THE FATE OF HEAVY METALS IN HIGHWAY STORMWATER RUNOFF:
THE CHARACTERIZATION OF A BIORETENTION BASIN IN THE MIDWEST

BY

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Abstract

The usual wear of automobiles and road surfaces deposits numerous environmental pollutants on roadways and parking lots, including heavy metals such as copper, zinc, lead, nickel and cadmium. During rainfall and snow events, these metals are washed from the paved surface in stormwater runoff or plowed onto shoulders where they are trapped in snow and ice. The metal contaminants carried in the stormwater runoff and eventual snowmelt often enter nearby surface waters and contribute to their degradation as well as threaten the survival of aquatic organisms at all levels of the food chain. This pathway of heavy metal contamination has become a significant concern due to increased urbanization and roadway construction.

Bioretention is a best management practice used to remove heavy metals and other pollutants from stormwater runoff and snowmelt that utilizes the inherent physical and chemical properties of soil compounds. As runoff passes through a bioretention basin, heavy metals are deposited in mulch and soil layers through processes including sedimentation and filtration as well as adsorption and complexation to soil compounds such as organic matter, clay and metal oxides. Numerous factors affect the retention of these metals, including the use of deicing salts. Deicing salts in highway runoff are thought to hinder heavy metal removal by interfering in the chemical attraction between metals and soil compounds.

Investigations, including a pilot column study and field experiments at an existing bioretention basin in Johnson County, Kansas, documented the effectiveness of bioretention in removing elevated levels of heavy metals, particularly copper, from highway stormwater runoff in the Great Plains region. Total suspended solids (TSS) and dissolved and total metal concentrations were analyzed in influent and effluent runoff samples from the field bioretention basin. The column study included tracer and retention tests that investigated water and dissolved copper retention, respectively, in two columns.

Removal rates of particulate-associated metals (based on concentration) from runoff samples were 90 percent or greater for lead, nickel, copper, cadmium and zinc.

From March to November 2007, the bioretention basin removed an average of 33 percent of total copper and 47 percent of dissolved copper from runoff samples. The TSS removal rate was 80 percent. Short-term dissolved copper retention was achieved in the laboratory column study. The two columns retained 91 and 94 percent of dissolved copper from the influent solution during the final tests.

Table of Contents

Chapter 1

Introduction

As increasingly tight regulations on point source pollutants become established, focus is turning towards the effects of non-point source pollutants on surface water quality. Stormwater runoff and snowmelt from highways and paved parking lots are a significant contributor of non-point source pollutants, including heavy metals. These metals are deposited on roadways and paved surfaces through the normal wear of automobiles and are then carried in runoff to surface waters during storm events. Heavy metals are also transported in snowmelt when snow plowed onto the shoulder of roadways melts during warmer temperatures. Due to increased urban development and construction of road networks, stormwater runoff management has become a greater priority, as a larger volume of precipitation cannot penetrate into soil and becomes runoff (Durand et al., 2004; Hsieh & Davis, 2005).

In a given watershed, stormwater runoff volume increases linearly with the percentage of impervious surface (Schueler, 1987). Long-term stream flow monitoring and hydrologic models show that developed suburban areas have 2 to 4 times the annual runoff of pre-development areas, partially due to construction methods that increase soil compaction and reduce infiltration (Burges et al., 1998). In high density areas, annual runoff volume levels can be 15 times greater than pre-development levels (Spinello & Simmons, 1992). In a watershed near Indianapolis, Indiana, the urban area increased by 18 percent between 1973 and 1991, resulting in an 80 percent increase in annual urban runoff volume (Bhaduri et al., 2000).

When stormwater flows over roadways and parking lots, it picks up trace heavy metals, including copper (from wear of bushings and bearings), zinc (from tire attrition), lead (from paint marking the rights-of-way), nickel (from steel parts attrition) and cadmium (from tire attrition and diesel oil) (Amrhein et al., 1992). Zinc, copper, cadmium and lead levels in highway stormwater runoff and snowmelt from heavily traveled roadways are often above ambient background levels and can exceed U.S. Environmental Protection Agency (EPA) and state surface water

discharge criteria on an event basis (Sansalone & Buchberger, 1997). Heavy metals are persistent pollutants that can be especially concentrated in runoff when intense, short-duration summer storms follow a lengthy, dry period during which these contaminants have accumulated on road surfaces (Munger et al., 1995). Contaminant metals also reach very high levels in snowbanks, particularly in regions that receive numerous, consecutive snowfall events (Sansalone & Glenn III, 2002). Snowmelt concentrations of heavy metals can be several orders of magnitude higher than those in stormwater runoff (Sansalone & Buchberger, 1996). Some scientists have estimated that highway runoff contributes 35 to 75 percent of the total metal contaminant inputs to receiving waterways (Ellis et al., 1987).

Between 1979 and 1983, the EPA created the Nationwide Urban Runoff Program (NURP) to evaluate the quality of urban stormwater runoff. Table 1 shows concentrations of a few major contaminants identified by NURP and shows that urban runoff tends to have elevated levels of these contaminants compared to concentrations typically found in runoff from undeveloped or agricultural lands (USEPA, 1983). In the Indiana watershed study, urbanization caused annual concentrations of copper, zinc and lead to increase by more than 50 percent (Bhaduri et al., 2000).

Table 1: Median Event Mean Concentrations of Contaminants in Urban Runoff (adapted from [USEPA, 1983]). Values in μg/L except as noted.

Contaminant	Residential	Commercial	Non-Urban
TSS (mg/L)	101	69	70
Total Pb	144	104	30
Total Cu	33	29	---
Total Zn	135	226	195

Heavy metals do not break down to less harmful compounds, and can remain in the local environment for a prolonged period of time. As a result, even small concentrations in runoff may result in long-term accumulation of heavy metals to levels that could contribute to the degradation of surface water quality in streams,

ponds and lakes and threaten aquatic organisms at all levels of the food chain. Heavy metal ions are extremely mobile, and, therefore, readily available to aquatic biota. Ionic species can be detrimental to the recipient, especially in the case of cadmium (Dean et al., 2005). When the Final Rule for Phase II Storm Water under the National Pollutant Discharge Elimination Systems (NPDES) regulations was circulated in October 1999, environmental scientists and professionals at the national regulatory level began to focus on the impacts of metal contaminants in roadway runoff. Soon after, state and local departments of transportation began to focus on the development of treatment solutions for stormwater runoff (Glenn III & Sansalone, 2002).

