed metal concentrations in

both the influent and effluent for bed 1 at a slope of 8:1. For metals that were not

detected, half of the detection limit was used when calculating adsorbed concentrations.

In the influent, every metal existed at a higher average concentration in the adsorbed

form than dissolved, except for Ni, which had an average dissolved concentration of

0.788 mg/L and an average adsorbed concentration of 0.574 mg/L; therefore, Ni was

predominantly in the dissolved form and may behave differently than the other metals. In

addition to Ni, Cd had nearly equal parts of dissolved and adsorbed concentrations in the

influent, with an average dissolved concentration of 0.108 mg/L and an average adsorbed

concentration of 0.170 mg/L, and Zn also was significant in the dissolved form at

0.139 mg/kg. In the effluent, no dissolved metals were detected.

When looking at percent removals from the 8:1 slope of each metal, Ni and Cd had some of lowest percent removals at 97.4% and 90.1%, which corresponds with each of these metals having higher dissolved concentrations in the influent. Cr, Cu, Fe, and Pb, which are all nearly entirely sorbed in the influent, have higher percent removals ranging from 97.2% to 99.4%. Zn also had the second lowest percent removal at 95.8%, with significant concentrations in the dissolved form, but still higher in the adsorbed form. When looking at the metals that sorbed to the soil versus those that were taken up into the plant (roots + grass) within the bed (see Table 3.5), Ni, Cd, and Zn, all with significant concentrations in the dissolved form, were predominantly taken up into the plant, with the highest mass accumulated in the roots. Cu and Pb, which had high average percent removals within the bed, were the metals with the most significant soil accumulation and were entirely sorbed in the influent. Clearly, metals with high dissolved fractions were predominantly removed from the stormwater by uptake into the plant, while metals that were highly sorbed were predominantly removed by settling of suspended matter. Cr was an exception to this behavior, because it was entirely sorbed, yet it did not accumulate above background concentrations in the soil. Also, though Cu accumulated significantly in the soil, a greater amount was also taken up into the roots. Fe accumulation could not be determined because Fe concentrations after testing were not statistically different than background concentrations.

Table 3.6: Influent and Effluent Average Dissolved and Adsorbed Metal Concentrations in Bed 1 at a Slope of 8:1

	Influent		Effluent	
	Average Dissolved Conc (mg/L)	Average Adsorbed Conc (mg/L)	Average Dissolved Conc (mg/L)	Average Adsorbed Conc (mg/L)
Cd	0.108	0.170	<0.002	0.007
Cr	<0.007	0.342	<0.007	<0.007
Cu	<0.009	0.519	<0.009	0.018
Fe	0.042	14.1	<0.003	0.401
Ni	0.788	0.574	<0.017	0.008
Pb	<0.055	2.658	<0.055	<0.055
Zn	0.139	1.068	<0.005	0.067
La	0.115	34.2	<0.007	0.186

The average adsorbed lanthanum concentrations and total suspended solids ratios in the influent and effluent were also compared to determine how much of the tagged suspended solids in the effluent originated from the influent. For the 8:1 slope of bed 1, the added suspended solids to the influent were tagged with lanthanum, so they could be traced going through the bed. The average adsorbed La/TSS ratio decreased considerably between the influent and effluent, at 73,700 in the influent and 12,900 in the effluent. Because of this decrease, influent suspended solids must have settled within the bed. Thus, 99.4% of the added TSS settled on the bed. This percentage was calculated by subtracting the effluent average adsorbed La concentration from the influent average adsorbed La concentration and dividing by influent average adsorbed La concentration times 100. This percentage can be compared with the overall EMC TSS % removal of 94.2% for the 8:1 slope of bed 1, which does not distinguish between influent TSS and the TSS eroded from the bed. In addition, 82.5% of the TSS in the effluent originated not from the influent, but eroded from the bed itself, which was calculated by subtracting the

effluent mg La adsorbed/kg TSS ratio from the influent mg La adsorbed/kg TSS ratio and

dividing by the influent mg La adsorbed/kg TSS ratio times 100.

There was near complete settling of the TSS on the bed, and Cr, Cu, Pb, and Fe,

which were all strongly sorbed in the influent, were captured within the bed by sorbing to

the TSS and then settling. Once these metals were settled within the bed, they were

available to be taken up by the grass and roots. Fe was not at concentrations in the grass

and roots above background concentrations, so uptake could not be identified. Cu and Pb

were two of the three metals that had significant concentrations within the bed soil (see

Table 3.5). Cd, Ni, and Zn, which were the only metals that had significant

concentrations in the dissolved form, were likely directly taken up by the roots and

leaves. This can further be confirmed, because Ni and Zn had no significant

accumulation in the bed soil, while Cd had some, but it was still less than the total mass

of the leaves and roots combined (see Table 3.5).

3.1.8   Chemical Fractionation Analysis

Contaminated soil samples I2 and I4 were collected from bed 1 where the

simulated stormwater initially hit the bed, following the set of high concentration

experiments. The top one inch of soil was used from each of the two cores, and

triplicates were conducted on each core. Blank soil samples conducted in triplicate were

obtained from the same soil used to fill the bed, but this soil was uncontaminated.

Results from the sequential extraction procedure gave the concentrations of Cd, Cr,

Cu, Fe, Ni, Pb, and Zn within each of the following soil fractions: water soluble (F1),

exchangeable (F2), carbonate (F3), Fe-Mn oxide (F4), and organic (F5). The water

soluble fraction deals with metals that can be leached out of the soil when water is present. Metals in this fraction are the most soluble, and most easily transported and bioavailable for plants because they are not strongly bound to the soil. The exchangeable fraction deals with metals that are adsorbed on the soil surface, and can easily be sorbed and desorbed, and therefore easily transported as well (Zerbe et al., 1999). The sorption-desorption process can be affected by changes in the ionic composition of water. The carbonate fraction deals with metals that are associated with sediment carbonates. This particular fraction is susceptible to pH changes in the water. Iron and manganese oxides are considered the reducible phase (Olajire et al., 2003), and exist as nodules within soil and can also coat soil. These oxides attract metals and scavenge them; however, under anoxic conditions they are considered thermodynamically unstable. Metals can be bound to different types of organic matter in soil, and under oxidizing conditions the organic matter can be degraded, thus releasing the soluble metals into the environment. However, metals within the organic fraction are least likely to become remobilized and bioavailable for plants. These fractions are related to solubility, and remobilization and thus transport decreases in the following order: water soluble > exchangeable > carbonate > Fe-Mn oxide > organic. Each figure displays the concentrations of each metal in the different fractions, where standard deviations are given for those triplicate samples where more than one was detected.

3.1.8.1 Cadmium

Cd was not detected in the blank soil samples for every fraction except the exchangeable fraction. Based on average concentrations, Cd was present at highest

concentrations in the organic fraction at 2.00 mg/kg for sample I4 with a high standard deviation, but was not detected in sample I2. The next highest Cd concentrations were in the exchangeable fraction at 0.63 mg/kg for sample I2 and 0.58 mg/kg for sample I4; however, these concentrations were not significant, because they were below a background concentration of 0.89 mg/kg (see Table 3.7). Cd concentrations were detected within the Fe-Mn oxide fraction, with concentrations of 0.42 mg/kg and 0.41 mg/kg, with lowest concentrations in the carbonate fraction.

Since Cd was only detected in one of the triplicate I4 samples and none of the I2 samples for the organic fraction, this concentration will not be considered. In addition, it has been found that Cd does not seem to form stable organic complexes (Olajire et al., 2003). Olajire et al. (2003) determined that in soil collected where metal contamination was from agricultural activities, industrial activities such as metal smelting, and domestic activities such as the disposal of waste, Cd was at the highest concentrations in the residual fraction, followed by the exchangeable and carbonate fractions. This proved that some of the Cd was bioavailable for plant uptake, since metals within the exchangeable and carbonate fractions are more easily remobilized than the residual fraction. Their results are similar to these results in that the highest concentration of Cd was present in the Fe-Mn oxide fraction, where Cd cannot become easily remobilized, followed by the carbonate fraction, where Cd has a higher bioavailability (see Figure 3.56). Cd is of serious environmental and health concern since it is a very hazardous and carcinogenic metal. Overall, Cd was associated with each fraction in the following order: Fe-Mn oxide > carbonate, eliminating the fractions where metal concentrations were

below blank concentrations. Cd was not detected in the water soluble fraction for any of

the soil samples.

Table 3.7: Cadmium Concentrations (Mean ± SD, n = 3) in each Geochemical Fraction of Two Contaminated Soils and One Uncontaminated Soil (blank)

	Samples		
	Blank	I2	I4
	mg/kg		
Water Soluble	<0.13	<0.13	<0.13
Exchangeable	0.89 ± 0.44	0.63 ± 0.08	0.58 ± 0.1
Carbonate	<0.13	0.34 ± 0.12	0.34 ± 0.09
Fe-Mn Oxide	<0.13	0.42 ± 0.11	0.41 ± 0.16
Organic	<0.13	<0.13	2.00 ± 1.08
Sum of all fractions	0.89	1.39	3.33

Figure 3.56: Average Cd concentrations associated with the five sequential fractions for all soil samples

3.1.8.2 Chromium

Cr was detected in the blank soil samples for every fraction except the water

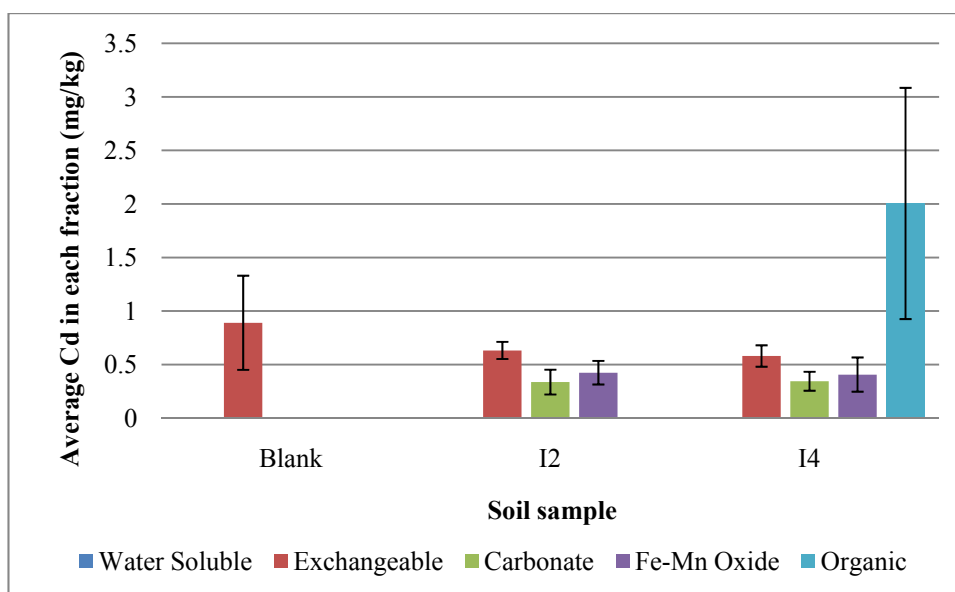soluble fraction. Based on average concentrations, Cr was highest in the organic fraction,

with statistically significant ($\alpha = 0.05$) concentrations of 2.99 mg/kg for sample I2 and

2.72 mg/kg for I4 (see Table 3.8). Cr was next highest in the Fe-Mn oxide fraction, with

statistically significant concentrations in samples I2 and I4. Cr concentrations in the

exchangeable and carbonate fractions for soil samples I2 and I4 were not statistically

significant. Cr was not detected in the water soluble fraction for any of the soil samples,

similar to Cd.

Figure 3.57 further displays how Cr was associated with each of the five fractions,

with the organic fraction clearly representing the highest concentration of Cr. Because Cr

was predominantly associated with the organic and Fe-Mn oxide fractions, its

bioavailability was lower than Cd, and can therefore not easily be taken up by plants or

remobilized from the soil. Overall, Cr was associated with each fraction in the following

order: organic > Fe-Mn oxide.

**Table 3.8: Chromium Concentrations (Mean ± SD, n = 3) in each Geochemical
Fraction of Two Contaminated Soils and One Uncontaminated Soil (blank)**

	Samples		
	Blank	**I2**	**I4**
	mg/kg		
Water Soluble	<0.07	<0.07	<0.07
Exchangeable	0.81 ± 0.13	0.77 ± 0.03	0.83 ± 0.14
Carbonate	0.35 ± 0.05	0.36 ± 0.12	0.30 ± 0.06
Fe-Mn Oxide	0.7 ± 0.05	1.05 ± 0.02	0.99 ± 0.1
Organic	1.6 ± 0.04	2.99 ± 0.19	2.72 ± 0.04
Sum of all fractions	3.46	5.17	4.84

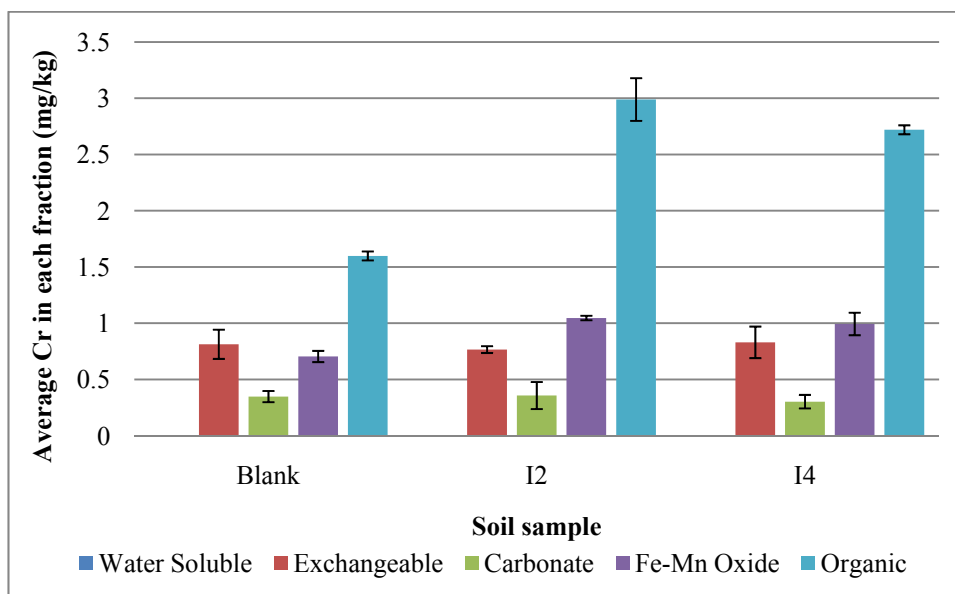**Figure 3.57: Average Cr concentrations associated with the five sequential fractions for all soil samples**

3.1.8.3 Copper

Unlike Cd and Cr, Cu was detected in the blank samples for every fraction. In the contaminated soil samples, Cu concentrations were well below blank Cu concentrations for every fraction (see Table 3.9). For the exchangeable fraction, Cu was not detected in any of the contaminated samples. Figure 3.58 further displays this, where blank Cu concentrations were higher than the contaminated soil samples for each fraction, but Cu in the contaminated samples was highest in the organic fraction.

This trend was different for the Olajire et al. (2003) sequential extraction procedure. They found the greatest amount of Cu to be in the residual fraction, followed by the organic and exchangeable fractions. Preciado and Li (2006) found Cu to be one of the most easily remobilized metals, with highest concentrations in the exchangeable fraction, and Tessier et al. (1979) also found Cu to have the highest concentrations in the

nonresidual fractions. It is possible that Cu was not detected in any fractions above

background because it could have already been taken up into the plant.

Table 3.9: Copper Concentrations (Mean ± SD, n = 3) in each Geochemical Fraction of Two Contaminated Soils and One Uncontaminated Soil (blank)

	Samples		
	Blank	**I2**	**I4**
	mg/kg		
Water Soluble	0.32 ± 0.07	0.15 ± 0.02	0.13 ± .02
Exchangeable	0.38 ± 0.02	<0.04	<0.04
Carbonate	3.32 ± 0.03	0.62 ± 0.07	0.61 ± 0.04
Fe-Mn Oxide	2.56 ± 0.26	1.23 ± 0.06	1.14 ± 0.09
Organic	11.5 ± 2.64	9.87 ± 0.53	10.5 ± 0.85
Sum of all fractions	18.08	11.87	12.38

Figure 3.58: Average Cu concentrations associated with the five sequential fractions for all soil samples
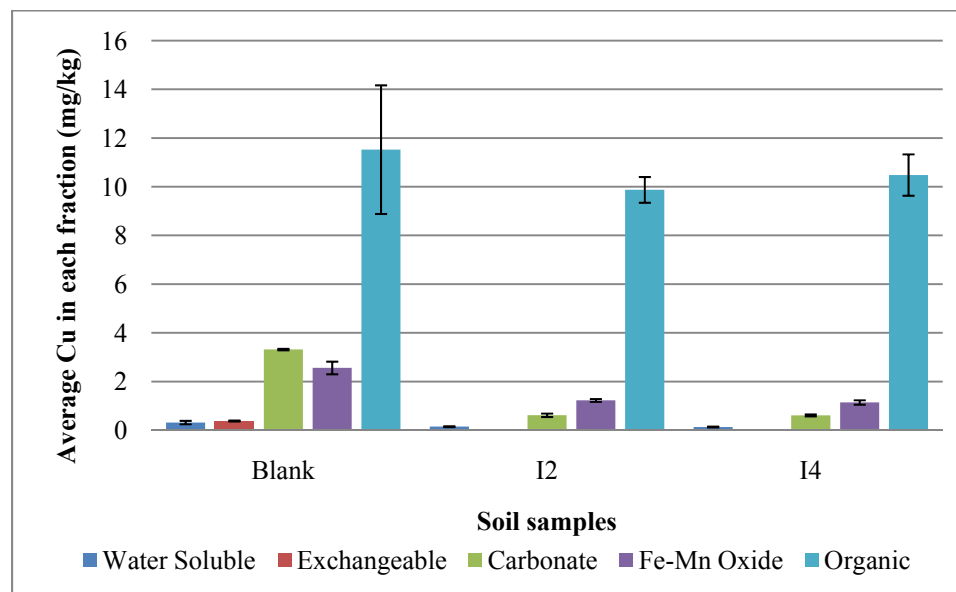
3.1.8.4 Iron

Fe was detected in the blank soil samples for every fraction, similar to Cu. Fe in the contaminated soils was not detected above the average blank concentration of 0.42 mg/kg and 14.2 mg/kg for the exchangeable and carbonate fractions (see Table 3.10). Average Fe concentrations were highest in the Fe-Mn oxide fraction, at 1705 mg/kg for I2 and 1688 mg/kg for I4, above the blank concentration of 1505 mg/kg. Average Fe concentrations were next highest in the organic fraction, at 773 mg/kg for I2 and 876 mg/kg for I4, above the blank concentration of 653 mg/kg. Average Fe concentrations were lowest in the water soluble fraction, at 2.95 mg/kg for I2 and 3.06 for I4, above the blank concentration of 1.03 mg/kg, and cannot be seen in Figure 3.59 since the concentrations are much lower than the other fractions.

The sequential extraction results from Preciado and Li (2006) corresponded to these results, where Fe concentrations were highest in the Fe-Mn oxide fraction. Because Fe concentrations were highest in the Fe-Mn oxide fraction and organic fraction, the bioavailability and remobilization of this metal will be low. The low Fe concentrations in the water soluble fraction of the contaminated soil samples were higher than the blank samples; therefore, a low concentration of Fe could become remobilized, since the water soluble fraction is considered the most bioavailable fraction. Overall, Fe was associated with each fraction in the following order: Fe-Mn oxide > organic > water soluble.