Due to the variable nature of stormwater quality, both spatially and temporally, it is difficult to set and enforce concentration-based limits on stormwater runoff. Therefore, the NPDES program requires permitted entities to create and implement stormwater pollution prevention plans that utilize best management practices to prevent the contamination of stormwater and receiving waters. Best management practices include a variety of structures that may perform pollution prevention and/or treatment activities (USEPA, 2000).

Bioretention basins are a type of best management practice that is constructed alongside roadways and adjacent to parking surfaces to retain and treat stormwater runoff and snowmelt from urban landscapes. These basins utilize the physical, chemical and biological properties of sediment, microorganisms and vegetation to remove contaminants from runoff. They also store water for a period of hours or days allowing runoff to enter receiving waters at a slower rate. Initially, bioretention basins were designed to decrease flooding associated with impermeable sites in urban areas, but more recently, basins have been increasingly used to reduce contaminant concentrations in stormwater runoff and snowmelt before it enters surface waters.

Water quality enhancement through bioretention occurs when contaminant metals are removed from stormwater runoff through physical and chemical processes including sedimentation, filtration, adsorption and complexation. Particulate-bound

metals are removed as runoff filters through mulch and sandy soil layers. Dissolved metals are trapped when they repartition through physiochemical transformation reactions to vegetation and sediment constituents (organic matter, clay and metal oxides), including adsorption and complexation (Davis et al., 2003). The resulting "treated" runoff is then released from the basin and will eventually reach surface waters. Bioretention basins have proven effective in the removal of low levels of metal contaminants in large volumes of water; however, recent research suggests that the ability of sediments to trap heavy metals may be compromised by the presence of deicing salts from winter road maintenance. Deicing salts have been shown to alter the physical and chemical relationship between heavy metals and sediment compounds in bioretention basins, thus affecting the performance of bioretention systems and increasing metal loading to receiving waters (Weiss et al., 2006; Durand et al., 2004).

Statement of the Problem

Laboratory and pilot-scale experiments suggest that bioretention is an effective system for the removal of heavy metal contaminants in highway stormwater runoff. However, more data are needed to assess their performance in the climate, meteorological and environmental conditions and traffic patterns commonly found in the Great Plains region. The purpose of this study was to examine heavy metal loading in highway stormwater runoff in the Kansas City metropolitan area and the heavy metal removal capacity of an existing bioretention basin located in Lenexa, Kansas. Water quality characteristics including pH, conductivity, TSS and total and dissolved metal concentrations were evaluated in influent and effluent stormwater samples. Laboratory soil columns were constructed to further test dissolved heavy metal removal through bioretention.

Definition of Terms

The following terms are defined to clarify the meaning and scope of this study (Mid-America Regional Council, 2008; Winogradoff, 2002):

Adsorption. Ionic attraction that holds a gaseous, liquid or dissolved substance to a solid surface.

Best Management Practice. Structural or non-structural solutions to prevent or control the discharge of stormwater pollutants and minimize runoff to U.S. waters.

Bioretention. Upland water quality control practice that utilizes the chemical, biological and physical properties of plants, microbes and sediment for the removal of pollutants from stormwater runoff.

Complexation. Formation of molecules through the combination of ligands and metal ions.

Deicing Salt. Salt compounds applied to roadways to decrease the freezing point of snow and ice.

Overflow Structure. Device for releasing stormwater when the inflow to a bioretention basin exceeds the designed outflow.

First Flush. Initial quantity of runoff from a storm or snowmelt event that often contains elevated contaminant concentrations.

Filtration. Removal of particles from stormwater runoff as it passes through the mulch and soil layers of a bioretention basin.

Impervious Surface. Surface that prevents water infiltration.

Sedimentation. Settling of suspended solids on the surface of the mulch or sediment layers due to the decreased pace and ponding of runoff inside a bioretention basin.

Snowmelt. Runoff that results after the melting of plowed snow.

Stormwater Runoff. Water that flows over impervious surfaces, such as roadways, during and after storm events

Total Suspended Solids. Suspended matter in stormwater runoff that can be removed by a 0.45 μm nylon filter.

Chapter 2

Review of the Related Literature

The behavior and eventual fate of heavy metals in bioretention basins depend on the physical nature of the metal (dissolved or particulate) and its affinity for and reactivity with sediment compounds. Dissolved heavy metal species are inherently very mobile; however, they readily complex with sediment constituents, such as organic matter and clay, through ion exchange reactions. Particulate species are much less mobile and are typically deposited through sedimentation and filtration. The movement of heavy metals through bioretention basins is also affected by chemical characteristics of the stormwater/soil solution, such as salinity, which is altered by the presence of deicing salts.

Bioretention

Bioretention is an upland method of water quantity and quality control that utilizes the physical, chemical and biological properties of soils, microbes and vegetation to remove pollutants from stormwater runoff (Winogradoff, 2002). Bioretention basins are shallow depressions constructed near impervious surfaces, including rooftops, roadways and parking lots and typically only require about five percent of the total impervious area to be effective. Compared to other best management practices, bioretention demonstrates some of the highest pollutant and nutrient removal efficiencies. As runoff approaches a basin, its velocity decreases as it passes over or through a pretreatment device and is then distributed within a ponding area (Mid-America Regional Council, 2008). Pollutant removal occurs as the runoff infiltrates the mulch and soil layers, through processes including sedimentation, filtration, volatilization, ion exchange, adsorption, decomposition, bioremediation and phytoremediation (Winogradoff). After passing through the soil matrix, the "treated" runoff is collected by an underdrain system that releases the water to a stormwater sewer system or directly to receiving water (Mid-America Regional Council). Only those processes and components of bioretention that are

relevant to the completed field and laboratory column studies will be further discussed.