Table 3.10: Iron Concentrations (Mean ± SD, n = 3) in each Geochemical Fraction of Two Contaminated Soils and One Uncontaminated Soil (blank)

	Samples		
	Blank	**I2**	**I4**
	mg/kg		
Water Soluble	1.03 ± 0.08	2.95 ± 0.35	3.06 ± 0.23
Exchangeable	0.42 ± 0.03	0.31 ± 0.10	0.43 ± 0.06
Carbonate	14.2 ± 0.92	4.96 ± 1.94	4.32 ± 0.24
Fe-Mn Oxide	1505 ± 70.1	1705 ± 57.2	1688 ± 12.2
Organic	653 ± 10.7	773 ± 51.9	876 ± 196
Sum of all fractions	2173.65	2486.22	2571.81
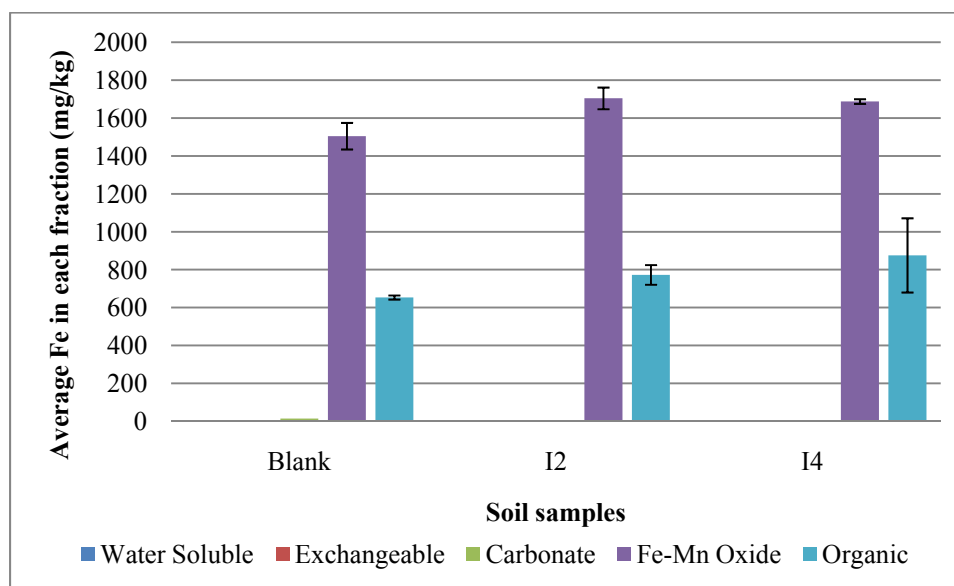
Figure 3.59: Average Fe concentrations associated with the five sequential fractions for all soil samples

3.1.8.5 Nickel

Ni was detected in the blank soil samples for every fraction, similar to Cu and Fe. Average Ni concentrations in the contaminated soils were not significantly different than the average blank concentrations for the water soluble fraction. In the exchangeable

fraction, Ni concentrations in the contaminated soils were on average below the blank concentrations (see Table 3.11).

Average Ni concentrations were highest in the Fe-Mn oxide fraction for I2 at 3.47 mg/kg, and in the organic fraction for I4 at 3.36 mg/kg, at statistically significant values (see Figure 3.60). Average Ni concentrations were next highest in the organic fraction for I2 at 3.18 mg/kg and in the Fe-Mn oxide fraction for I4 at 3.00 mg/kg, followed by the carbonate fraction, which was not statistically significant.

In the nonresidual fraction, Olajire et al. (2003) found the highest Ni concentrations in the exchangeable fraction, followed by the carbonate fraction, which differed from these results, because Ni concentrations in the contaminated samples were not above blank concentrations for the exchangeable fraction. Both Olajire et al. (2003) and Tessier at al. (1979) found Ni concentrations be highest in the residual fraction. Since Ni concentrations were highest in the Fe-Mn oxide and organic fractions, Ni is less likely to become remobilized and become bioavailable for plant uptake; however a low concentration could become remobilized since Ni concentrations were above blank concentrations for the water soluble and carbonate fractions. Overall, Ni was associated with each fraction in the following order for I2: Fe-Mn oxide > organic > carbonate, and for I4: organic > Fe-Mn oxide.

Table 3.11: Nickel Concentrations (Mean ± SD, n = 3) in each Geochemical Fraction of Two Contaminated Soils and One Uncontaminated Soil (blank)

	Samples		
	Blank	**I2**	**I4**
	mg/kg		
Water Soluble	0.44 ± 0.13	0.50 ± 0.16	0.47 ± 0.14
Exchangeable	1.87 ± 0.74	1.11 ± 0.41	1.25 ± 0.64
Carbonate	0.88 ± 0.39	1.62 ± 0.30	1.19 ± 0.23
Fe-Mn Oxide	0.88 ± 0.08	3.47 ± 0.27	3.00 ± 0.37
Organic	2.34 ± 0.11	3.18 ± 0.46	3.36 ± 0.33
Sum of all fractions	6.41	9.88	9.27
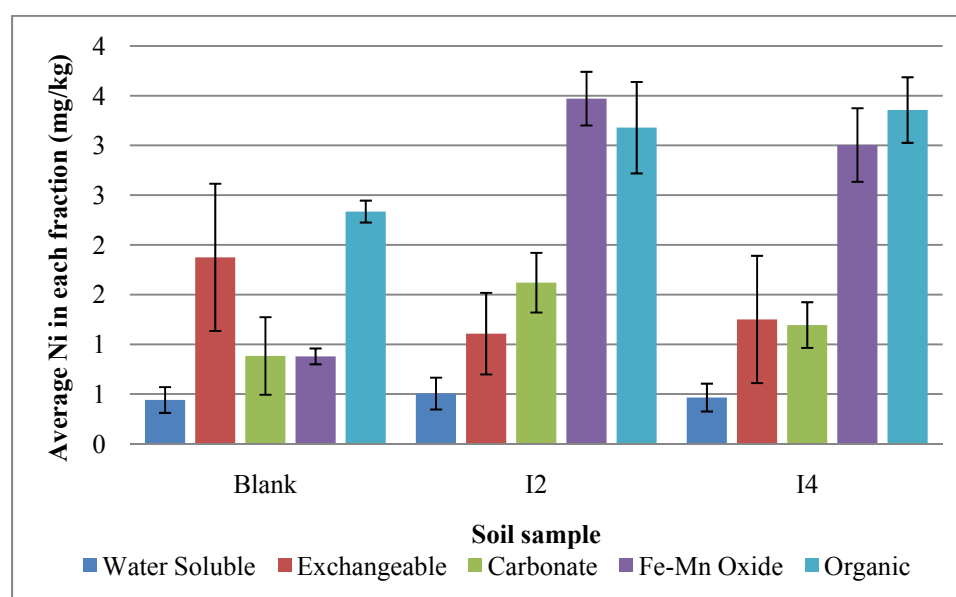
Figure 3.60: Average Ni concentrations associated with the five sequential fractions for all soil samples

3.1.8.6 Lead

Pb was detected in the blank soil samples for every fraction except the water soluble and organic fractions. In the water soluble fraction, Pb was also not detected in any of the contaminated soil samples. In the exchangeable fraction, average Pb

concentrations in the contaminated samples were not significantly different than the blank Pb concentrations.

Average Pb concentrations were highest in the Fe-Mn oxide fraction, at 8.08 mg/kg for I2 and 7.84 mg/kg for I4, followed by the organic fraction, with concentrations of 5.64 mg/kg for I2 and 4.92 mg/kg for I4 (see Table 3.12). The next highest Pb concentrations were in the carbonate fraction followed by the exchangeable fraction for I2, and the exchangeable fraction followed by the carbonate fraction for I4, however these concentrations were not significantly different from average blank concentrations for I4 (see Figure 3.61). Interestingly, Pb was not found at all in the organic fraction in the blank sample.

Olajire et al. (2003) found that Pb was primarily concentrated in the exchangeable fraction, and could easily become remobilized. These results were not similar to this study, because the highest Pb concentrations were found in the Fe-Mn oxide and organic fractions, and would therefore not easily become remobilized and bioavailable for plant uptake. Pb had a significant difference between the average blank concentrations for the exchangeable and carbonate fractions for I2 and not I4, and therefore a small amount of Pb could potentially become remobilized. Preciado and Li (2006) reported similar results, with Pb concentrations highest in the exchangeable and carbonate fractions. However, Turer and Maynard (2003) found that Pb was mostly related to the Fe-Mn oxide fraction of the soil, secondly to the carbonate fraction, and finally to the organic fraction, which is similar to the results of this study. Overall, Pb was associated with each fraction in the following order for this study:

Fe-Mn oxide > organic > carbonate > exchangeable for I2 and Fe-Mn oxide > organic for

I4, where Pb will most likely not become remobilized because of the high Pb

concentrations in the Fe-Mn oxide and organic fractions.

Table 3.12: Lead Concentrations (Mean ± SD, n = 3) in each Geochemical Fraction of Two Contaminated Soils and One Uncontaminated Soil (blank)

	Samples		
	Blank	**I2**	**I4**
	mg/kg		
Water Soluble	<0.81	<0.81	<0.81
Exchangeable	3.12 ± 1.34	3.27 ± 1.42	3.43 ± 1.64
Carbonate	2.25 ± 0.90	4.05 ± 0.53	2.79 ± 0.54
Fe-Mn Oxide	4.31 ± 0.73	8.08 ± 1.34	7.84 ± 2.14
Organic	<0.81	5.64 ± 1.30	4.92 ± 0.52
Sum of all fractions	9.68	21.04	18.98
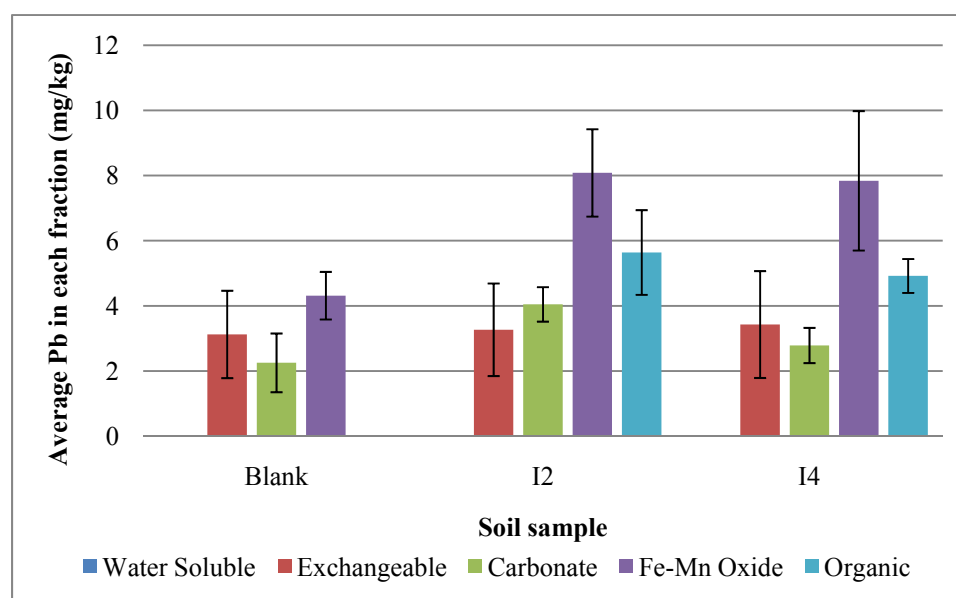
Figure 3.61: Average Pb concentrations associated with the five sequential fractions for all soil samples

3.1.8.7 Zinc

Zn was detected in the blank soil samples for every fraction except the water soluble fraction. Average blank Zn concentrations of 0.82 mg/kg and 0.62 mg/kg for the exchangeable and carbonate fractions were higher than the average Pb concentrations for the contaminated samples. Average Zn concentrations were highest in the Fe-Mn oxide fraction with concentrations of 3.20 mg/kg for I2 and 3.92 mg/kg for I4, similar to Fe, Ni, and Pb, followed by the organic fraction (see Table 3.13).

Olajire et al. (2003) found the highest Zn concentrations in the organic and residual fractions, followed by the exchangeable and Fe-Mn oxide fractions. Turer and Maynard (2003) found that Zn was mostly related to the iron and manganese oxide fraction of the soil, secondly to the carbonate fraction, and finally to the organic fraction. Preciado and Li (2006) also found the highest concentrations of Zn in the Fe-Mn oxide fraction, followed by the organic fraction, identical to the results of this study. Overall, Zn was associated with each fraction in the following order for this study: Fe-Mn oxide > organic (see Figure 3.62). Because Zn is at highest concentrations in these fractions, it is less likely to become remobilized.

Table 3.13: Zinc Concentrations (Mean ± SD, n = 3) in each Geochemical Fraction of Two Contaminated Soils and One Uncontaminated Soil (blank)

	Samples		
	Blank	**I2**	**I4**
	mg/kg		
Water Soluble	N.D.	N.D.	N.D.
Exchangeable	0.82 ± 0.43	0.17 ± 0.09	0.31 ± 0.13
Carbonate	0.62 ± 0.02	0.39 ± 0.15	0.43 ± 0.09
Fe-Mn Oxide	2.16 ± 0.05	3.20 ± 0.13	3.92 ± 0.13
Organic	1.18 ± 0.03	1.57 ± 0.09	1.61 ± 0.12
Sum of all fractions	4.78	5.33	6.27

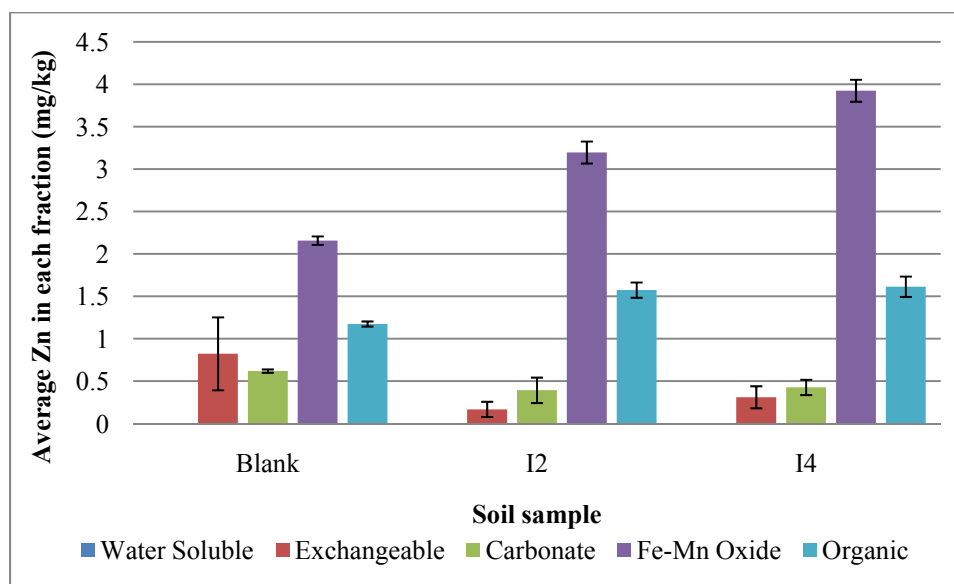**Figure 3.62: Average Zn concentrations associated with the five sequential fractions for all soil samples**

Overall, the majority of these metals existed in the fractions that would not easily remobilize the metals. Out of each of the metals, the Fe-Mn oxide fraction contained the highest metal concentrations for Fe, Ni, Pb, and Zn, followed by the organic fraction. For Cd and Cr, the organic fraction contained the highest concentration of these metals,

followed by the Fe-Mn oxide fraction. Cu was unusual, because none of the fractions in the contaminated soil samples had concentrations above the blank soil samples. Fe was the only metal that had concentrations above the blank soil samples in the water soluble fraction, even though it was at the lowest concentration. In general, the order of contamination was Fe > Pb > Ni > Zn > Cr > Cd > Cu. Since the Fe-Mn oxide and organic fractions contained the highest concentrations of every metal except Cu in the nonresidual fraction of the soil, these metals will less likely become remobilized, than if they were predominantly in the exchangeable and carbonate fractions. This is most important for Pb and Cd, which significantly accumulated in the bed soil.

3.2   Low Concentration Experiments

In this series of tests, a low concentration of contaminants, as described in Table 3.14 was delivered to a different bed during an initial first flush period, followed by a longer flow period with tap water and a lower flow rate. The low concentration experiments more accurately represent actual highway stormwater runoff, which is why they were discussed in addition to the high concentration experiments. The low concentrations used for these tests represent the lower 95% confidence interval for the contaminants reported in the literature for the roadway runoff, although several were elevated above detection limits. A total of four tests were conducted which included the following: 1) an 8:1 slope (7.13°) with a medium flow rate, 2) a 4:1 slope (14.0°) with a medium flow rate, 3) a 2:1 slope (26.6 °) with a medium flow rate, and 4) a 2:1 slope (26.6 °) with a high flow rate. The medium flow simulation used an initial flow rate of 3.99 gpm for 15 min followed by a flow rate of 1.11 gpm for 45 min. The high flow

simulation used an initial flow rate of 5.54 gpm for 6 min followed by a flow rate of 1.20

gpm for 24 min.