Components

The standard components of a bioretention basin are selected to encourage and achieve certain physical and biological processes, as well as to naturally self-perpetuate to improve the effectiveness of these processes. Components blend and overlap with time through root and plant growth, organic decomposition and the growth of macro and microorganisms. This blending lends to the development of a natural soil horizon and a stable configuration that will increase the life span of the system (Winogradoff, 2002).

In the ponding area, at the surface of a filter layer composed of a sandy soil medium, is a layer of mulch, which acts as a filter for solids suspended in the pooled runoff. The mulch layer provides a level of pretreatment, through filtration and sedimentation, before the runoff enters the actual soil matrix. The mulch layer also facilitates organic decomposition and the growth of microorganisms as well as adsorption and the bonding of heavy metals. Studies at the University of Maryland have exhibited extensive heavy metal entrapment in the mulch layer through organic complexation (Winogradoff, 2002). The mulch layer is often the largest sink for heavy metals in stormwater runoff and has demonstrated 74 percent removal of zinc in a study by Muthanna et al. (2007a).

After stormwater has passed through the soil medium and the heavy metals have had a chance to complex with or adsorb to various sediment compounds (these processes are discussed in length in the following paragraphs), the "treated" runoff reaches a perforated, horizontal underdrain or outlet pipe buried a few feet below the surface. The underdrain provides a discharge point for the runoff and helps control infiltration rates by increasing the ability of the soil to drain quickly (Winogradoff, 2002). Occasionally, strong storms cause high stormwater flow events and the volume of runoff entering a basin is more than the ponding area can contain or an underdrain can effectively drain in an adequate period of time. For these situations,

bioretention basins often contain an overflow structure. When water in the pooling area reaches a depth of usually one foot or more, the excess water will enter the overflow structure where it is directed outside of the bioretention basin in a way that will not cause erosion to surrounding soils (Mid-America Regional Council, 2008).

Removal Capacity

In a bioretention study performed at the University of Maryland, two basins were monitored to quantify water quality improvements to stormwater runoff from a parking lot. Twelve data sets were analyzed for zinc concentrations, and nine data sets were analyzed for copper and lead concentrations. With each set, the median output metal concentration was lower than the input concentration, indicating successful water quality improvement. The percent removal of copper, lead and zinc were 76 percent, 57 percent and 83 percent, respectively (Davis et al., 2003). Another study at the University of Maryland showed improved heavy metal removal efficiency with increased soil depth. The following efficiencies were exhibited at depths of one and three inches, respectively: 90 to 93 percent for copper, 93 to 99 for lead and 87 to 99 for zinc (Winogradoff, 2002).

Properties of Contaminant Heavy Metals

The majority of studies analyzing highway runoff and snowmelt show that of the total heavy metal composition, the majority of metals are found as particulates. Forty to fifty percent of particulate mass is from pavement wear, and 20 to 30 percent is from tire wear. The remaining particulates originate from engine and brake wear and urban atmospheric deposition (Kobriger & Geinopoles, 1984). The particulate size distribution in urban highway runoff ranges from <1 to 9,500 μm (Muthanna et al., 2007b). Copper, zinc, lead and nickel, in particular, are carried into bioretention basins largely bound to particulates and are thus easily entrapped in the mulch and soil layers through sedimentation and filtration. In a study conducted by the California Department of Transportation (DOT) over a four-year period, the mean

total metal concentrations of copper, zinc, lead and nickel at 34 highway sampling sites were 33.5, 187.1, 47.8 and 11.2 μg/L, respectively (Kayhanian et al., 2007).

Of all the heavy metals commonly found in highway runoff, copper, zinc and cadmium are the most likely to exist in the dissolved state. The following mean dissolved metal concentrations were recorded in the California DOT study: 14.9 μg/L Cu, 68.8 μg/L Zn and 0.24 μg/L Cd (Kayhanian et al., 2007). Ellis et al.'s (1987) research on urban stormwater runoff in London found that dissolved portions of lead, copper and zinc in runoff constituted 1-10 percent, 20-40 percent and 30-50 percent of all metal constituents, respectively.

These metals travel to bioretention basins along with a heterogeneous mixture of organic and inorganic ligands that they readily complex with through ion exchange reactions (Lee et al., 2000). These ligands include bicarbonate, chloride, nitrate, phosphate, sulfate, iron sulfides and dissolved organic matter. Metals can also form oxide and hydroxide complexes. Heavy metal adsorption on these organic and inorganic constituents exhibits an ageing effect that typically causes solubility and extractability to decline with time (Swift & McLaren, 1991). Metal complexes boost the tendency for metal precipitation which means the heavy metals can be more easily trapped in sediments through sedimentation and filtration (Dean et al., 1995).

Adsorption and Ion Exchange

When sediment constituents contain zones of negative charge, which often surround clay particles and organic matter, they can bind and release positively charged ions from the soil solution and are said to have cation exchange capacity. Depending on the pH of a soil solution, H^+ ions may be more or less strongly bound to the hydroxide and organic acid groups found on clay particles and organic matter, respectively. Typically, a significant number of H^+ ions are dissociated, leaving negative charges that can attract and bind other cations such a Ca^{2+}, Mg^{2+}, Al^{3+}, Na^+ and heavy metals (Sansalone & Buchberger, 1997). Research by Durand et al. (2004) has shown that cadmium is readily found in the "exchangeable" phase, when a metal

is complexed through cation exchange. Lead is another metal that undergoes exchange complexation, and it tends to displace sodium and calcium on charged surfaces (Scott & Wylie, 1980). In samples of urban highway runoff, the majority of zinc, copper and lead ions are bound to particulates less than 100 μm, suggesting that a portion of retained metals are too small to settle out through mechanical filtration and that specific and non-specific adsorption is a dominant process in heavy metal removal through bioretention (Muthanna et al., 2007b).