**Table 3.14: Low Simulated Stormwater Concentrations and Tap Water
Concentrations**

	Low Concentration (µg/L)	Tap Water (µg/L)
Cd	20	5
Cr	25	5
Cu	35	9
Fe	250	84
Ni	95	18
Pb	215	43
Zn	10	16
	Low Concentration (mg/L)	
TSS	9	0

3.2.1   Suspended Solids Results

Figure 3.63 through Figure 3.66 depict the suspended solids concentrations for the

four low concentration tests. The solid lines represent the average concentration of the

samples collected for the first flush of the test, followed by the average concentration of

the samples collected for the tail end of the test. Sieved soil (<0.841 mm) was mixed

with two influent vessels at target concentrations of 9 mg/L for the initial low

concentration flow of 3.99 gpm and no soil was added in the second influent vessel and

used clean water with a lower flow rate of 1.11 gpm. Actual concentrations measured in

the influent flow as it sprayed onto the distributor plate for the low concentration portion

of the tests varied greatly from the target concentration on more than one occasion;

however, the average influent concentrations for a few of tests were relatively close to the
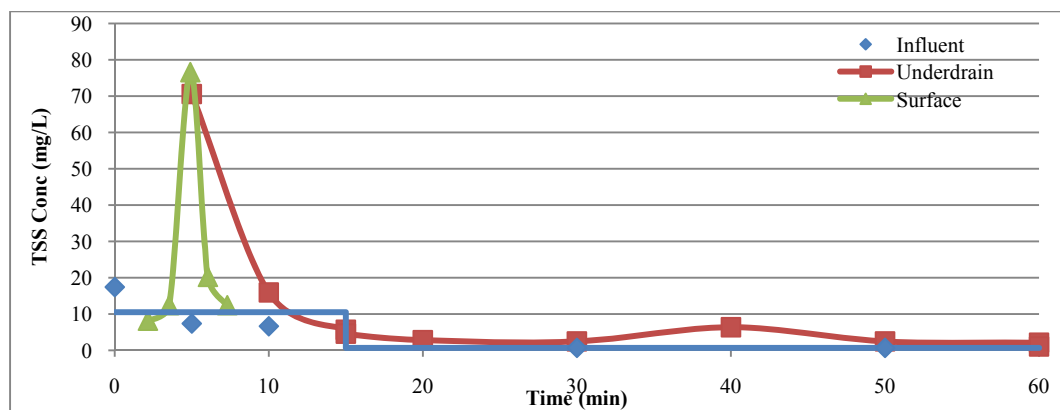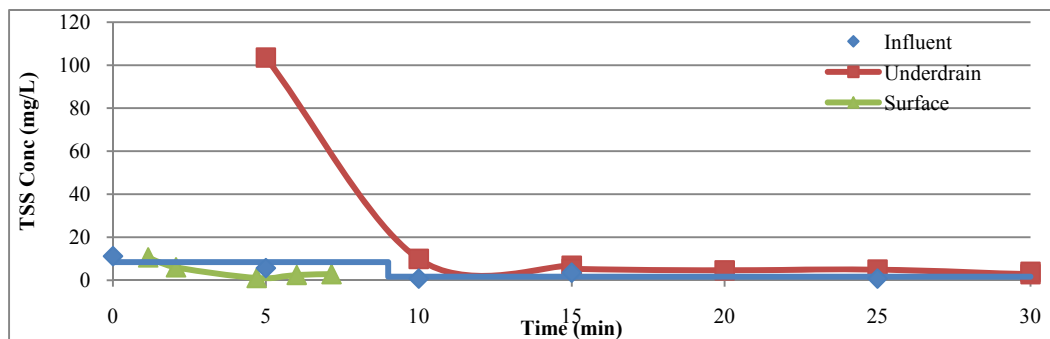target concentration of 9 mg/L.
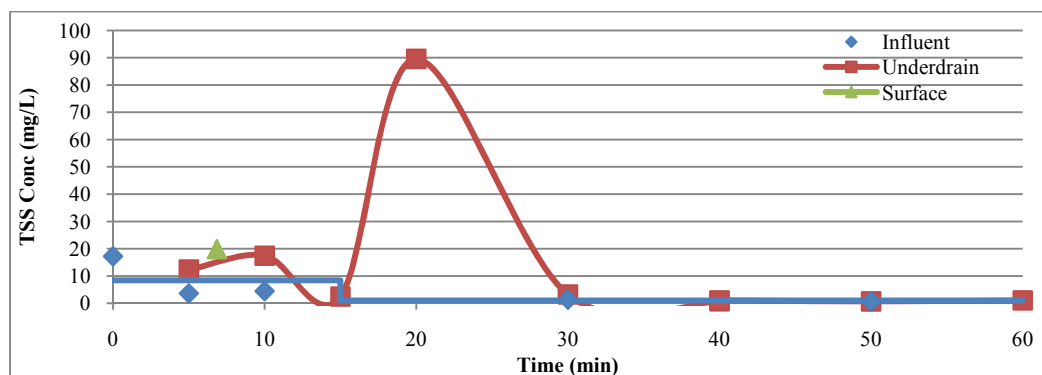
Figure 3.63 Concentration of suspended solids in 8:1 slope, medium flow rate
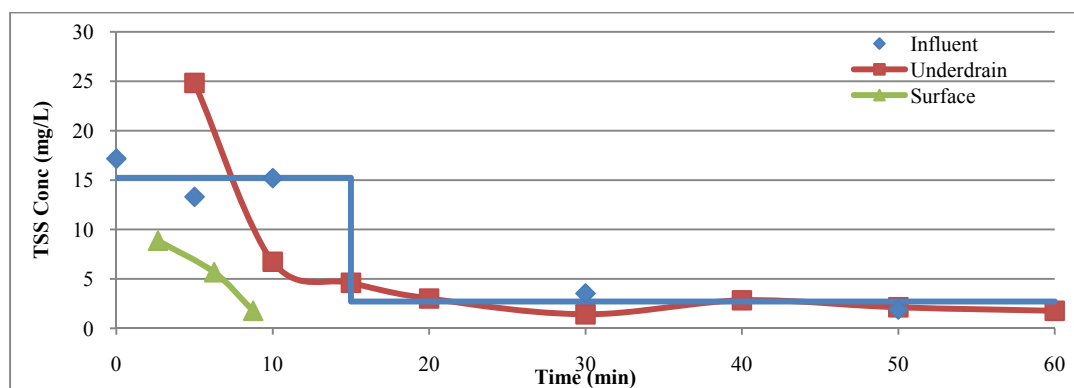
Figure 3.64 Concentration of suspended solids in 4:1 slope, medium flow rate

Figure 3.65 Concentration of suspended solids in 2:1 slope, medium flow rate

Figure 3.66 Concentration of suspended solids in 2:1 slope, high flow rate

For the low concentration test with a medium flow, influent concentrations averaged 8 mg/L, 15 mg/L, 11 mg/L, and 8 mg/L. The 8:1 medium flow test and 2:1 high flow test were within a 15% margin of the target concentration of 9 mg/L. However, the 4:1 and 2:1 medium flow tests were only within a very poor margin of the target concentration. Suspended solids concentrations decreased during the lower flow rate for the tailing 45 min for the first three tests and 21 min for the last test, and averaged 1 mg/L, 3 mg/L, 0.7 mg/L, and 2 mg/L.

For the first three medium flow tests, surface runoff was only generated during the first 15 min of the test. Once the concentration and flow decreased for the tailing 45 min, all the water delivered to the bed infiltrated and no surface samples could be collected. Sediment concentrations in the surface runoff exhibited unusual trends for each test. For each of the tests except the 4:1 medium flow test, a few of the surface sediment concentrations were higher than the influent sediment concentrations. For example, the 8:1 medium flow test had a single surface sediment concentration of 20 mg/L, which was well above the average influent concentration of 8 mg/L for the first

flush portion of the test. This higher suspended sediment concentration in the surface was from additional sediment eroding from the bed itself. The 2:1 medium flow test had a very large spike in sediment concentration at around 5 min. The surface samples collected around 6 and 7 min also had sediment concentrations above the influent sediment concentrations. The 4:1 medium flow test was unlike the other two, and each of the 3 surface sediment samples had decreasing concentrations that were below the influent. The 2:1 high flow run did not generate more TSS in the surface runoff, which was not consistent with bed 1. The first collected sample had a sediment concentration slightly above the influent average of 8 mg/L at 11 mg/L. The other four collected samples had sediment concentrations slightly below the influent average. Baseline suspended solids concentrations averaged 7 mg/L, which was slightly below the average surface suspended solids concentration for each slope and test. It appears that when utilizing the low concentration simulated stormwater runoff, sediment concentrations do not differ greatly between slopes. When accumulated over the entire storm, the percent removals of the event mean concentration were 50.4% for the 8:1 test, 26.9% for the 4:1 test, and 16.7% for the 2:1 high flow test. The percent removals for the 2:1 medium flow test could not be computed because influent suspended solids concentrations were much lower than the surface concentrations, and percent removals were negative. Based on the other tests, an increase in slope caused percent removals to gradually decrease.

In addition to collecting surface samples, groundwater samples were also collected from the underdrain. The underdrain sediment concentrations exhibited slightly similar trends to the surface sediment concentrations because the majority of the collected

underdrain samples had sediment concentrations above the influent sediment concentrations. For the first 15 min of the 8:1 medium flow test, the first two sediment samples test were above the average influent concentration of 8 mg/L at 12 mg/L and 17 mg/L. The third sediment sample was below the average influent concentration at 2 mg/L. For the tail end portion of the test, the sediment sample collected at 20 min had an unusually large spike in sediment concentration at 90 mg/L, but the other collected samples had low sediment concentrations that were around the influent average of 1 mg/L. The other three tests had similar sediment concentration trends. For example, the sample collected at 5 min had a large spike in sediment concentration for all three tests at 25 mg/L, 71 mg/L, and 104 mg/L. As the slopes increased, this spike in concentration also increased. It is possible that an increase in slope causes more sediment to be released from the bed, as seen from the percent removals. The other sediment samples gradually decreased in concentration, and were slightly above the tail end average influent concentrations, except the tail end portion of the 4:1 medium flow test, which had sediment concentrations that were slightly below the average influent concentration of 3 mg/L. Baseline underdrain suspended solids concentrations averaged 11 mg/L, which is only slightly lower for the 8:1 test and 2:1 medium and high flow tests; however, this concentration is higher than the 4:1 medium flow test when compared with average underdrain concentrations for each test.

3.2.2   Total Metals Results

Total metals were determined by ICP-OES analysis following acid digestion. These samples were not filtered prior to digestion, and results represent the combined

total of metals dissolved in the water and sorbed to suspended solids. Table 3.14 displays

the low target concentrations of simulated stormwater runoff and tap water

concentrations. For the medium flow rate test with an 8:1 slope, total metals

concentrations are displayed in Figure 3.67 through Figure 3.73. Measured influent

concentrations for Cd, Cr, Ni, and Pb were somewhat lower than the target concentrations

for the first flush portion of the test. For example, the low target concentration for Cd

was 20 μg/L, and the average measured influent concentration was 9 μg/L. Cu, Fe, and

Zn had higher measured influent concentrations than the target concentrations. For

example, the low target concentration for Cu was 35 μg/L, and the averaged measured

influent concentration was 84 μg/L. For the remaining 45 minutes of the test, measured

influent concentrations were not detected for Cd, Cr, Ni, and Pb, but were for Cu, Fe, and

Zn. Zn exhibited very high influent concentrations throughout the duration of the test,

and most likely arose from high concentrations of Zn in the tap water. Cr, Ni, and Pb

were within a 40% margin of the target values, while Cd was within a 60% margin of the

target values. Overall, the influent concentrations remained fairly constant over time for

every metal despite their differences from the target concentrations.

Collected surface runoff was only generated for the first 15 min during the initial

higher flow rate of the 8:1 medium flow test. Each of the metals except Fe and Zn were

not detected in the surface runoff sample, with the following detection limits for Cd, Cr,

Cu, Ni, and Pb: 8 μg/L, 6 μg/L, 12 μg/L, 18 μg/L, and 77 μg/L. Fe remained below

200 μg/L, while Zn remained below 50 μg/L. In the surface baseline samples, none of

the metals were detected except Fe and Zn, with concentrations below 135 μg/L and

40 µg/L, respectively. EMC percent removals for Cd, Cr, Cu, Fe, Ni, Pb, and Zn were as

follows: 66.3, 85.4, 94.7, 40.4, 87.3, 77.8, and 69.8. In the 8:1 slope test, Cu and Ni had

the highest percent removals out of the metals. Underdrain samples also had every metal

not detected except Fe and Zn, with the same detection limits as the surface samples. Fe

remained below 420 µg/L, while Zn remained below 90 µg/L. Figure 3.70 shows an

initial spike in Fe concentration, with all the other samples above the influent

concentrations. Figure 3.73 has very erratic Zn concentrations in the underdrain samples,

and some are above and below influent concentrations. In the underdrain baseline

samples, each metal was not detected except for Fe and Zn, with concentrations below

500 µg/L and 35 µg/L. Zn baseline concentrations remained below the experimental

underdrain concentrations, but Fe had higher baseline concentrations, which means that

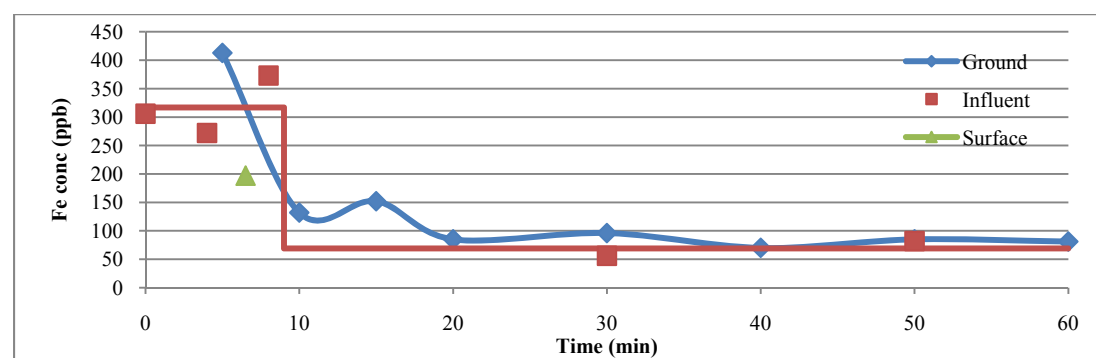Fe occurs in naturally high concentrations in the tap water or soil.
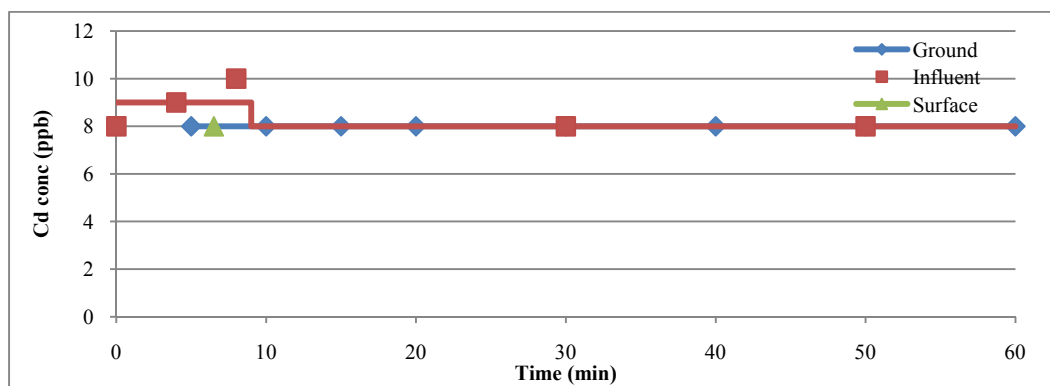
Figure 3.67 Total concentration of cadmium in 8:1 slope, medium flow rate
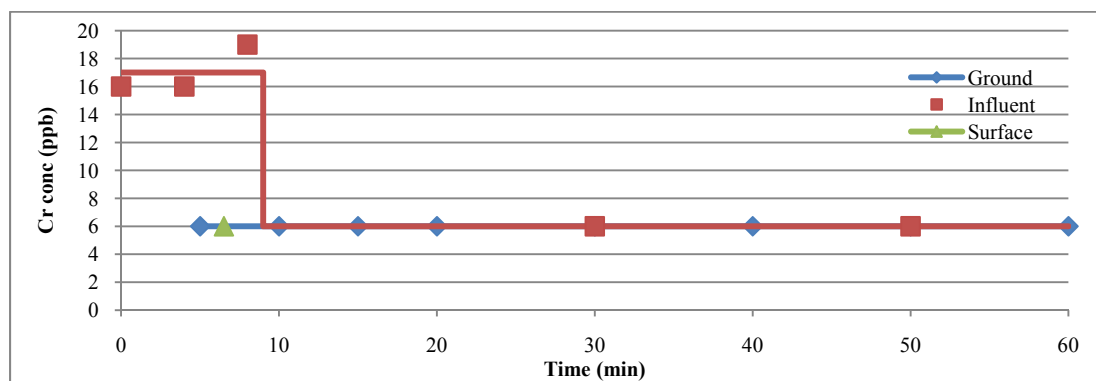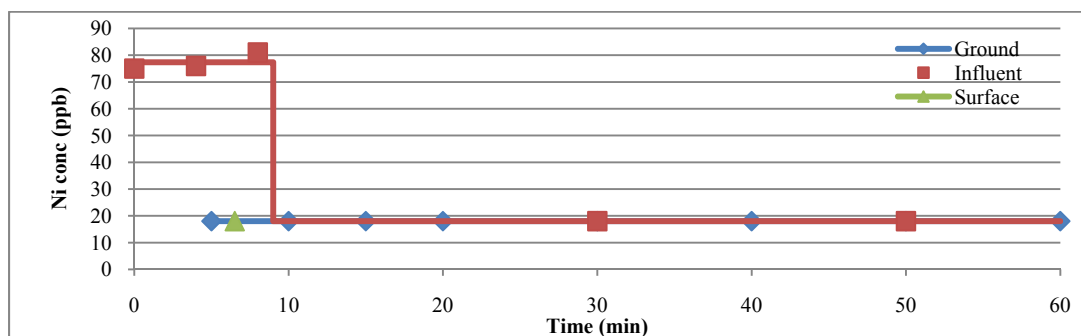
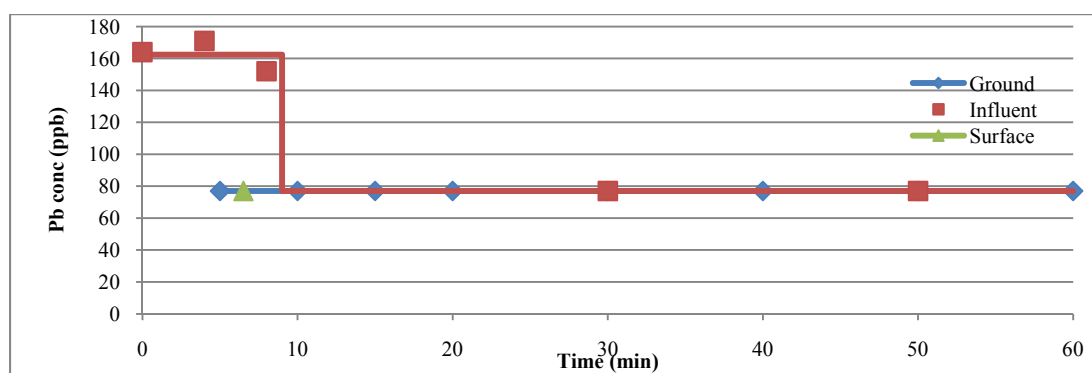**Figure 3.68 Total concentration of chromium in 8:1 slope, medium flow rate**
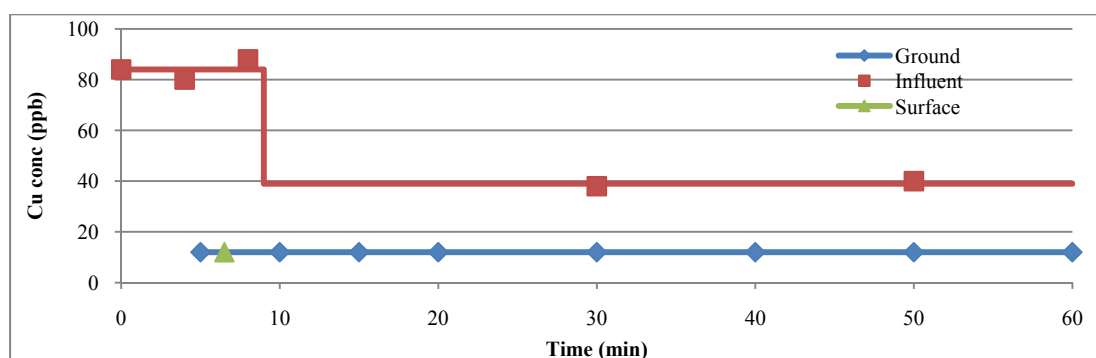
Figure 3.69 Total concentration of copper in 8:1 slope, medium flow rate

Figure 3.70 Total concentration of iron in 8:1 slope, medium flow rate

Figure 3.71 Total concentration of nickel in 8:1 slope, medium flow rate

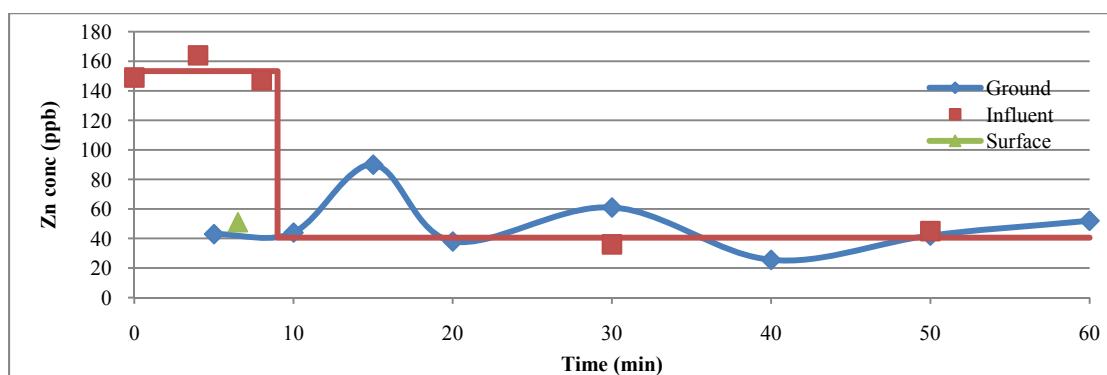**Figure 3.72   Total concentration of lead in 8:1 slope, medium flow rate**

Figure 3.73 Total concentration of zinc in 8:1 slope, medium flow rate

For the medium flow rate test with a 4:1 slope, total metals concentrations are displayed in Figure 3.74 through Figure 3.80. When compared with the 8:1 slope test, the influent metal concentrations vary slightly. Unlike the 8:1 slope, Cr was not detected

in the influent for the entire duration of the test with an average detection limit of 17 μg/L. Similar to the 8:1 slope, Cd and Pb had initial influent concentrations that were slightly lower than the low target concentrations; except for this slope Ni had influent concentrations higher than low target concentrations. Cu, Fe, and Zn also had higher influent concentrations than the low target concentrations. For the first flush portion of the test, the influent concentrations were erratic and not consistent, particularly for Cu, Ni, Pb, and Zn. For Cd and Pb, which had slightly lower average influent concentrations than the low target concentrations, were within a 27% and 16% margin of the low target concentrations. The tailing portion of the test had very consistent influent metal concentrations, where Cd, Cr, and Ni were not detected with average detection limits of 9 μg/L, 11 μg/L, and 27 μg/L respectively.