Clay Minerals

Aluminosilicate clays are secondary minerals with crystalline structures. The two types of layers that characterize clay structures are silicon layers and layers dominated by aluminum, iron and magnesium. These layers are held in place by shared oxygen atoms. Silicate clay minerals possess a net negative charge that attracts cations, including heavy metal ions, dissolved in the soil solution. This negative charge results from ionic substitutions within silicate clays, and because it arises inside the crystalline structure, it cannot be neutralized through covalent bonding of cations and is said to be permanent. Negative charge on clays is also found at the edges of particles where hydroxide groups are found. Although the high, specific surface area of clays improves their capacity to trap metal pollutants, some clays also have inherent limitations as heavy metal adsorbers, including low loading capacity, small metal-ion binding constants and low metal selectivity (Schlesinger, 1997).

Clay minerals concentrate heavy metal ions in sediments through surface ion exchange reactions and by formation of inner- and outer-sphere complexes with Si-O and Al-O groups (Liebens, 2001). Copper and zinc adsorb to clay particles as Cu-OH and Zn-OH complexes through ion exchange reactions which have been observed on the clay minerals, kaolinite and chlorite (Celis et al., 2000). In a study that examined heavy metal adsorption on clay particles, 30 percent of the added amount of zinc adsorbed to clay surfaces (Liebens). According to a study by Schmitt et al. (2002),

particulate concentrations of heavy metals are directly correlated to the clay content of sediments.

Organic Matter

Anaerobic decomposition occurs frequently in bioretention basins because the sediment is intermittently saturated due to wet/dry cycles. When soils are saturated, the pore spaces are filled with water, inhibiting the diffusion of oxygen from the atmosphere into these pores, and any oxygen already in the soil is quickly depleted by microorganisms using it for aerobic respiration. Anaerobic decomposition is often incomplete and results in the accumulation of significant amounts of organic carbon in bioretention basin sediments (Schlesinger, 1997).

Humic and fulvic acids play an important role in the cycling and accumulation of heavy metals in sediments (Gier & Johns, 2000). The surface of these acids are composed of numerous chains of carboxyl and hydroxyl functional groups that often dissociate in solution, allowing the organic acids to form complexes with heavy metal cations (Nriagu & Coker, 1980). Metal binding by organic solids (humus) occurs through complexation of a metal with a deprotonated ligand, such as a phenolic, carboxylic, sulfhydryl or amine group. Fulvic acid, the soluble fraction of organic matter, has such a strong affinity for lead, nickel and copper that it promotes dissolution of these contaminant metals from adsorption sites on clay minerals. It also suppresses heavy metal adsorption on silicate minerals and iron and aluminum oxides (McBride & Hendershot, 1997). Generally, metals preferentially accumulate on humic acids versus fulvic acids (Gier & Johns).

The majority of copper in bioretention basin sediments is associated with organic matter, as it forms stable organic complexes, particularly with humic substances. The affinity of copper for organic matter was documented by Durand et al. (2004) with respect to sediments of different origins. In a study that introduced copper and zinc to a column soil matrix containing dissolved organic matter, the subsequent formation of organometallic complexes indicated that the sorption

frequency for zinc is low while the majority of copper was bound to the organic matter (Muthanna et al., 2007b). The McBride and Hendershot (1997) study further showed that the high affinity relationship between copper and dissolved organic matter can also result in the leaching of copper due to the increased solubility of copper when it is bound to dissolved organic matter. In fact, the presence of dissolved organic matter is a more important factor in the retention of copper than the form in which copper enters the soil media. Lead solubility is also correlated with organic matter content, while cadmium solubility is found to be negatively correlated to the content of organic matter in soil.

Iron and Manganese Oxides

In bioretention systems with intermittently flooded sediments, iron and manganese may be present in different oxidation states. Soluble Fe^{2+} and Mn^{2+} are found in high concentrations in flooded, low-redox sediments while insoluble Fe^{3+} and Mn^{4+} dominate in the presence of oxygen, in dry, aerated soil or at the water-sediment interface. In oxygenated sediment layers, iron and manganese often precipitate as crystalline oxide and hydroxide minerals (Schlesinger, 1997).

Iron and manganese oxides are not especially strong adsorbers of most heavy metals under acidic conditions, but humic matter adsorbed on oxides increases metal adsorption at low pH (Zachara et al., 1992). The sorption of lead and cadmium onto the surface of mineral oxides is primarily dominated by traditional cationic exchange (Nriagu & Coker, 1980).

Deicing Salts

In most areas that experience cold winters, especially across the northern U.S. "snow belt", roadways, parking lots and sidewalks are treated through the application of deicing salts to discourage the formation of slippery, icy surfaces by decreasing the freezing point of water. As road systems expand due to increased urbanization and the growth of suburban areas, snow and stormwater are exposed to increasing amounts of deicing salts.

The most commonly used deicing salts are sodium chloride (usually applied as a rock salt) and calcium chloride (applied as a liquid or granule) (Novotny & Olem, 1994). The quantity of deicing salts used in the United States every year usually ranges between eight and eleven million tons depending on the severity of the winter (Norrstrom & Bergstedt, 2001).

Snow plowed onto a highway shoulder is directly exposed to traffic and winter road maintenance practices; so in a very short period of time, significant levels of heavy metal pollution and deicing salts can accumulate. This accumulation is compounded by the porous matrix of snow, the high surface area of snow and ice crystals, and freeze/thaw cycles (Federal Highway Administration, 1999). Due to the significantly longer residence time of snow compared to stormwater, heavy metals in snow are more likely to partition towards the particulate phase (Sansalone & Glenn III, 2002).

In areas where deicing salts are not used, highway runoff can contain salt concentrations as low as 10 ppm (Federal Highway Administration, 1999). In the Mammoth Lakes and Lake Tahoe areas in California, by contrast, the average chloride concentration in runoff during the winter months is 8 mmol/L, and a maximum of 58 mmol/L has been recorded (Goldman & Hoffman, 1975). Salt levels in snowmelt vary with the quantity of chemicals applied and the intensity of subsequent rainstorms or snowmelt events (Paddock & Lister, 1990). According to Åsteböl et al. (1996), 75 to 90 percent of the salt added to roadways eventually enters the roadside environment through snowmelt or splashing and is usually deposited within 10 meters of the roadway. Chloride ions from deicing salts are also known to corrode motor vehicles and bridge structures which can result in increased heavy metal concentrations on the road surfaces and subsequently in snowmelt (U.S. Department of Transportation, 1999). This increased heavy metal pollution and chloride anions and associated calcium and sodium cations from deicing salts eventually contaminate superficial soils and surface waters (Sansalone & Glenn II, 2002). NaCl is highly soluble in water and easily percolates through permeable

sediment to the subsurface where heavy metals are trapped in bioretention basins (Norrstrom & Bergstedt, 2001).

The normal use of deicing salts often causes an increase in the salinity of receiving environments due to the increased presence of chloride ions, which travel easily because they do not participate in chemical reactions (Paddock & Lister, 1990). Increases in the salinity of runoff affects heavy metal partitioning and is thought to increase metal mobilization in bioretention basins (Glenn III & Sansalone, 2002). The chloride and acetate ions from deicing compounds such as NaCl and calcium magnesium acetate (CMA) trigger the release of metals from ion exchange sites on sediment constituents in the top 20 cm of the soil column (U.S. Department of Transportation, 1999). In a study that looked at metal mobilization in roadside soils subjected to varying concentrations of deicing salts (NaCl and CMA), high-concentration salt solutions mobilized more cadmium than low-salt solutions. These results support hypotheses that heavy metals common to highway surfaces may be mobilized through complexation with acetate and chloride by a cation exchange process.

In addition to anion activity, salt cations (Mg, Ca and Na) displace heavy metals from cation-exchange sites on sediments, resulting in elevated concentrations of heavy metals and other cations in surface waters. Calcium and magnesium ions are better competitors for exchange sites than sodium ions. In addition, there is some evidence that acetate forms stronger ligand-metal ion pairs than chloride (Amrhein et al., 1992). The strong bond that forms between acetate ions and heavy metals and the superior displacement abilities of calcium and magnesium ions, suggest that the use of CMA may be more detrimental than NaCl in the release of heavy metals to surface waters. The Glenn III & Sansalone study (2002) lends support with the finding that cadmium mobilization is strongly associated with sodium, calcium and chloride ions in roadside soil samples.

Another factor that contributes to metal mobilization is organic matter mobilization which increases when exposed to runoff with high salinity, especially

when the source is NaCl. Humic and fulvic acids are commonly mobilized under conditions of high exchangeable sodium and low electrolyte concentrations (Amrhein et al., 1992). In the Amrhein et al. study that used columns containing roadside soils to investigate metal mobilization, the concentration of copper, lead, nickel and iron in the leachate solutions increased when the salt concentration was increased, suggesting competitive exchange and ligand complexation between the salt ions and the native organic matter. Soluble copper has a stronger affinity for soluble organic matter compared to lead and zinc, and this attraction is stronger for free metal Cu^{+2} and organic matter than with total soluble copper and organic matter, suggesting that free metal activity is controlled by sorption (McBride & Hendershot, 1997). Another study found that cadmium was the only tested metal that did not follow this trend, as cadmium is only weakly associated with organic matter (Glenn & Sansalone, 2002). Some research has contradicted this trend and suggested that calcium salts decrease the solubility of copper-organic complexes and, thus, their mobility (Römkens, 1993).

Summary

Numerous studies have shown that bioretention is an effective practice for the removal of heavy metal contaminants associated with highway stormwater runoff and snowmelt. In addition to sedimentation and infiltration, metals are trapped in the soil layer through the exchange of ions with clay, organic matter and metal oxides. Dissolved ions from deicing salts can interfere with the adsorption and complexation of metal contaminants through competitive exchange at adsorption sites, resulting in increased metal mobilization through bioretention basins.

Chapter 3

Field Study Location and Methods

<u>Purpose</u>

The performance of bioretention systems depends on geographical variables including traffic type and frequency, average rainfall, frequency and duration of storms, and the types of surrounding vegetation and soil. Therefore, the construction of these systems must account for local climate, meteorological, and environmental factors. Compared to other regions of the country, the Great Plains typically have shorter, more intense storms, and soils found in the Midwest typically have a higher clay and lower sand content than coastal soils, which slows drainage and causes longer periods of standing water (Peltier et al., 2008).

As studies have shown, bioretention basins have the potential to significantly improve the water quality of stormwater runoff from highways and paved surfaces. However, relatively little research has been conducted to date to characterize the composition and treatment of highway stormwater runoff, especially in regards to dissolved metals, under conditions commonly found in Kansas and generally representative of the Great Plains region. In order to obtain additional information on these issues, a monitoring program was implemented at an existing bioretention basin in Lenexa, Kansas, and soil columns were utilized in the laboratory. The purpose of the field study was to collect data on total and dissolved heavy metal loading in highway stormwater runoff, under local hydrological conditions, and on the heavy metal removal capacity of a newly installed bioretention basin. The soil columns were constructed to investigate dissolved metal removal in bioretention-type soil complexes on a small-scale. Information gained through this study could greatly contribute to the development of construction and management plans for bioretention systems in the Great Plains region.