The surface and underdrain samples exhibited slightly different trends than the 8:1 slope test, but the surface runoff was still only generated during the first flush period of the test. In the surface runoff, the only metals that were not detected throughout the entire test were Cd, Cr, and Cu with average detection limits of 9 μg/L, 13 μg/L, and 8 μg/L respectively. Ni and Pb were not detected for the first 6 min of the test, with average detection limits of 27 μg/L and 79 μg/L. Zn was not detected at around 2 min with a detection limit of 6 μg/L. At around 8 min, Ni was detected below 65 μg/L, while Pb was detected below 140 μg/L. From 6 to 9 min when the surface runoff stopped, Zn was detected below 50 μg/L. Fe was the only metal detected below 130 μg/L throughout the duration of the surface runoff. Similar to the 8:1 test, the baseline surface sample concentrations were not detected for each metal except Fe and Zn. These baseline

concentrations were higher for Fe, and only slightly lower for Zn. Percent removals for Cd, Cu, Fe, Ni, Pb, and Zn were as follows: 53.5, 91.3, 57.6, 62.8, 55.2, and 75.1. Cr was not included in the percent removals because influent concentrations were not detected. Cu and Zn had the highest percent removals out of all the metals. When comparing the 8:1 and 4:1 slope tests, Ni and Pb had a significant drop in percent removals, but the rest of the metals remained about the same.

In the underdrain, Cd, Cr, Cu, and Pb were the only metals that were not detected throughout the entire test with average detection limits 9 μg/L, 14 μg/L, and 5 μg/L respectively. Ni was not detected throughout the entire test with an average detection limit of 32 μg/L, except at 20 min when it was detected at 57 μg/L. Zn was mostly detected throughout the entire test below 95 μg/L, but was not detected from 15 to 20 min with a detection limit of 6 μg/L. Similar to the 8:1 test, Figure 3.77 had an initial spike in Fe concentration, and then gradually decreasing with concentrations mostly above influent concentrations. Zn had tail end underdrain concentrations below influent concentrations. In the baseline samples, concentrations of Fe and Zn were the only detected metals, and these concentrations were above the experimental underdrain concentrations, which further prove that Fe and Zn occur naturally in high concentrations in the tap water or soil.
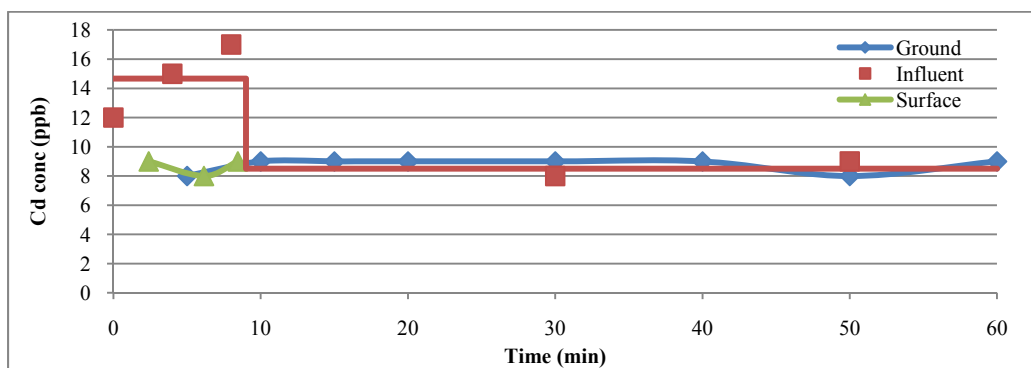
Figure 3.74 Total concentration of cadmium in 4:1 slope, medium flow rate

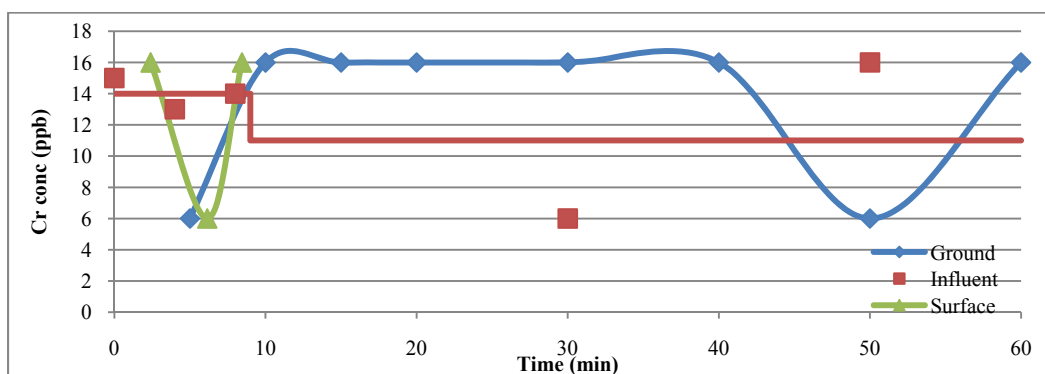**Figure 3.75 Total concentration of chromium in 4:1 slope, medium flow rate**

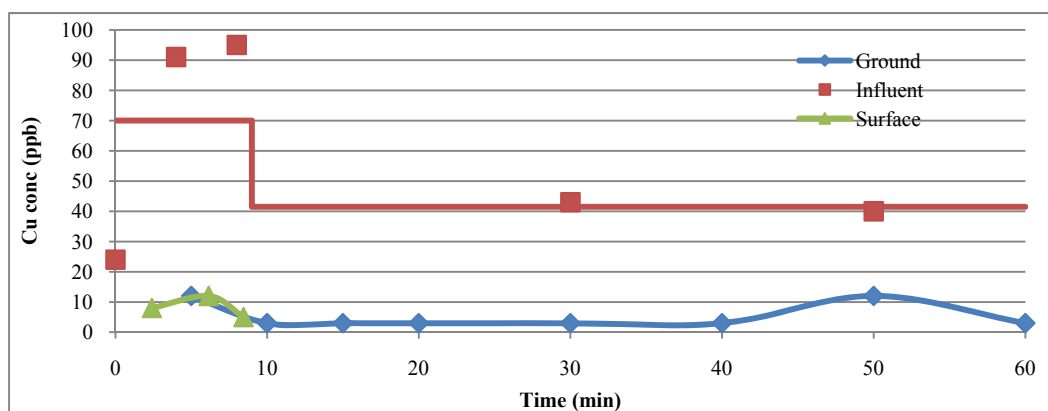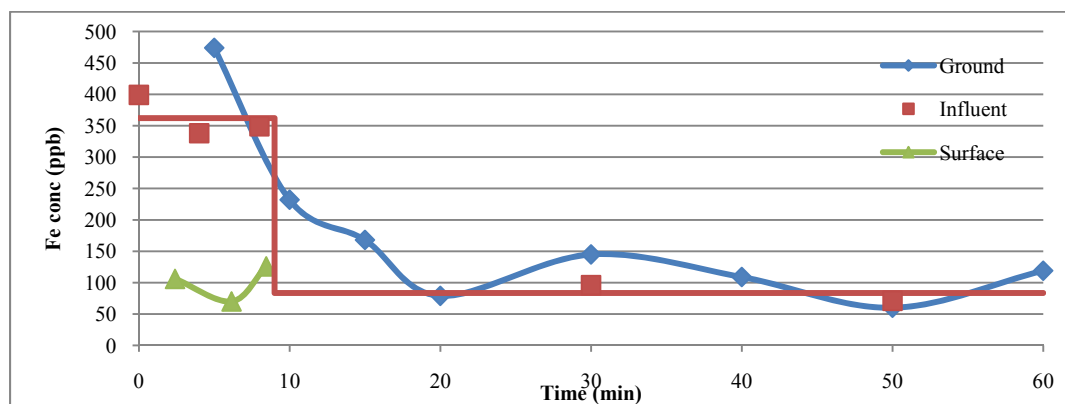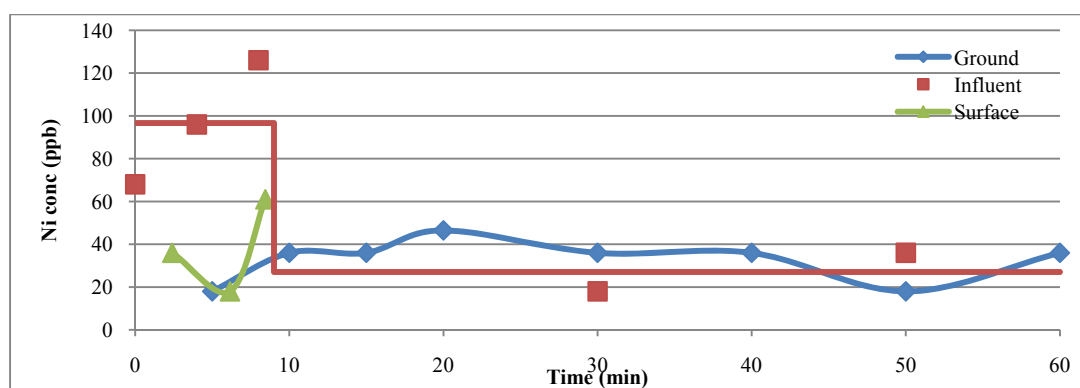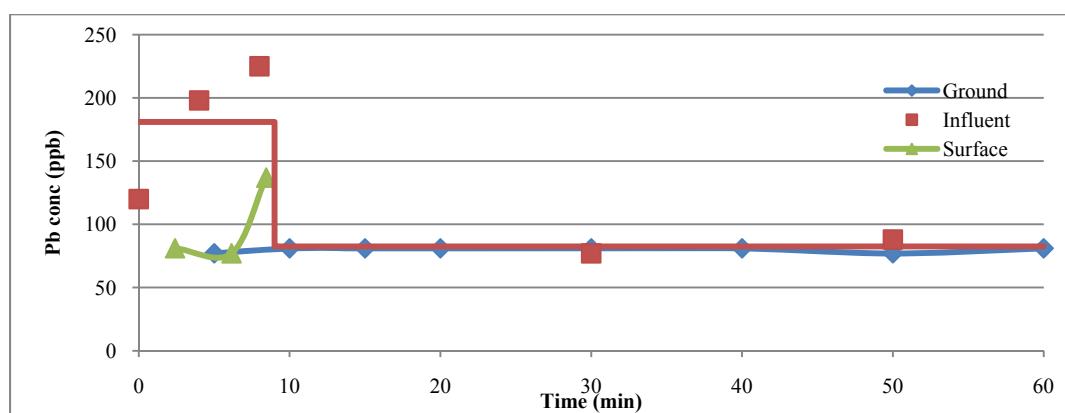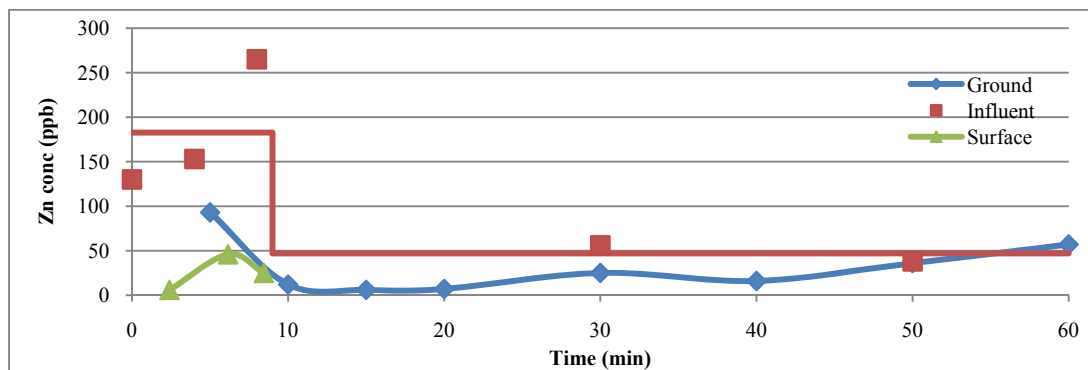**Figure 3.76 Total concentration of copper in 4:1 slope, medium flow rate**

Figure 3.77 Total concentration of iron in 4:1 slope, medium flow rate

Figure 3.78 Total concentration of nickel in 4:1 slope, medium flow rate

Figure 3.79 Total concentration of lead in 4:1 slope, medium flow rate

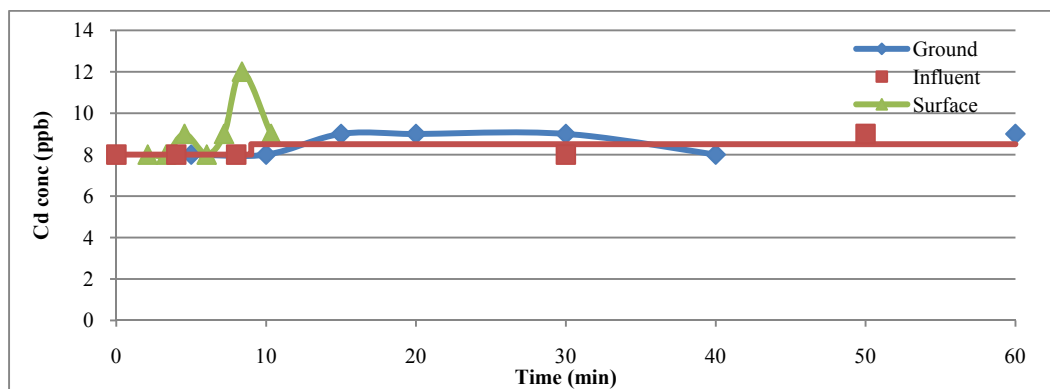**Figure 3.80 Total concentration of zinc in 4:1 slope, medium flow rate**

Figure 3.81 through Figure 3.87 portray the 2:1 slope test with a medium flow rate. Similar to the 8:1 medium flow rate test, Cd, Cr, Ni, and Pb had initial average influent concentrations slightly lower than the low target concentrations. Cd and Cr were the furthest from their target concentrations, each within a 60% and 44% margin respectively. Ni was within a 24% margin of its low target concentration, while Pb was the closest to its low target concentration within a 1% margin. Cu, Fe and Zn had initial average influent concentrations slightly higher than the low target concentrations. Cd was the only metal that was not detected in the influent for the entire test, with a detection limit of 8 µg/L. In the tailing end of the test, Cr and Pb were not detected with average limits of 11 µg/L and 79 µg/L respectively. The rest of the metals were detected and consistent, except Cr and Ni, which had concentrations below and above the influent average.

Even with the 2:1 slope, surface runoff virtually ceased to be generated after the first flush of the storm. In the surface samples, Cd, Cr, and Pb were the only metals not detected throughout the entire test with average detection limits of 9 µg/L, 12 µg/L, and

79 µg/L. Ni was not detected throughout the entire test except at 10 min at 66 µg/L, with

an average detection limit of 27 µg/L, which can be seen from the spike in concentration

in Figure 3.85. Cu was not detected throughout most of the test with an average detection

limit of 7 µg/L, except at 2 min and 4 min, detected below 20 µg/L. Fe and Zn were

detected throughout the entire test below 590 µg/L and 60 µg/L. Figure 3.84 shows a

spike in Fe concentration at 4 min and 10 min which was above the average influent

concentration, with increasing concentrations from 6 min to 10 min in the surface runoff.

Zn had surface concentrations well below the average influent concentration. In the

baseline samples, concentrations of Fe and Zn were the only detected metals, where these

concentrations were lower for Fe and higher for Zn when compared with the average

experimental surface concentrations, unlike the 4:1 slope test. Overall, the surface runoff

concentrations gave percent removals for Cr, Cu, Ni, Pb, and Zn as follows: 42.9, 92.3,

70.8, 68.0, and 74.8. Cd and Fe were not included in the percent removals, because they

were not detected in the influent. Because Fe was not detected in the influent, but was

detected above baseline concentrations in the runoff, soil eroded from the bed could

contain high concentrations of Fe, which would also explain the suspended solids

concentrations above influent concentrations that were not detected. For the 2:1 medium

flow test, Cu and Zn had the highest percent removals. When compared to the other

slopes, these percent removals are similar, and an increase in slope did not affect percent

removals very much.

For the underdrain, there is a gap in the figures between 50 min and 60 min

because the samples were lost. In the underdrain samples, Cd, Cr, and Cu were the only

metals that were not detected throughout the entire test with average detection limits of

9 µg/L, 13 µg/L, and 6 µg/L respectively. Pb was not detected throughout the entire test

with an average detection limit of 80 µg/L, except at 15 minutes at 158 µg/L. Ni was not

detected throughout the entire test with an average detection limit of 28 µg/L, except at

15 min and 60 min detected below 50 µg/L. Fe and Zn were the only metals detected

throughout the entire run below 830 µg/L and 30 µg/L respectively. Similar to the other

two tests, Fe has an initial high spike in concentration and then decreases over time, as

seen in Figure 3.22, and Zn had consistently low underdrain concentrations that are

below the influent average, as seen in Figure 3.87. In the baseline samples, Fe and Zn

were the only detected metals, which remained above average experimental underdrain

concentrations for both metals.