The field study took place at a bioretention basin near Lenexa, Kansas in Johnson County, approximately 0.25-mile north of Highway K-10 (Figure 1). The basin has a surface area of approximately 0.1 acres, and it receives runoff from a 0.83-acre drainage area of which approximately 0.33 acres is impervious surface. Stormwater runoff from Mize Boulevard, a four lane arterial highway, enters the basin through a storm sewer and exits directly into Mize Lake, a 7.5-acre lake created in 2004. During the sample collection period, extensive housing development was occurring to the west of Mize Boulevard and created construction-vehicle traffic. Stormwater sampling took place after rainfall events from December 2006 through November 2007. Samples were not collected for every rain event during this period, most notably those events that occurred within 24-48 hours of each other.
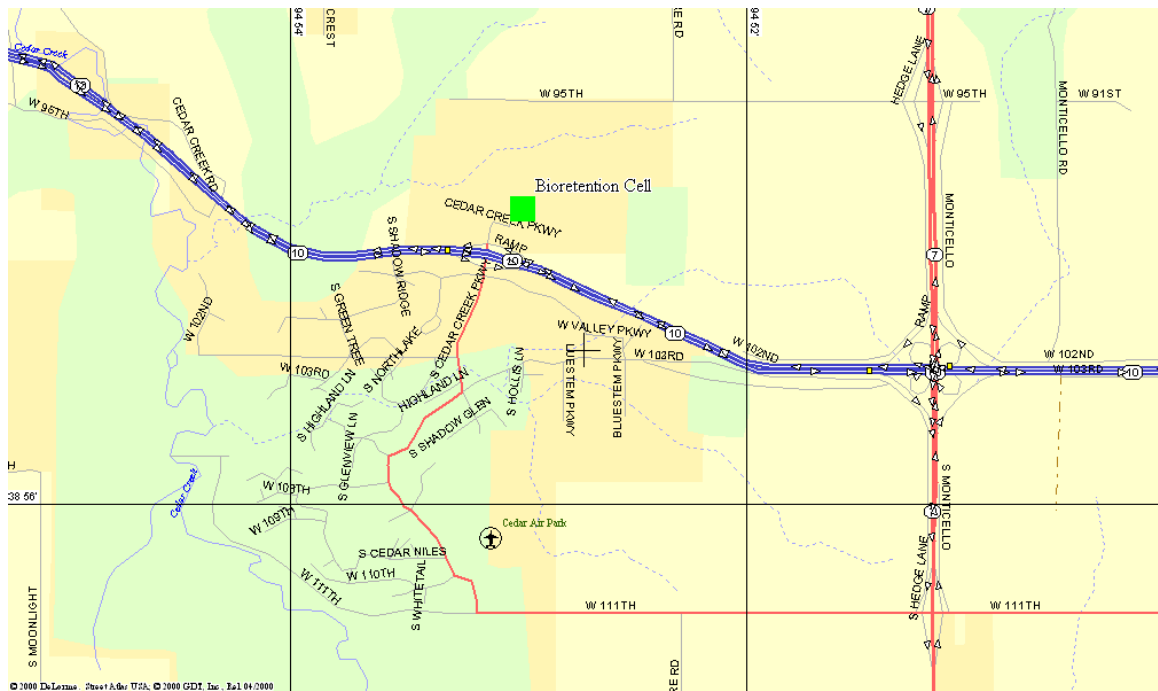

Figure 1. Map showing bioretention basin location near Lenexa, Kansas in Johnson County.

Basin Description

After a storm event, runoff from Mize Boulevard flowed through a tube secured to the road pavement into a collection bottle placed in a mesh trap suspended in the sewer drain (Photos 3 and 4). The sewer drain is located just uphill on the other side of the pavement walkway depicted in Photo 1. Runoff not collected in the bottle filters through the mesh trap, flows through the length of the concrete storm sewer and empties directly into the ponding area of the bioretention basin (Photo 2). At the surface of the ponding area is a 2.5-inch wood chip mulch layer which overlays a 2.6-foot sandy soil layer. When collection started in December 2006, the basin was newly constructed, and vegetation was only established primarily along the perimeter of the basin. By fall 2007, approximately 80 percent of the basin was covered with emergent wetland vegetation.

The underground drain pipe for the basin empties the "treated" stormwater into the overflow structure which is located at the south end of the basin (Photos 1 and 5). Stormwater effluent then flows through a surface-level outfall pipe and is discharged into Mize Lake. During intense, lengthy storms, when the water in the ponding area reaches a depth between one and two feet, the water by-passes the underground drain pipe route and empties directly into Mize Lake via the overflow structure. The darker, copper-colored surface layer in Photo 6 is a 1 to 2 millimeter bio-film which also coats the inside of the underground drain pipe.

The bioretention basin experienced numerous wet/dry cycles during the collection period. After a significant storm event, water remained in the ponding area for an average of two to three days, but often longer during the winter months. The soil matrix was moist during most of the year, especially two or three inches from the surface.

Collection Methods

Water samples were collected at three locations within the bioretention basin. The first location was in the storm sewer entrance at the street surface. Runoff flowed through a tube from the street into a collection bottle placed in the mesh trap.

Samples collected at this location will be referred to as "sewer samples" in Chapter 4. The second collection site was at the storm sewer outfall, right before the stormwater emptied into the ponding area and contacted the sediment matrix. These samples were captured by a Teledyne ISCO 3700 programmable auto-sampler. A 4210 flow meter connected to the auto-sampler used an ultrasound device to detect changes in the distance between the detector and the floor of the storm sewer due to the flow of stormwater. When the runoff depth reached an approximate depth of 1 inch, the auto-sampler was triggered to collect samples. The sampler was set to collect 500 mL samples every five minutes for as long as conditions were met or until 16 samples were collected, resulting in a single, composite sample for each storm event. A one-liter, representative sample was then taken from the large, composite sample and kept for analysis. Samples collected by the auto-sampler will later be referred to as "auto-sampler samples." The third collection site was at the underground drain pipe inside the overflow structure. "Treated" runoff was collected at this location right before it flowed into Mize Lake. Samples were collected in a pan positioned under the drain pipe which was then emptied into a collection bottle. These samples will be called the "drain pipe samples."

Starting in December 2006, initial samples were collected from the sewer and drain pipe for contaminant screening. When the auto-sampler was installed in March 2007, runoff samples were collected from all three locations. From March 2007 to November 2007, 23 samples were collected from both the sewer and drain pipe locations. Due to operational issues with the auto-sampler, only 15 samples were collected by the auto-sampler during this period. Table 2 (Appendix I) contains TSS and dissolved and total copper concentrations from all collected samples. Rainfall data was collected from Johnson County ALERT rain gage stations located within three miles of the field site. The cumulative rainfall prior to each sample collection date and tabulated runoff curve values based on ground cover in the watershed were used to determine the runoff data (Figure 2).

Photo 1. Bioretention cell and Mize Lake in March 2007.

Photo 2. Ponding area of cell in March 2007.

Photo 3. Mesh trap in storm sewer holding collection bottle.