Figure 3.81 Total concentration of cadmium in 2:1 slope, medium flow rate
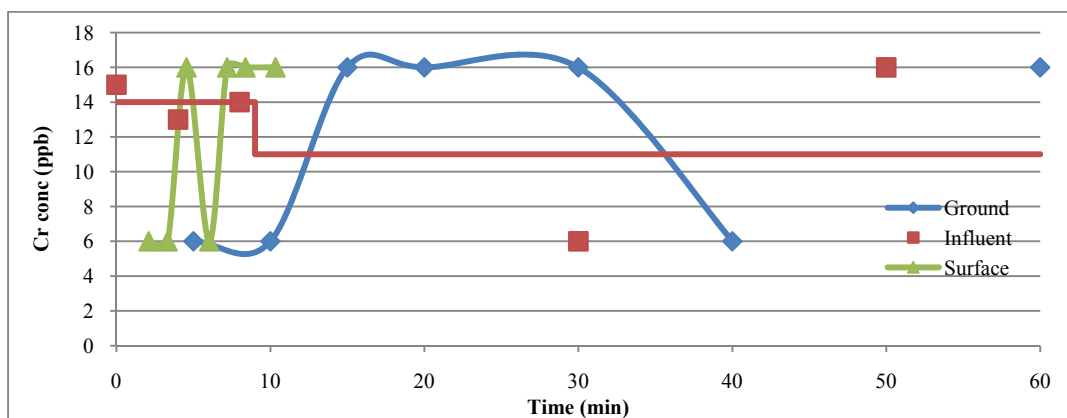
Figure 3.82 Total concentration of chromium in 2:1 slope, medium flow rate
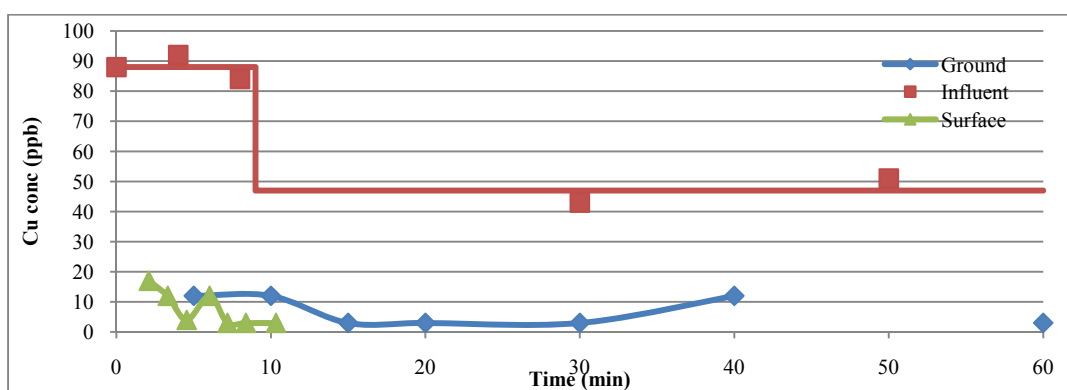
Figure 3.83 Total concentration of copper in 2:1 slope, medium flow rate

Figure 3.84 Total concentration of iron in 2:1 slope, medium flow rate
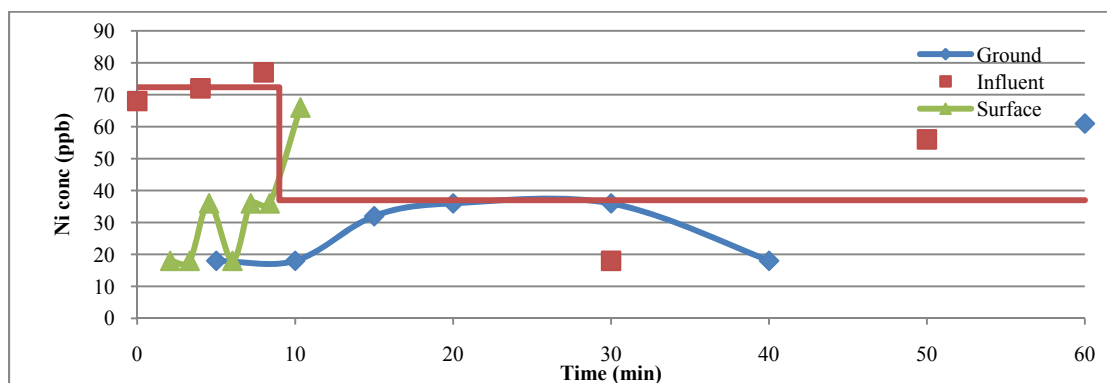
Figure 3.85 Total concentration of nickel in 2:1 slope, medium flow rate

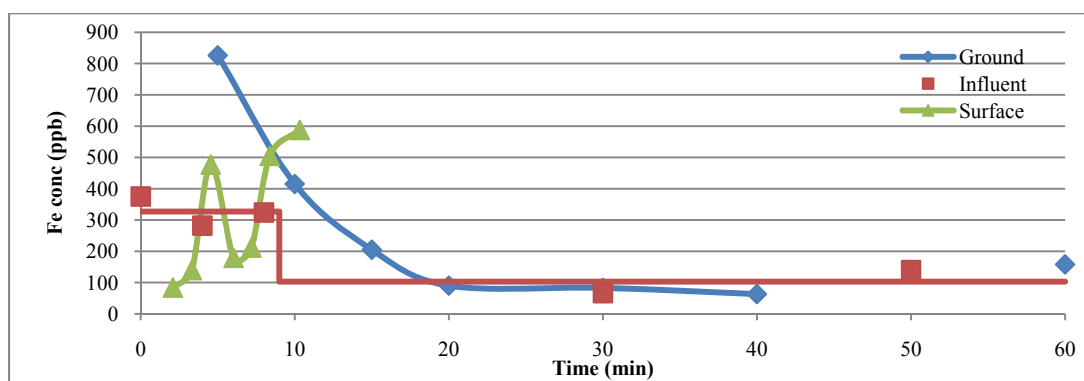**Figure 3.86 Total concentration of lead in 2:1 slope, medium flow rate**

Figure 3.87 Total concentration of zinc in 2:1 slope, medium flow rate

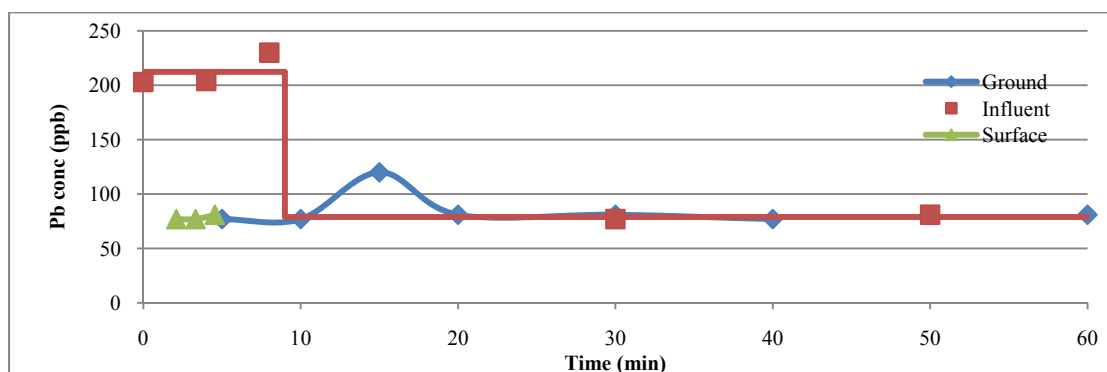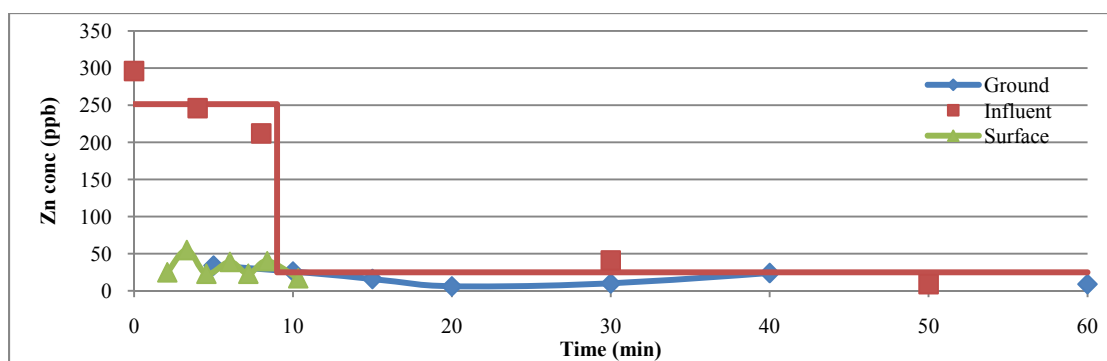Figure 3.88 through Figure 3.94 portray the fourth test, which consisted of a 2:1 slope with a high flow rate. For the high flow simulation, an initial flow rate of 5.43 gpm was maintained for 6 min and then followed by a flow rate of 1.18 gpm for 29 min.

Similar to the 2:1 medium flow rate test, Cd, Cr, Ni, and Pb had influent concentrations that were below the low target concentrations for the first flush portion of the test. How far these metals were from their respective target concentrations varied greatly, where Cd was within a 43% margin, Ni and Pb were within a 20% margin, and Cr was within a 4% margin. Cu, Fe, and Zn had influent concentrations that were above the low target concentrations. In the tail end portion of the test, Cd, Cr, Ni, and Pb were not detected with detection limits of 8 μg/L, 6 μg/L, 18 μg/L, and 77 μg/L. Cu, Fe, and Zn were detected throughout the entire test, and were detected nelow 90 μg/L, 580 μg/L, and 250 μg/L respectively. Out of these metals, Cu was the only one that remained consistent with the average influent concentrations as seen in Figure 3.90. At 25 min there was a large spike in Fe concentration for the tail end portion of the test at 575 μg/L (see Figure 3.91).

Surface runoff was not generated throughout the entire test, unlike in bed 1. This difference could have been due to the construction of the bed itself. In the surface samples, Cd, Cr, and Pb were not detected throughout the duration of the test, similar to the 2:1 medium flow rate test. Cu and Ni were only detected within the first minute at 15 μg/L and 37 μg/L. Beyond the first minute, Cu and Ni were not detected with limits of 12 μg/L and 18 μg/L respectively. Similar to the other tests, Fe and Zn were detected throughout the entire test, and were detected below 165 μg/L and 80 μg/L. Both Fe and Zn surface concentrations remained below average influent concentrations. In the baseline samples, concentrations of Fe and Zn were the only detected metals. Similar to the other tests, these concentrations were higher for Fe and Zn when compared with the

average experimental surface concentrations. Average EMC percent removals for Cd,

Cr, Cu, Fe, Ni, Pb and Zn are as follows: 60.5, 76.9, 88.6, 76.4, 76.7, 66.8, and 71.3. For

the 2:1 high flow test, Cr and Cu had the highest percent removals. Once again, these

percentages remained similar to the other slopes.

In the underdrain samples, Cd, Cr, Cu, Ni and Pb were not detected throughout

the duration of the test, somewhat similar to the 2:1 medium flow rate test, with detection

limits of 8 µg/L, 6 µg/L, 12 µg/L, 18 µg/L, and 77 µg/L, respectively. Fe and Zn were

detected throughout the entire test, with concentrations below 2000 µg/L and 105 µg/L,

respectively. As with the other tests, Fe had a large spike in concentration at 5 min, and

then decreased past this time below average influent concentrations (see Figure 3.29). Zn

concentrations consistently remained below average influent concentrations (see Figure

3.94). In the baseline samples, concentrations of Fe and Zn were the only detected

metals, where the average baseline Fe concentration was higher than the average

experimental underdrain concentrations, and the average baseline Zn concentration was

the same as the experimental average Zn concentration.
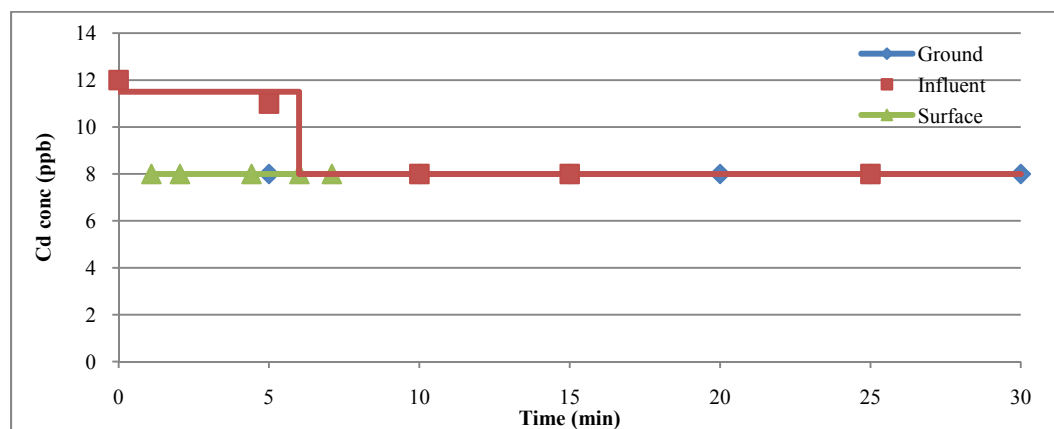
Figure 3.88 Total concentration of cadmium in 2:1 slope, high flow rate

Figure 3.89 Total concentration of chromium in 2:1 slope, high flow rate

Figure 3.90 Total concentration of copper in 2:1 slope, high flow rate
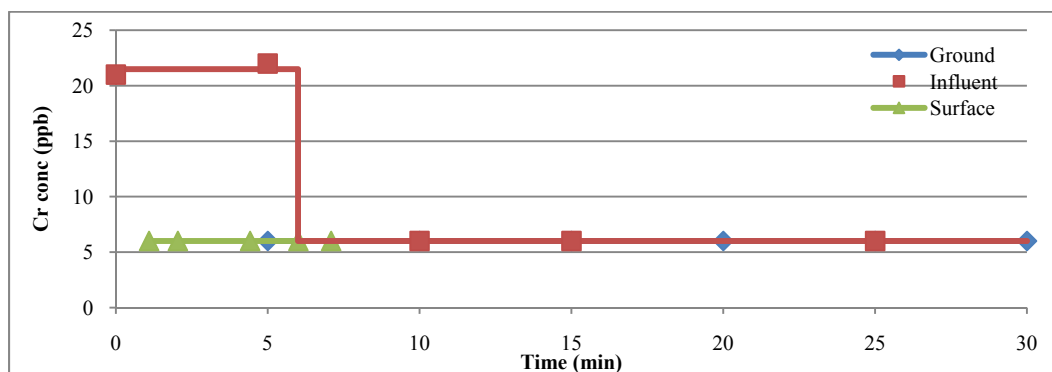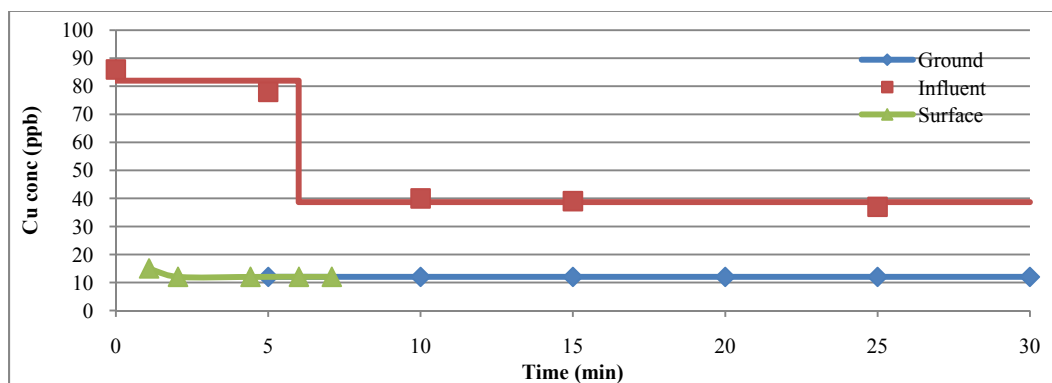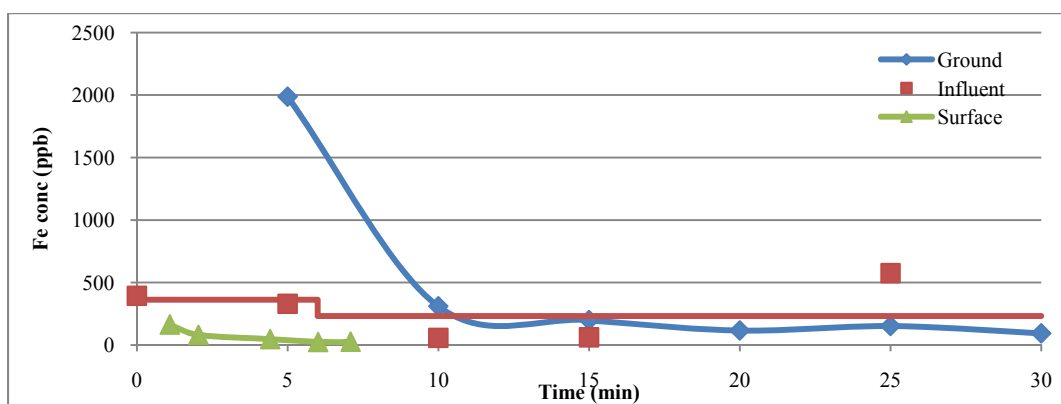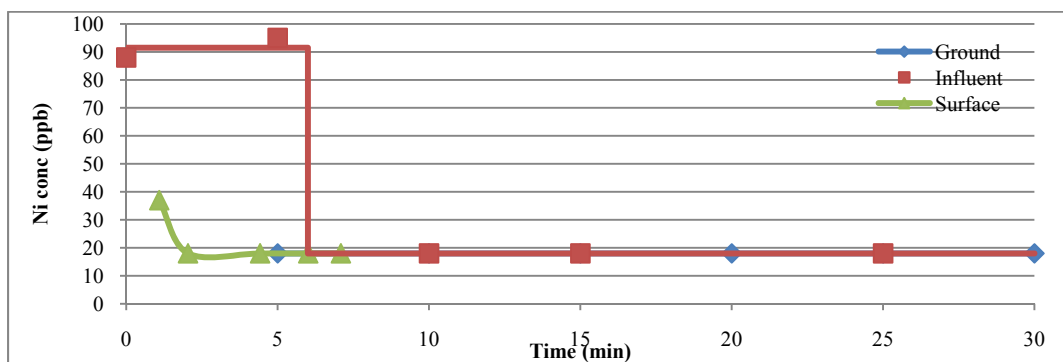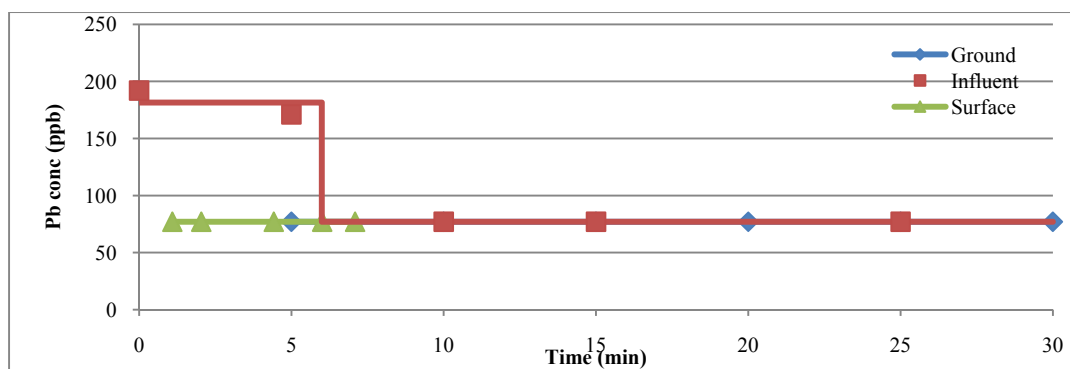

Figure 3.91 Total concentration of iron in 2:1 slope, high flow rate

Figure 3.92 Total concentration of nickel in 2:1 slope, high flow rate

Figure 3.93 Total concentration of lead in 2:1 slope, high flow rate
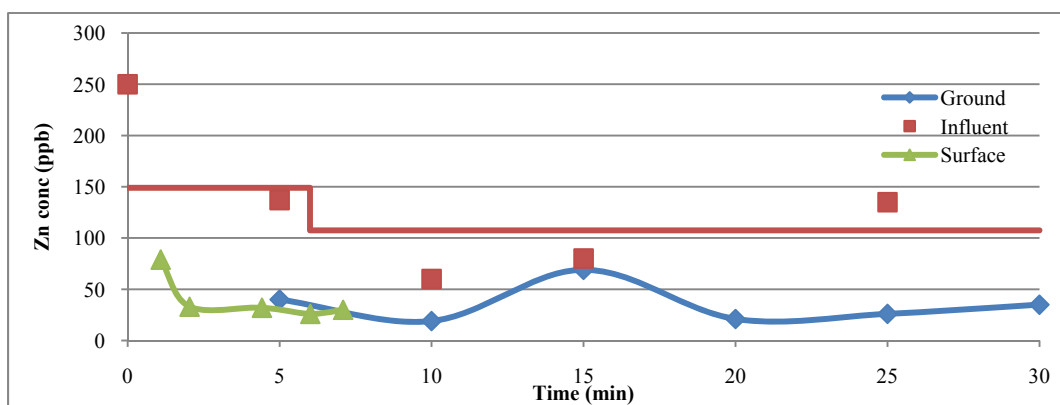
Figure 3.94 Total concentration of zinc in 2:1 slope, high flow rate

3.2.3   Dissolved Metals Results

Dissolved metal samples were collected on-site by filtering the samples with a 0.45 μm syringe filter. These samples were preserved with acid and analyzed by ICP-OES. Figure 3.95 through Figure 3.100 exhibit a few of the dissolved metals for the 8:1 medium flow test and 4:1 medium flow test. For the first flush portion of the 8:1 medium flow test, influent Cr and Fe concentrations exhibited similar trends, where they were detected as soon as the test started, but were not detected for the remaining 15 min, with detection limits of 6 μg/L and 4 μg/L, respectively; however, Cr was not detected in the tail end portion of the test, and Fe was with concentrations below 25 μg/L, which was similar to Fe in the 4:1 test. In the 4:1 medium flow test, Cr was not detected throughout, with a detection limit of 6 μg/L.   Also in the 4:1 medium flow test, the first collected influent sample spilled; therefore no metal concentrations were available. In both the 8:1 and 4:1 medium flow tests, Cd, Ni, and Zn were detected during the first flush portion of the test in the influent, with concentrations below 20 μg/L, 90 μg/L, and 75 μg/L, but were not detected in the tail end of the test, with detection limits of 3 μg/L, 25 μg/L, and 4 μg/L, respectively. Cu was the only metal detected throughout the entire test with concentrations below 55 μg/L in both the 8:1 and 4:1 medium flow tests. However, Cu and Fe were unlike the other metals because the influent concentrations in the tail end portion of the test were higher than the first flush portion, which was similar to Zn in bed 1. In the tail end portion of the test, Cu and Fe were consistently below average influent concentrations.

In the surface samples, Cu was the only detected metal in both the 8:1 and 4:1 medium flow tests, with a concentration of 8 µg/L for the 8:1 test and an average concentration of 10 µg/L for the 4:1 test, although these values were far below dissolved influent concentrations of 35 µg/L to 55 µg/L. In the underdrain, Fe was the only detected metal for both the 8:1 and 4:1 tests, with concentrations below 55 µg/L, and was above influent concentrations in both tests, indicating leaching out of the soil.
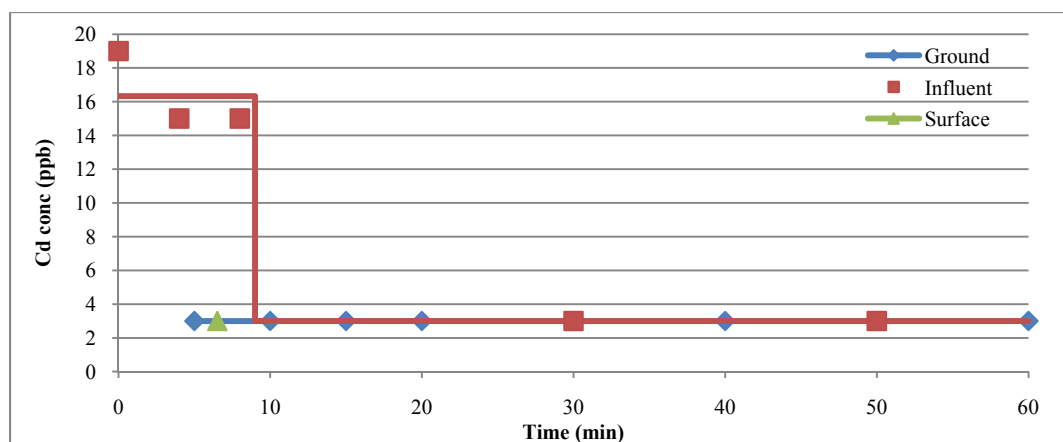
Figure 3.95 Dissolved concentration of cadmium in 8:1 slope, medium flow rate
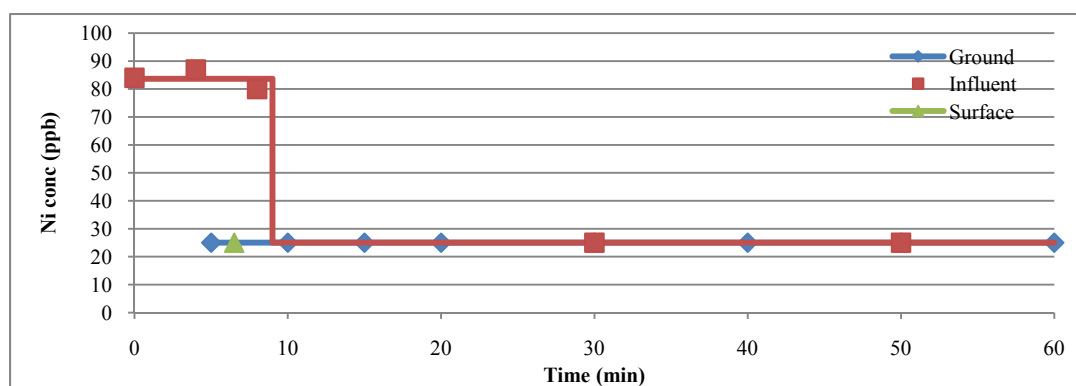
Figure 3.96 Dissolved concentration of nickel in 8:1 slope, medium flow rate
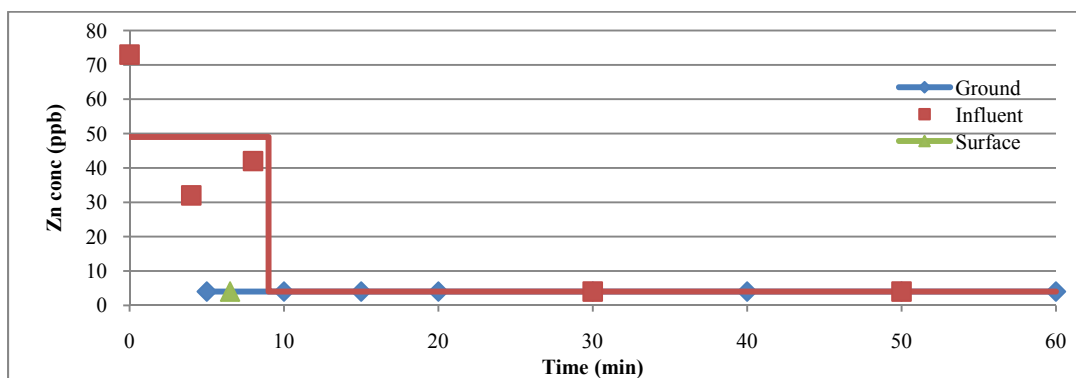
Figure 3.97 Dissolved concentration of zinc in 8:1 slope, medium flow rate

Figure 3.98 Dissolved concentration of cadmium in 4:1 slope, medium flow rate

Figure 3.99 Dissolved concentration of nickel in 4:1 slope, medium flow rate

Figure 3.100 Dissolved concentration of zinc in 4:1 slope, medium flow rate

The 2:1 medium flow test metals results were similar to the 2:1 high flow test results, where a few of the dissolved metals are displayed in Figure 3.101 through Figure 3.106. Similar to the 8:1 and 4:1 medium flow tests, both the 2:1 medium and high flow tests exhibited detectable influent, surface, and underdrain concentrations only with Cu throughout the entire test. In the 2:1 high flow test, Cd was detected throughout the entire test with influent concentrations below 20 µg/L. In the 2:1 medium flow test, Cd was detected throughout the entire test with concentrations below 30 µg/L, except at 50 min with a detection limit of 2 µg/L. Ni, Cr, and Zn exhibited similar trends for both tests. They were detected in the first flush portion of the test with concentrations below 95 µg/L, 10 µg/L, and 185 µg/L, respectively, and were not detected or close to detection limits in the tail end portion of the test, with detection limits of 15 µg/L, 2 µg/L, and 3 µg/L, respectively. Once again, Cu and Fe had an unusual trend with the tail end concentrations higher than the first flush concentrations.

In the surface samples for both the 2:1 medium and high flow tests, Cd and Cr were detected, but were close to detection limits. Ni, Pb, and Zn were not detected in the

surface and underdrain samples, with detection limits of 15 µg/L, 20 µg/L, and 3 µg/L.

Fe was not detected in the surface samples, except for a few samples close to the

detection limit, but was detected in the underdrain samples with concentrations below

60 µg/L. These concentrations were above influent concentrations, indicating leaching

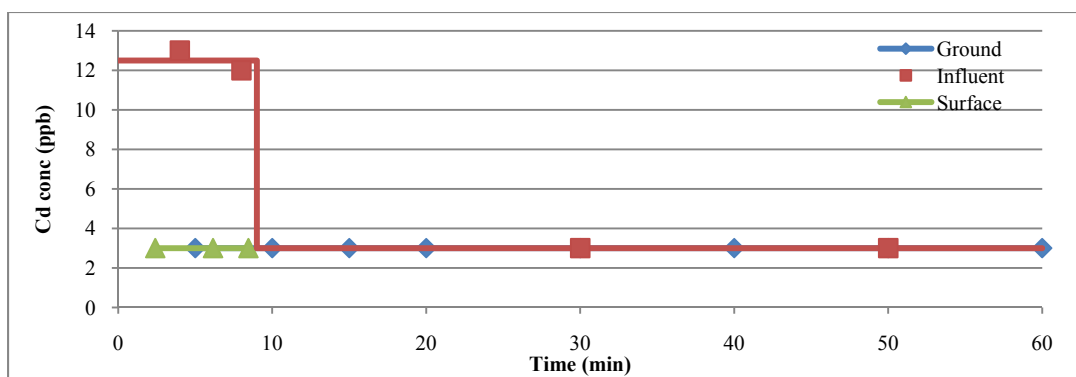out of the soil, similar to the 8:1 and 4:1 medium slope tests.

Figure 3.101 Dissolved concentration of cadmium in 2:1 slope, medium flow rate
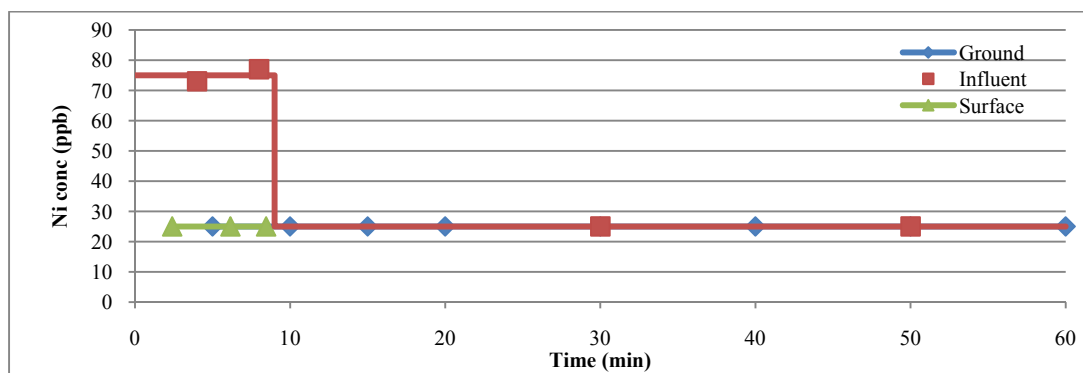

Figure 3.102 Dissolved concentration of nickel in 2:1 slope, medium flow rate

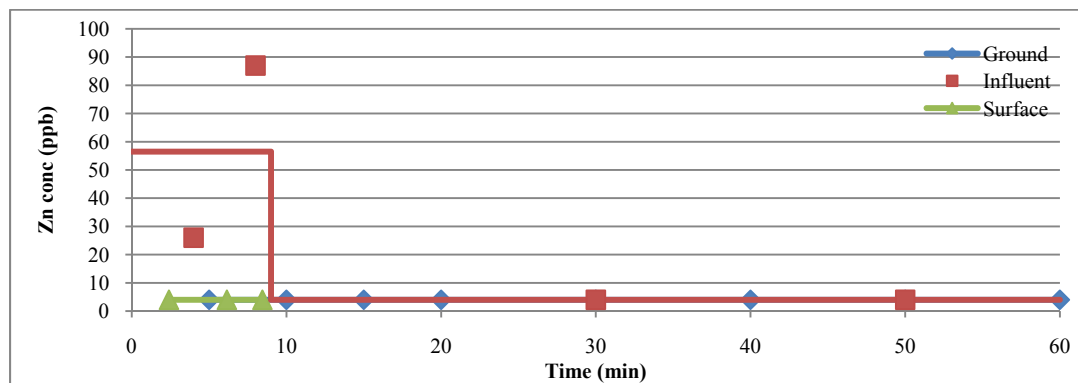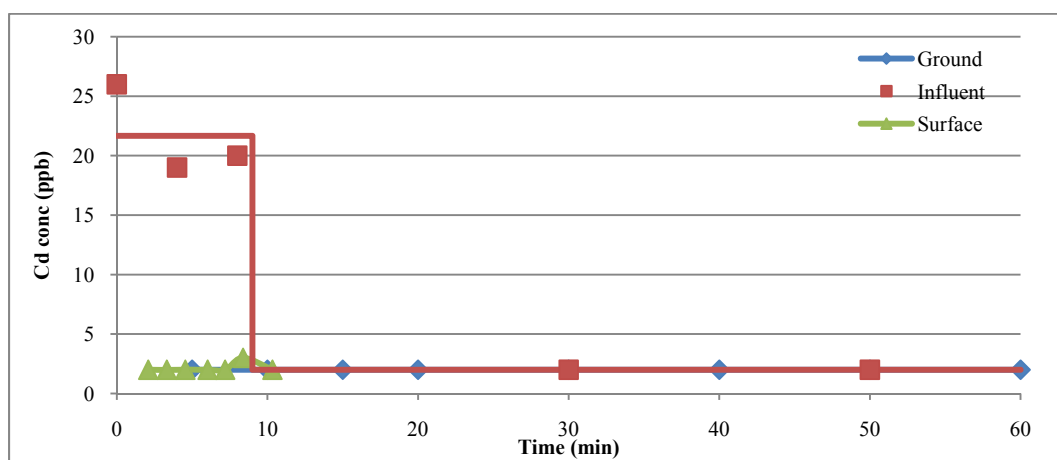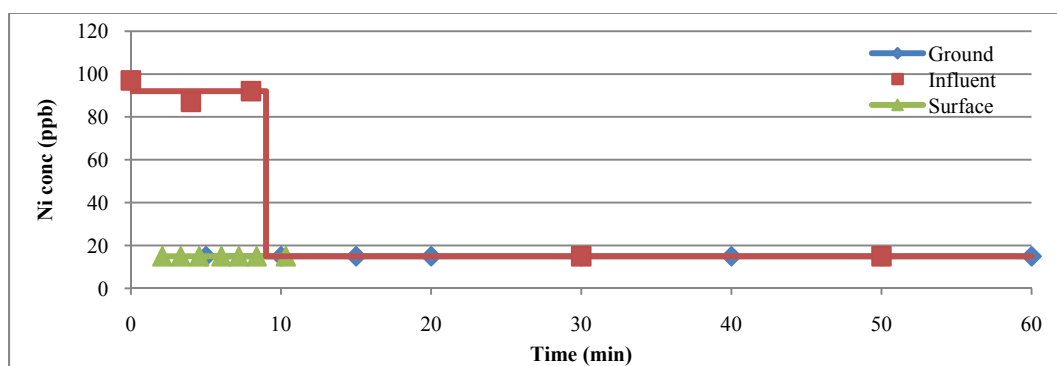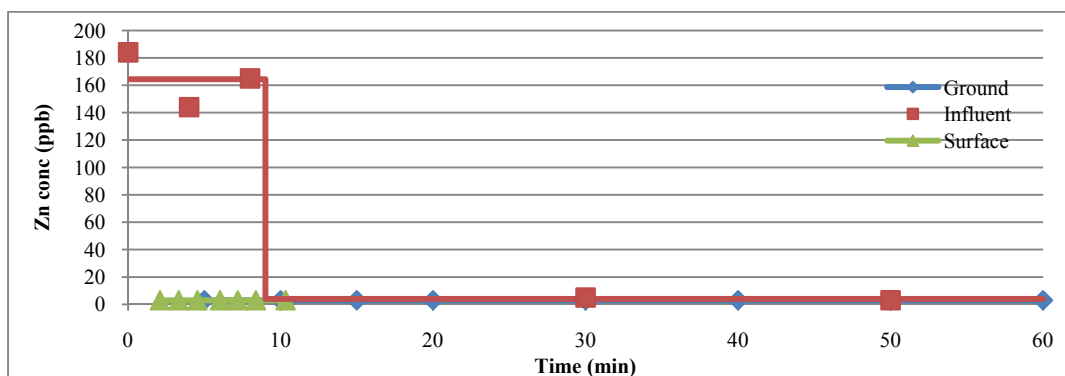**Figure 3.103 Dissolved concentration of zinc in 2:1 slope, medium flow rate**
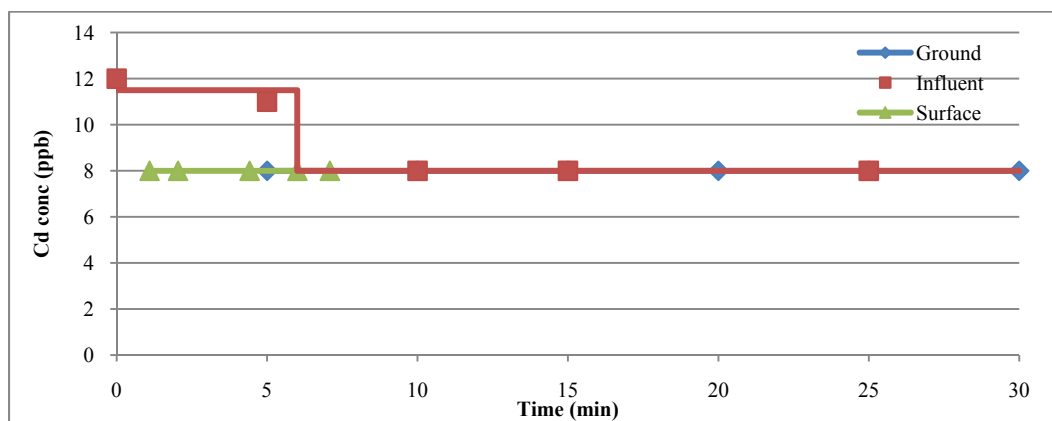
Figure 3.104 Dissolved concentration of cadmium in 2:1 slope, high flow rate
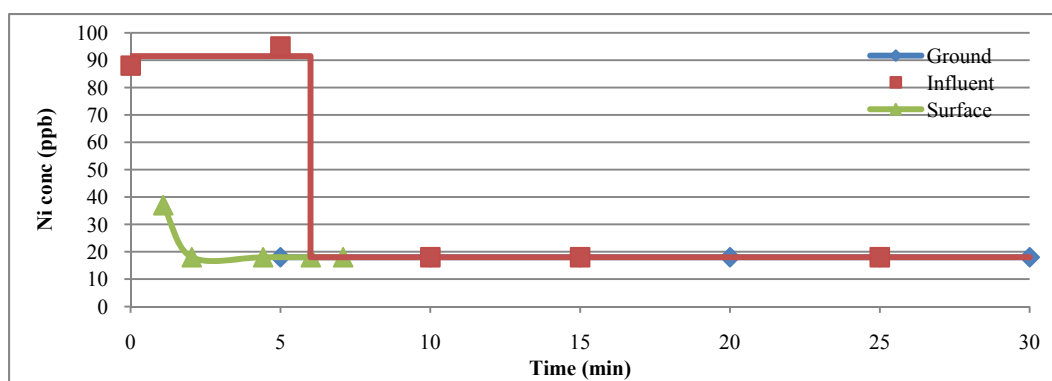
Figure 3.105 Dissolved concentration of nickel in 2:1 slope, high flow rate
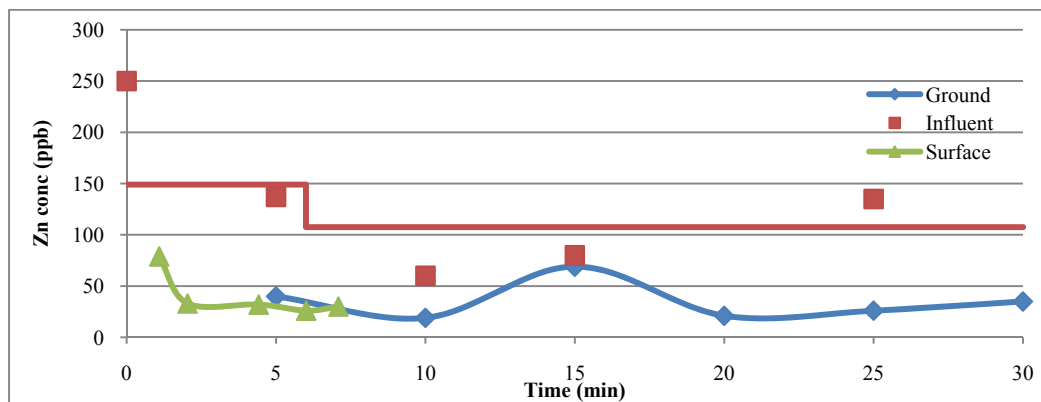
Figure 3.106 Dissolved concentration of zinc in 2:1 slope, high flow rate