Photo 4. View of sewer from road and collection tube.

Photo 5. View of overflow structure at far end of bioretention basin close to Mize Lake.

Photo 6. Inside of overflow structure showing drain pipe and orange biofilm.

Laboratory Methods

In addition to determining the total and dissolved concentrations of heavy metals in influent and effluent samples, water quality factors, including pH, conductivity and TSS, were also measured to further characterize highway stormwater runoff in northwestern Kansas. For each collected sample, pH measurements were taken at the site with a Thermo field meter. Samples were then transported to the laboratory where they were stored at 4 °C until further analysis. TSS tests were conducted according to the 2540D procedure in <u>Standard Methods for the Examination of Water and Wastewater</u> (Clesceri, 2005).

For dissolved metal analysis, water samples were passed through a 0.45 μm nylon filter and preserved with trace metal grade, concentrated nitric acid. Nitric acid digestion in a SCP Science DigiPrep MS digestion block, at a 10:1 sample:acid ratio, followed by filtration through a 0.45 μm nylon filter prepared the samples for total metal analysis. Inductively-coupled plasma mass spectrometry (ICP-MS) was used to determine both dissolved and total metal concentrations for the following metals typically found in highway runoff: copper, zinc, cadmium, nickel and lead. The ICP-MS method was used to screen the initial winter 2006 and spring 2007 samples. Based on these initial results, only copper was analyzed in subsequent samples. These samples were analyzed through flame or graphite-furnace atomic absorption depending on the concentrations encountered.

Chapter 4

Results of Field Study

Precipitation and Runoff

Rainfall in 2007 was greater than usual in northeastern Kansas; the Lenexa area received approximately 110 percent of the yearly average rainfall (Peltier et al., 2008). Rainfall data from 20 storm events sampled between April and October 2007 are depicted in Figure 2, which shows the collection date and the cumulative rainfall and runoff levels since the last collected sample. On nine sampling days, more than 1.0 inch of rain had fallen since the previous sample was collected. It was initially thought that the highest total copper concentrations in sewer samples would follow periods of minimal rainfall because copper would have a greater chance of accumulating on the road surface. However, the data indicated no correlation between total metal concentration and the number of days between storm events or between total metal concentration and runoff volume.
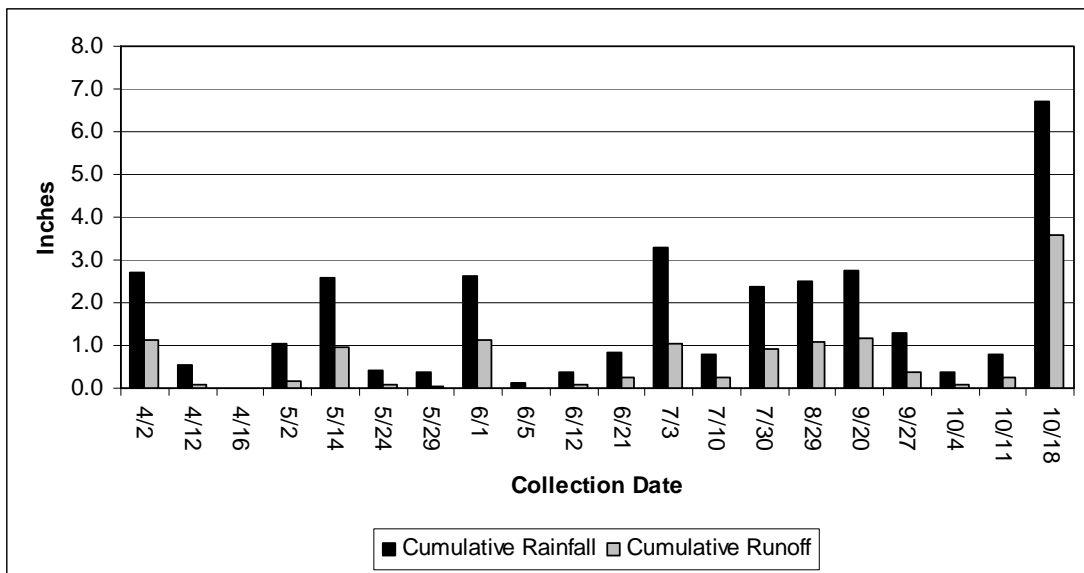

Figure 2. Cumulative rainfall and runoff since last collected sample.

Water Quality Parameters

Table 3 provides information on the water quality parameters tested on the stormwater runoff at all three collection sites. The average and median pH of samples collected at the sewer and auto-sampler are very similar, while the pH of drain pipe samples was lower on average. These results are similar to those from the Muthanna et al. (2007b) study which showed lower pH values in outflow samples compared to inflow samples from a bioretention basin in both April and August. This study also investigated metal solubility and found that the soluble fraction of lead and zinc were more correlated with pH than soluble copper. Laboratory studies testing heavy metal adsorption to sandy loam soils have shown that zinc adsorption occurs best at pH 6-8, while copper and lead tend to have the highest adsorption rates at pH 5-8 (Davis et al., 2001).

The conductivity values in Table 3 do not include measurements from December 2006 and 2007. Conductivity values of sewer samples collected in December were, on average, 197 times greater than typical values for samples collected during the rest of the study. Typical December values for drain pipe samples were 28 times greater. These elevated values are due to the presence of dissolved deicing salts in the highway surface runoff. On average, the auto-sampler values were almost 40 percent less than the sewer values, while drain pipe values were approximately 76 percent greater than the sewer values. The greater conductivity values in the drain pipe samples could be explained by the evaporation of runoff as it passed through the bioretention basin, resulting in the same total salt mass in a smaller volume of water. Another possible explanation is that the soil was leaching anions, which would cause increased conductivity values.