3.2.4   Resuspension Results

After the four tests were completed on the bed, resuspension tests were conducted to determine the amount of tagged suspended solids that could remobilize. Four resuspension tests were conducted that represented each slope and flow rate used for the initial testing. For the initial 8:1 slope performance test, target concentrations of La tagged suspended solids were added to the influent; 9 mg/L for the first flush portion and none for the tail end of the test. Subsequent tests did not tag the suspended solids that were added to the influent. As displayed in Figure 3.107, the first three collected influent samples exhibited tagged suspended solids concentrations that were slightly lower than the target concentration for the first flush, with an average tagged suspended solids concentration of 6 mg/L, and an average La concentration of 372 μg/L. The last two collected influent samples exhibited tagged suspended solids concentrations much lower than the first three samples, with an average tagged suspended solids concentration of 0.03 mg/L, and a nondetectable amount of La for the tail end of the test.
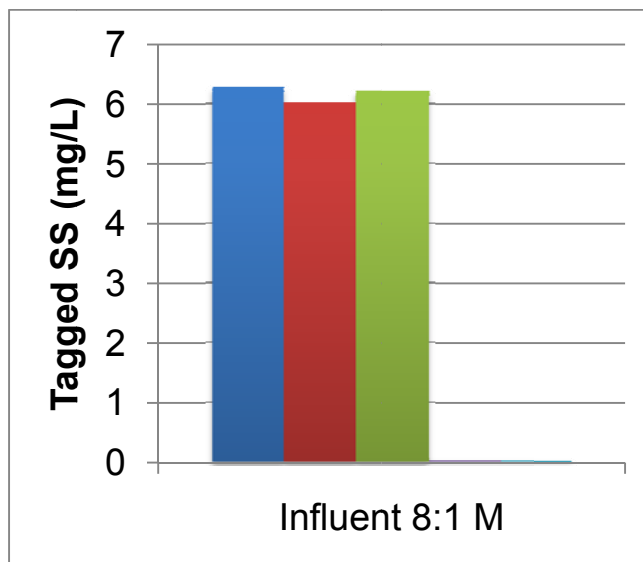
Figure 3.107: Influent tagged suspended solids concentration in 8:1 slope, medium flow rate for bed 3

Figure 3.108 displays the tagged suspended solids concentrations in the surface runoff samples for each test on bed 3, four performance tests and four resuspension tests. As seen from this figure, the tagged suspended solids concentrations were highest for the 8:1 medium flow test, with a tagged suspended solids concentration of 0.65 mg/L and La concentration of 39 μg/L. It was during this test that the tagged suspended sediment was being released in the influent. These surface runoff concentrations were well below the average influent tagged suspended solids concentration of 6 mg/L and average La concentration of 372 μg/L. The fraction of La tagged soil in the samples greatly decreased from around 0.70 in the influent to 0.03 in the surface samples. This low surface runoff concentration showed that the majority of the added suspended solids were settling within the bed, and a very small amount flowed over the bed without settling. The majority of the total suspended sediment in the runoff (average of 5 mg/L for this

run, see Figure 3.63) was eroded from the bed itself and did not originate from the

influent water. Additional evidence of this was the baseline TSS concentrations in

surface runoff which averaged 1.8 mg/L with only tap water as the influent. La was not

detected in any of the three remaining performance tests or the four resuspension tests at

detection limits of 3 μg/L to 8 μg/L. Based on this data, it appears that the tagged

suspended solids initially added to the 8:1 medium flow influent did not become

resuspended for any slope or flow rate.
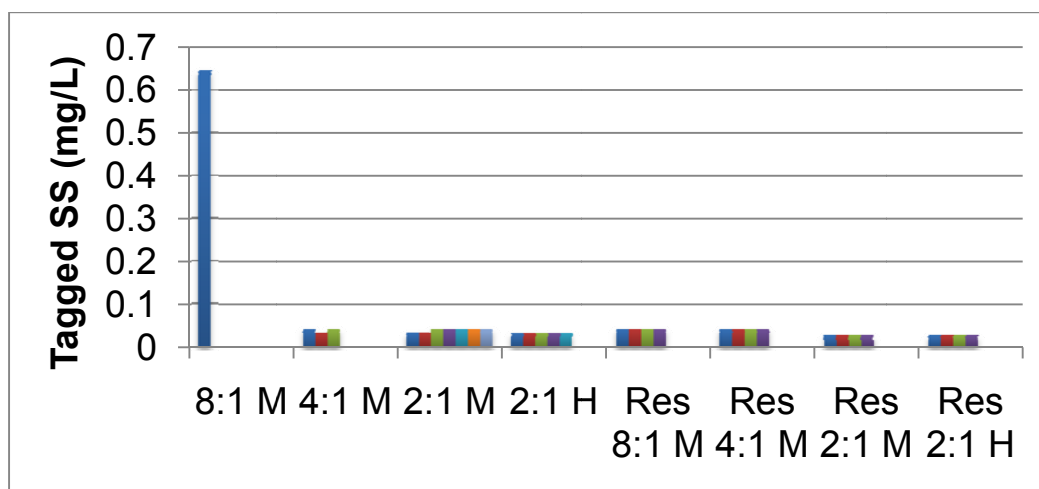
Figure 3.108 Tagged suspended solids concentrations for experimental and resuspension tests for bed 3

3.2.5 Efficiency of Vegetated Biofilters to Mitigate Highway Stormwater Runoff

Figure 3.109 displays the average percent removals of the event mean

concentration for each total metal and total suspended solids of the performance tests for

bed 3. Metals that were not detected in the influent exhibited a percent removal of zero,

since effluent concentrations were higher. The low concentration simulated stormwater

better represented actual highway stormwater runoff concentrations; therefore, the

removal efficiencies of this bed more accurately depict how efficiently a vegetated

biofilter would perform along a highway. It can be seen from this figure that average

percent removals were lower than the high concentration tests over each metal (see

Figure 3.109), except Cu, which had the highest percent removals for each test (average

92%), which was similar to the average copper percent removal of 97% for bed 1.

Suspended solids had very low percent removals for the low concentration tests (average

24%), where TSS percent removals decreased with an increase in slope. This percentage

was much lower than the average TSS percent removal for the high concentration tests of

93%. This large difference was most likely due to a very low concentration of TSS that

was initially added to the influent for the first flush of the tests. Because the bed

continuously erodes a low level of TSS, as influent concentrations approach that level,

removal efficiencies decrease dramatically.

When comparing with each slope, the percent removals for each metal did not

remain consistent, particularly for Cd, Cr, Fe, and Ni. For Cd, Cr, and Ni had highest

percent removals at the 8:1 slope, with decreasing percent removals for the 4:1 and 2:1

(medium) slopes, followed by an increase for the 2:1 (high) slope. Cd exhibited a zero

percent removal at the 2:1 (medium) slope and Cr at the 4:1 slope. Fe had the highest

percent removal at the 2:1 (high) slope, with a zero percent removal at the 2:1 (medium)

slope, similar to Cd. For the low concentration set of tests, the 8:1 slope had the best

percent removals for the majority of the contaminants, and an increase in slope portrayed

a slightly lower range of percent removals. The lower simulated stormwater
concentrations had significantly lower overall percent removals compared with bed 1.
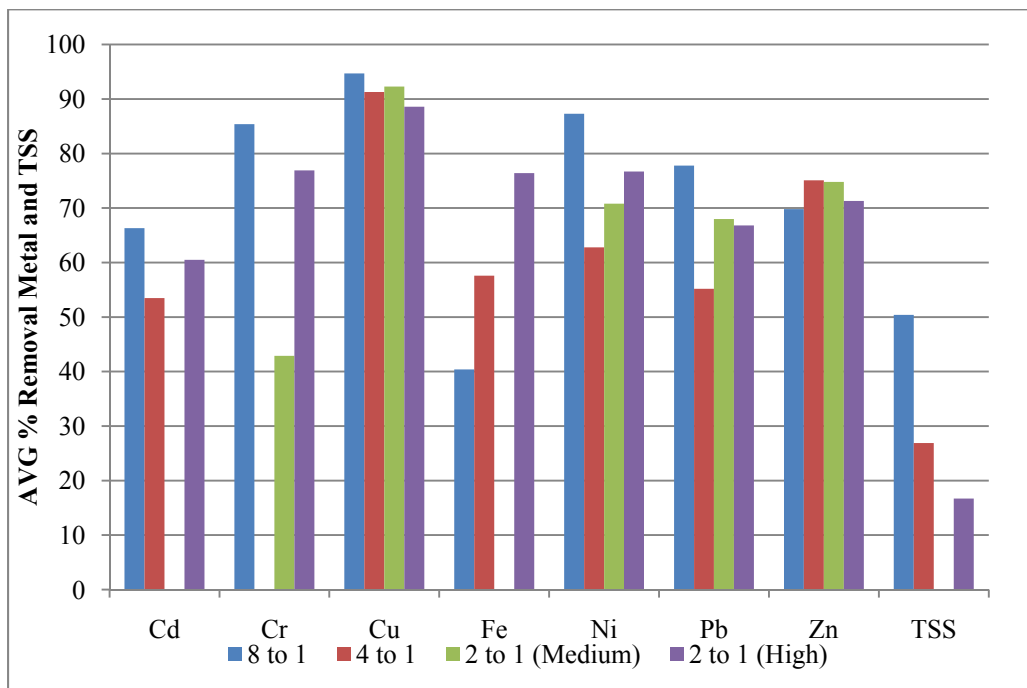
Figure 3.109: Average percent removals of event mean concentration for total metals and total suspended solids for bed 3

3.2.5.1 Comparison with Other Vegetated Biofilter Studies

The percent removals from previous vegetated biofilter studies were more closely
related to the percent removals from the low concentration tests than the high
concentration tests. Several of the previously mentioned studies were conducted on
actual highways with vegetated biofilters; therefore, the stormwater runoff concentrations
more closely resembled the low concentration simulated stormwater runoff. Average
percent removals for our tests for the event mean concentration of TSS, Cd, Cr, Cu, Fe,

Ni, Pb, and Zn were as follows for the low concentration tests: 24%, 45%, 51%, 92%, 44%, 74%, 67%, and 73%.

Stagge and Davis (2006) conducted vegetated biofilter tests on a four lane highway median in Maryland during 18 storm events. They reported TSS percent removals between 65-71% and zinc percent removals between 30-60%, which were slightly higher than the TSS values reported for this biofilter study and slightly lower than the Zn values, but still closer than the high concentration percent removals. Another study from Barrett (2005) observed 42 storm events and determined the efficiency of adjacent vegetated biofilters: TSS percent removal of 48%, zinc removal of 54%, and copper removal of 24%. Li et al. (2008) studied the capacity of two Texas highway medians to mitigate highway stormwater runoff and determined TSS and Pb percent removals as follows: 68% and 48%. Each of these studies concluded that based on these percent removals, the vegetated biofilters were efficient in mitigating highway stormwater runoff. Despite the lower percent removals for the low concentration tests, these percentages are more common for actual storm events, and still represent the efficiency of the vegetated biofilter in these tests.

3.2.6 Metal Accumulation in Grass, Soil, and Roots

Five soil cores were initially collected from the bed from random locations to determine the baseline metal concentrations. After completion of all performance and resuspension tests, twenty-five cores were collected throughout the bed, five replicates at five different locations down the length of the bed. As described previously, the cores were separated into grass, roots, and soil fractions, and each fraction was digested and

analyzed for metal concentrations. The metals added to the influent included Cd, Cr, Cu, Fe, Ni, Pb, and Zn. Figure 3.110 through Figure 3.116 display the concentrations (mg of metal/kg of dry matter) of each metal within the grass, soil, and roots down the length of the bed. Because five core samples were collected at each distance along the bed, average values were plotted and error bars at each point on the graph represent one standard deviation. The solid horizontal lines on each graph represent the average background concentrations of the grass, soil, and roots before any tests were conducted.

In terms of the highest concentrations of metals accumulating within the media, each metal exhibited different trends. Cd, Cu, Pb, and Zn exhibited the highest concentrations detected in the roots. Cu had soil concentrations below baseline concentrations. Cr and Fe had the highest concentrations detected in the soil, next highest in roots, and low concentrations were detected in the grass. Ni was unusual and had the highest concentration detected in the grass, next highest in the roots, and lowest in the soil. In terms of the spatial distribution of metals, concentrations typically decreased along the length of the bed with highest concentrations detected at a distance of 1 foot from the beginning of the bed, the location where the polluted water was delivered to the bed.

Out of all these metals, Zn was the only metal that had a statistically significant ($\alpha = 0.05$) amount of accumulation throughout the bed in the grass, soil, and root media (see Figure 3.116). Highest concentrations were found in the roots and grass. Even though the standard deviations were large for some of the root samples, the differences were statistically significant. Cu was also detected at elevated concentrations throughout

the bed in the roots and grass, with highest concentrations at a distance of 1 foot (see

Figure 3.112). Cd similarly had elevated concentrations in roots along the length of the

bed (see Figure 3.110). Except at a distance of 1 foot, all concentrations of Cd in grass

were indistinguishable from background; however, Ni had statistically significant

elevated concentrations in the grass at 1 foot. In the roots, Ni was above background

concentrations significantly at 1 foot, 3 ft, and 12 ft. Even though above background

concentrations along the length of the bed, Ni accumulation in the soil was not

statistically significant (see Figure 3.114). Cr had elevated concentrations in the soil,

with concentrations above background along the entire length of the bed, and

accumulated at a significant level throughout the length of the bed as well. Even though

Cr had lower concentrations in the grass, there was a statistically significant amount of

accumulation at 1 foot and 6 ft along the bed (see Figure 3.111). Fe also had elevated

concentrations in the soil, with concentrations above background significantly at 1 foot

and 9 ft. Fe did not have a significant amount of accumulation in any of the grass or root

samples (see Figure 3.113). Pb was only statistically significant in the grass at 1 foot (see

Figure 3.115).
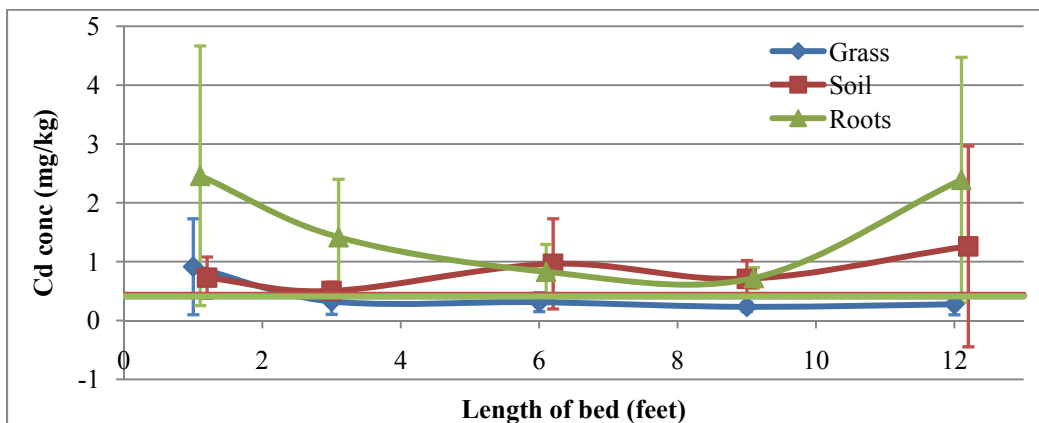
Figure 3.110 Concentration of Cd throughout Length of Bed
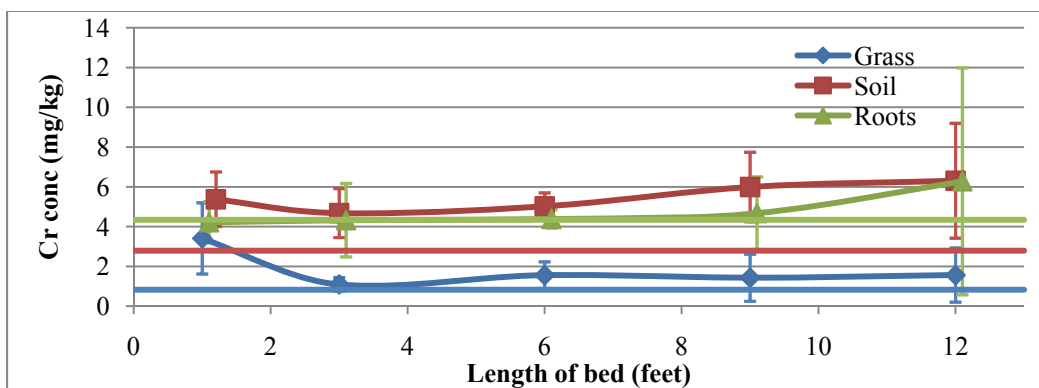
Figure 3.111 Concentration of Cr throughout Length of Bed
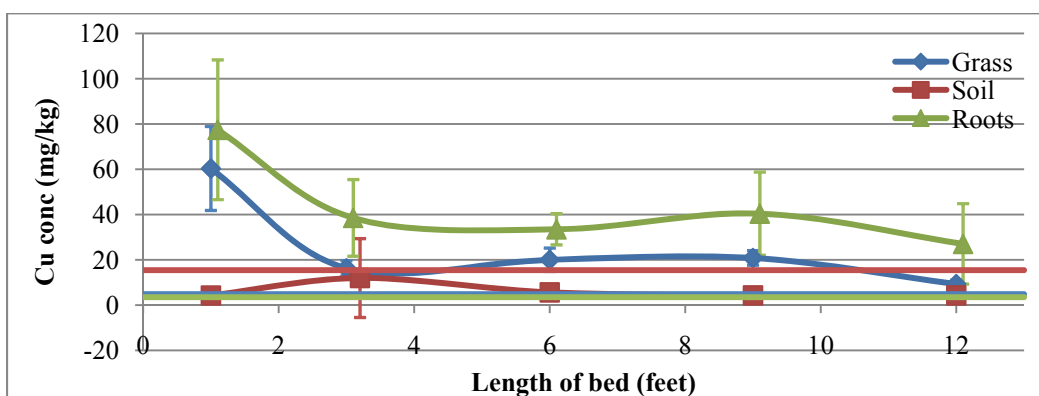
Figure 3.112 Concentration of Cu throughout Length of Bed
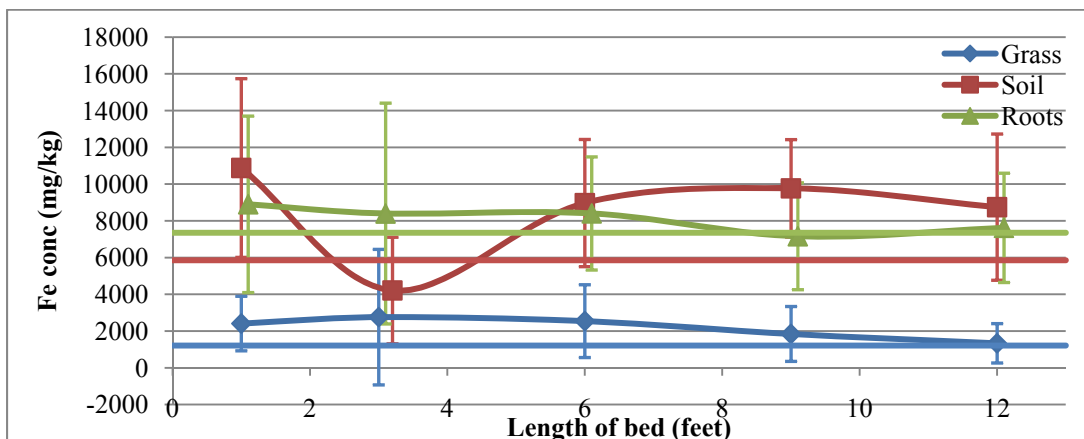
Figure 3.113 Concentration of Fe throughout Length of Bed
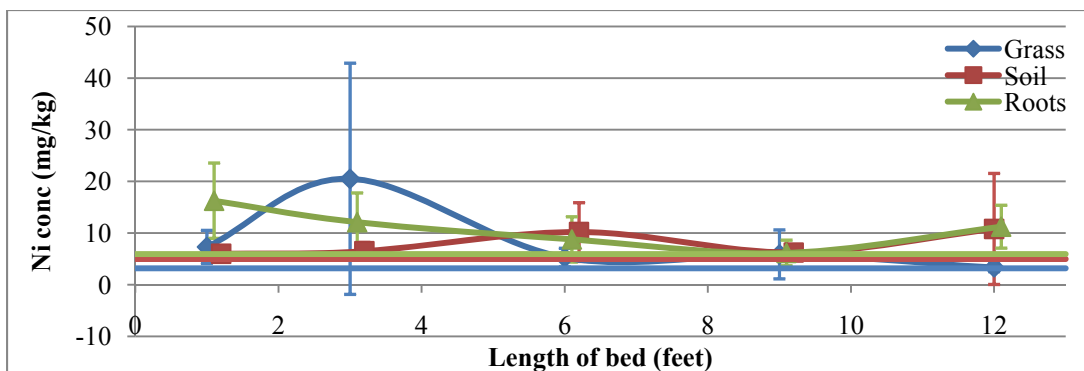
Figure 3.114 Concentration of Ni throughout Length of Bed
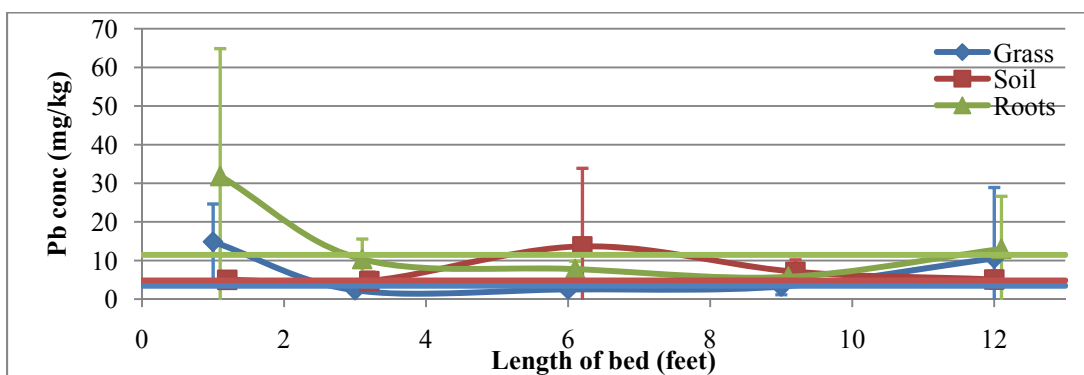
Figure 3.115 Concentration of Pb throughout Length of Bed
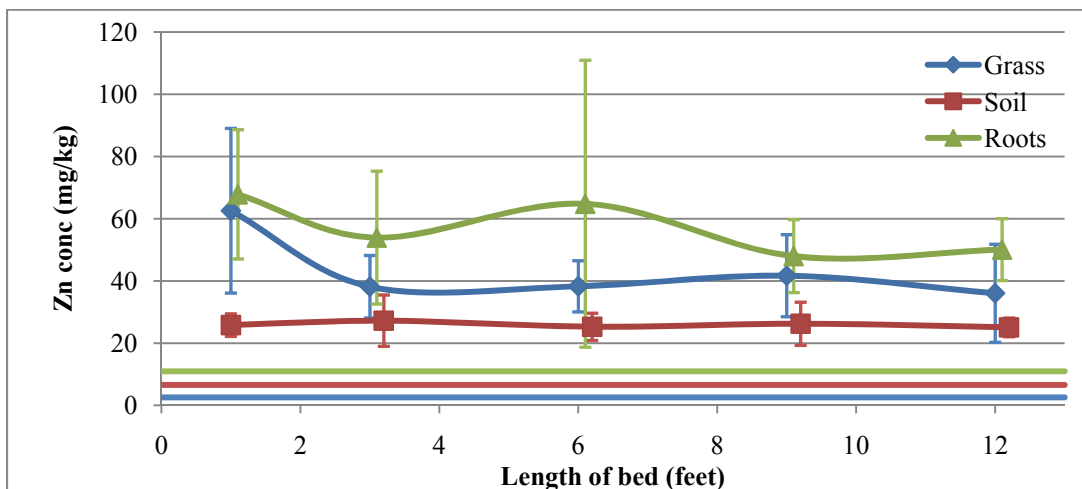
Figure 3.116 Concentration of Zn throughout Length of Bed

In the roots, every metal except Cr, Fe, and Pb showed a statistically significant amount of accumulation along the length of the bed. Cu and Zn accumulated significantly down the entire length of the bed. Cd and Ni only accumulated significantly at the 1, 3, and 12 ft locations, and Cd also accumulated at the 6 ft location. Highest concentrations for Cu and Zn were found in the roots. Cu accumulated to the highest concentration in roots at 77 mg/kg.

In the grass, all of the metals except Cd and Fe accumulated significantly in the tissues, where Cu and Zn accumulated significantly down the entire length of the bed. Cr, Ni, and Pb accumulated significantly at 1 foot down the bed, and Cr also accumulated significantly at 6 ft. Highest concentrations for Pb were found in the grass, with a concentration of 15 mg/kg. Considering not only the metals that significantly accumulated in the soil, Cu, Ni, Pb, and Zn accumulated in the vegetation at higher concentrations than in the soil. There are two explanations for the higher concentrations in vegetation than in the soil for these metals. It appears metals were taken up in the

plant and concentrated in the tissues as an active mechanism. However, this is exaggerated by reporting concentrations in terms of dry mass. Because vegetation has a much higher moisture content than soil, metals are greater concentrated in vegetation than soil during drying compared with the native conditions. On average, the moisture content of the root, grass, and soil samples from Bed 3 were 83.1%, 64.4%, and 10.5%. This was used to convert concentrations of mg/kg dry mass to mg/kg wet mass for the highest concentrations found in the bed (see Table 3.15).

After correcting for this distortion, soil concentrations were significantly higher than root and grass concentrations for Cd, Cr, Fe, Ni, Pb, and Zn, but root and grass concentrations for Cu were higher than soil concentrations. However, soil concentrations only significantly accumulated for Cr, Fe, and Zn. Therefore, it is likely that Cr, Fe, and Zn mainly adsorbed to the bed soil, while Cd, Cu, and Pb were preferentially taken up by the vegetation and then these metals were concentrated in their roots, including Ni, which had almost equal concentrations in the vegetation and roots.

Table 3.15: Maximum Core Concentrations in Bed 3 Per Wet Mass

mg/kg dry mass							
	Cd	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
roots	2.46	6.28	77.4	8898	16.3	31.9	67.9
grass	0.91	3.41	60.3	2760	20.5	14.9	62.6
soil	1.26	6.31	12.0	10879	10.8	13.7	27.2
mg/kg wet mass							
	Cd	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
roots	0.42	1.06	13.1	1504	2.75	5.39	11.5
grass	0.32	1.21	21.5	982.6	7.30	5.30	22.3
soil	1.13	5.65	10.7	9737	9.67	12.3	24.3

In the soil, Cr, Fe, and Zn accumulated significantly at maximum concentrations of 5.65 mg/kg, 9,737 mg/kg, and 24.3 mg/kg, which were higher than observed concentrations in vegetation for Cr, but lower in Zn. Fe was found at the highest concentration, but was also the highest concentration in the influent. The higher concentrations of metals in the soil compared to the vegetation indicated that the soil captured the majority of the metals, which was different than bed one. The total mass of the contaminant is better to track its fate than concentration. A mass balance was performed to determine the total mass of grass, roots, and soil in the bed. Extrapolating the relative mass of soil, roots, and grass from the cores over the extent of the bed, and assuming that the metals do not penetrate any deeper than the 2 in depth cores, the mass of contaminants collected by each media fraction was computed (see Table 3.16). Metals displaying a mass of zero in the table represent where their background metal concentrations were higher than the concentrations in the media; therefore, there was no observable metal accumulation in this media. This mass balance further shows that the vast majority of the metal mass was concentrated in the soil for all metals except Cu, which had a high background concentration in soil.

Table 3.16: Estimated Mass of Metal Accumulated in Different Media Over the Entire Bed

	Total in Top 2" of Bed (kg dry mass)	Cd (g)	Cr (g)	Cu (g)	Fe (g)	Ni (g)	Pb (g)	Zn (g)
Grass	46.3	0	0.042	0.44	49.2	0.28	0.12	2.01
Roots	29.1	0.035	0.016	1.18	21.3	0.14	0.0093	1.47
Soil	692	0.31	2.10	0	1865	2.48	1.95	30.1

3.2.7 Analysis of Total Suspended Solids and Adsorbed Metals

Table 3.17 displays the average dissolved and adsorbed metal concentrations in both the influent and effluent for bed 3 at a slope of 8:1. For metals that were not detected, half of the detection limit was used to compute an average. In the influent, every metal existed at a higher average concentration in the adsorbed form than dissolved, except for Ni, which was similar to bed 1 and was entirely dissolved. Zn was also significant in the dissolved form compared to the other metals, at 0.030 mg/L. In the effluent, no dissolved metals were detected and average adsorbed concentrations were lower than the influent concentrations for Cd, Cu, Fe, Pb, and Zn, but still higher than the non-detect dissolved concentrations. Similar to bed 1, Cr had an effluent average adsorbed concentration of zero, because it was not detected in both the total and dissolved forms.

When looking at the percent removals for the 8:1 slope of each metal, Ni did not have one of the lower percent removals, which was the case for bed 1 since it was highest in the dissolved form. Instead, Ni had one of the higher percent removals at 87.3%. Cd, Cr, Cu, Fe, Pb, and Zn, which were the metals at high concentrations in the adsorbed

form, had a large range of percent removals, from 40.4% to 94.7%. This broad range of

percent removals could be because a lower simulated stormwater concentration was used.

When looking at the metals that sorbed to the soil versus were taken up into the plant

(roots + grass) within the bed, Cr, Fe, and Zn were the three metals that had a statistically

significant amount of accumulation in the soil, and the mass of these metals was highest

in the soil. These were also some of the metals that were mostly in the adsorbed form.

Cd, Cu, Ni, and Pb had the highest accumulation in the soil, but these values were not

significant.

Table 3.17: Influent and Effluent Average Dissolved and Adsorbed Metal
Concentrations in Bed 3 at a Slope of 8:1

	Influent		Effluent	
	Average Dissolved Conc (mg/L)	Average Adsorbed Conc (mg/L)	Average Dissolved Conc (mg/L)	Average Adsorbed Conc (mg/L)
Cd	0.010	0.098	<0.003	0.003
Cr	0.004	0.008	<0.006	0.000
Cu	<0.009	0.062	<0.008	0.012
Fe	0.010	0.208	<0.003	0.196
Ni	0.055	0.000	<0.025	0.000
Pb	0.020	0.093	<0.034	0.022
Zn	0.030	0.078	<0.004	0.049
La	0.028	0.196	<0.003	0.038

The average adsorbed lanthanum concentrations and total suspended solids ratios

in the influent and effluent were also compared to determine how much of the tagged

suspended solids in the effluent originated from the influent. For the 8:1 slope of bed 3,

the suspended solids that were added to the influent were tagged with lanthanum, so they

could be traced going through the bed. The average adsorbed La/TSS ratio decreased

considerably between the influent and effluent, from 36,500 to 18,800. Because of this

decrease, influent suspended solids must have settled within the bed. Thus, 80.6% of the

added TSS settled on the bed. This percentage was calculated by subtracting the effluent

average adsorbed La concentration from the influent average adsorbed La concentration

and dividing by the influent average adsorbed La concentration times 100. This

percentage can be compared with the overall EMC TSS % removal of 50.4% for the 8:1

slope of bed 3, which does not distinguish between influent TSS and the TSS eroded

from the bed. In addition, 48.5% of the TSS in the effluent originated not from the

influent, but eroded from the bed itself, which was calculated by subtracting the effluent

mg La adsorbed/kg TSS ratio from the influent mg La adsorbed/kg TSS ratio and

dividing by the influent mg La adsorbed/kg TSS ratio times 100.

80.6% of the added TSS from the influent settled on the bed, and Cd, Cr, Cu, Fe,

Pb, and Zn, which all strongly sorbed in the influent, were captured within the bed by

sorbing to the TSS and then settling. Once these metals were settled within the bed, they

were available to be taken up by the roots and leaves; however, Cr, Fe, and Zn were

predominantly concentrated in the soil, while Cd, Cu, Ni, and Pb were available to be

taken up by the plant. This was similar to bed 1, except Cd also had significant

concentrations in the dissolved form for bed 1. Ni and Zn, which were the only metals

that had significant concentrations in the dissolved form, were likely directly taken up by

the roots and leaves, comparable to bed 1. Overall, it is more difficult to distinguish the

specific removal mechanisms within bed 3 since simulated stormwater concentrations were much lower than bed 1.

4   Conclusions

In this study, the efficiency of two vegetated biofilters to mitigate highway stormwater runoff was determined by comparing the influent contaminant concentrations with the effluent contaminant concentrations. Additionally, the removal mechanisms within the biofilters were determined. Once the removal mechanisms were established, the eventual fate of the contaminants within the beds was determined. Whether or not the contaminants primarily sorbed to the grass, soil, or roots helped establish their future mobility within the bed. Finally, how the metals were bound to the soil for bed 1 was ascertained through a sequential extraction procedure to further predict their future mobility. Conclusions from these vegetated biofilter tests include:

❖ From the high concentration experiments, percent removals from event mean concentrations were consistently high for the metals and total suspended solids over each slope, and average percent removals of metals ranged from 94.7% to 99.0%, with an average TSS percent removal of 92.8%. Cr and Pb had the highest average percent removals over all four slopes, which was probably because these were two of the metals entirely sorbed in the influent. A change in slope did not considerably affect percent removals, and these high percent removals proved the vegetated biofilter to be very efficient in mitigating simulated highway stormwater runoff with high contaminant concentrations.

❖ Based on the adsorbed La and TSS concentrations from bed 1, 99.4% of the added TSS to the influent settled on the bed, which represented near complete settling of the added TSS. Cu and Pb, which were both metals that strongly sorbed in the

influent, were removed by settling of the suspended matter. Cd, Ni, and Zn, which were predominantly in the dissolved form in the influent, were removed from the simulated stormwater by direct uptake into the plant. Also, 82.5% of the TSS in the effluent originated from erosion of soil from the bed.

❖ After Cr, Cu, and Pb adsorbed to the TSS in the influent and settled within the bed, they were also available to be taken up by the roots and leaves. Cr and Cu were predominantly taken up into the root portion, and Cu also had a significant amount of accumulation in the bed soil. Pb was the only metal that predominantly sorbed to the bed soil. Ni, Cd, and Zn were mainly taken up into the plant, with the highest mass accumulated in the roots, similar to Cr and Cu.

❖ Results from the sequential extraction procedure established that all of the metals except Cu gave highest concentrations in the Fe-Mn oxide and organic nonresidual fractions within the soil. Cu was unusual, because none of the fractions in the contaminated soil samples from bed 1 had concentrations above the blank soil samples. Because the majority of the metals were in the Fe-Mn oxide and organic fractions, they are not likely to become remobilized in the soil. These results mainly apply to Pb and Cd, which both significantly accumulated in the soil of bed 1. In general, the order of these concentrations within the soil was Fe > Pb > Ni > Zn > Cr > Cd > Cu.

❖ From the low concentration experiments, percent removals from event mean concentrations were much lower than the percent removals from the high concentration experiments. Similar to bed 1, a change in slope did not greatly

affect percent removals. Overall, Cu had the highest percent removals for each of the four tests, averaging 92.0%. The other metals ranged from 43.6% to 74.4%, with a much lower average TSS percent removal of 23.5%, much lower than bed 1. These low concentration experiments better represented actual highway storm events, and even though percent removals were lower, they correlated better with other biofilter studies.

❖ Based on the adsorbed La and TSS concentrations from bed 3, 80.6% of the added TSS to the influent settled on the bed. Cd, Cr, Cu, Fe, Pb, and Zn, which were all metals that were strongly sorbed in the influent, were removed by settling of the suspended matter. Ni and Zn were the only metals that were significant in the dissolved form. In addition, 48.5% of TSS in the effluent originated from erosion of soil from the bed, which was much lower than bed 1, which corresponds with the lower TSS percent removal of 50.4%.

❖ After Cd, Cr, Cu, Fe, Pb, and Zn adsorbed to the TSS in the influent and settled within the bed, they were also available to be taken up by the roots and leaves. Cr, Fe, and Zn had significant accumulation in the soil, while Cd, Cu, Ni, and Pb were available to be taken up by the plant, Cd and Cu predominantly in the roots, and Ni and Pb predominantly in the leaves. Ni and Zn, which were the two metals that were significant in the dissolved form, were most likely directly taken up by the plant since Ni had low accumulation in the soil, and Zn was the only metal that had significant accumulation in the grass, soil, and roots down the length of the bed.

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