Comparing samples from individual storm events reveals that TSS values in auto-sampler samples are, on average, 80 percent less than those in sewer samples. This value is strongly influenced by a single storm event in July during which the TSS concentrations at both sampling sites were almost equal. Excluding this storm from the results increases the average TSS removal to 85 percent. The average drain

pipe sample, on the other hand, has a TSS value that is only about 10 percent less than the mean auto-sampler sample. These results suggest that the majority of TSS is removed by the mesh trap in the storm sewer entrance and not through sedimentation in the mulch or soil layers. Table 3 shows that the highest TSS concentration collected at the drain pipe is greater than the highest concentration collected at the auto-sampler. Greater drain pipe values could be explained by the disruption of the bio-film coating in the drain pipe during sample collection. The median sewer and drain pipe TSS values for this study were comparable to levels reported by the U.S. EPA in the 1983 National Stormwater Survey (USEPA, 1983).

Table 3: Stormwater Quality. Detection limits for TSS were 1 μg/L.
(* excluding December samples)

	Sewer			Auto-Sampler			Drain Pipe		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
pH	7.60	7.71	7.15-8.21	7.55	7.56	7.11-8.35	7.10	7.12	6.03-7.61
Conductivity* (μS/cm)	220	216	102-383	127	114	87-256	922	830	197-1660
TSS (μg/L)	443	128	bdl-1969	28.2	7.2	bdl-124	25.41	8.00	bdl-240

Heavy Metals in Highway Runoff

Stormwater samples collected at the sewer site from March through May 2007 were screened for a range of total and dissolved heavy metals, including copper, zinc, cadmium, nickel and lead. Table 4 shows the median dissolved and total concentrations of these metals. Although zinc was most commonly found in total metal samples, copper was selected for further analysis because it was detected in almost all total and dissolved metal samples. Zinc, nickel and lead, on the other hand, were detected in less than half of the dissolved metal samples, and cadmium had the lowest total metal concentrations. Because the majority of zinc, copper, nickel and lead were found in the particulate fraction, these metals could more effectively be removed in the bioretention basin through sedimentation and filtration in the mulch and soil layers than cadmium.

Table 4: Median Metal Concentrations in Sewer Samples (ppb).

Metal	Total	Dissolved
Copper	17.5	0.90
Zinc	420	0.00
Cadmium	1.30	0.07
Nickel	14.5	0.00
Lead	18.0	0.00

Table 5 shows the mean and median values and the range of dissolved and total copper concentrations at the three sample collection sites between June 1 and November 27, 2007. Mean and median total copper concentrations decreased from one collection site to the next with the drain pipe samples having the lowest and least varied total copper concentrations. Although the same could be said about the mean and median dissolved copper concentrations, no discernible trend could be seen when comparing the dissolved copper concentrations during individual storm events. Because total copper concentrations decreased across the bioretention basin while TSS concentrations did not, the solids in the drain pipe samples must be something other than particulate metals, such as pieces of biofilm from inside the drain pipe.

Table 5: Dissolved and Total Copper Concentrations (µg/L).

	Dissolved			Total		
	Mean	Median	Range	Mean	Median	Range
Sewer	18.0	16.2	0-48.9	76.4	56.3	0-293
Auto-Sampler	13.5	6.91	0-55.8	40.1	25.0	12.4-124
Drain Pipe	3.93	0	0-8.52	18.5	18.4	0-39.0

Deicing Salts in Highway Runoff

Three sewer samples collected in December 2006 and 2007 contained substantially elevated dissolved salt concentrations as measured by conductivity. The conductivity values of these samples were much greater than the mean values seen in

Table 3. The maximum conductivity value was recorded on December 7, 2007 at 12,630 μS/cm, the day after a 2-4 inch snowfall. Elevated salt levels are characteristic of road salt application on Mize Boulevard and resulted in increased conductivity measurements from December 2006 through March 2007.


Metal Removal

Based on the ICP-MS analysis of sewer and drain pipe samples collected from March through May 2007, the bioretention system removed more than 90 percent of total copper, cadmium and lead concentrations on an event basis. The percent removal for nickel and zinc ranged from 13-91 percent and 62-91 percent, respectively. The lower removal values for nickel occurred for sewer samples with already very low nickel concentrations. Dissolved metal concentrations in the sewer samples were generally below the detection limit for cadmium, nickel and lead, although detectable levels of these metals, except for lead, were present in more than half of the drain pipe samples from the same storm events. Since auto-sampler samples were not collected during this sampling period, no data are available to directly determine whether total metal removal occurred primarily through infiltration in the mesh trap located in the storm sewer or in the mulch and soil layers in the bioretention basin. Although, based on the results of the copper examination of runoff samples, discussed below, total metal removal most likely occurred primarily in the mesh trap.

Copper concentrations in stormwater samples were furthered examined from June through November 2007. Average and median copper concentrations in samples are presented in Table 5. Both dissolved and total concentrations in stormwater decreased as it passed through the bioretention basin. The sewer samples generally had greater total copper concentrations than the auto-sampler and drain pipe samples. Because the total concentrations in the auto-sampler and drain pipe samples were lower and showed little variation between storm events, it is likely that most of the particulate-associated copper was deposited not in the mulch and soil layers of the

bioretention basin, but in the mesh trap immediately after the runoff entered the storm sewer. Although the dissolved copper concentration results did not show a discernible trend of removal within the bioretention basin throughout the year, the summer samples did produce some notable results. Drain pipe samples showed the lowest dissolved copper concentrations, and the biggest difference in concentration between sewer and drain pipe samples was seen during the summer months. Both total and dissolved copper concentrations do not appear to be strongly correlated within samples, suggesting multiple sources of copper in the bioretention basin.

Figure 3 shows removal percentages for TSS and dissolved and total copper on a per storm basis; these results include the storm sewer in the bioretention system. Averages of 77 percent total copper removal and 41 percent dissolved copper removal were calculated for an individual storm. When considering only the performance of the bioretention basin (excluding the mesh trap in the storm sewer), the average total and dissolved copper removal were 33 percent and 47 percent, respectively. This decreased total copper removal percentage suggests that a significant portion of particulate-associated copper is removed in the mesh trap. Figure 3 shows that TSS removal is not strongly correlated to total copper removal. This suggests that solid-associated copper may be adsorbed primarily to small particulates that are not affected by filtration through the mesh trap or the mulch and soil layers.
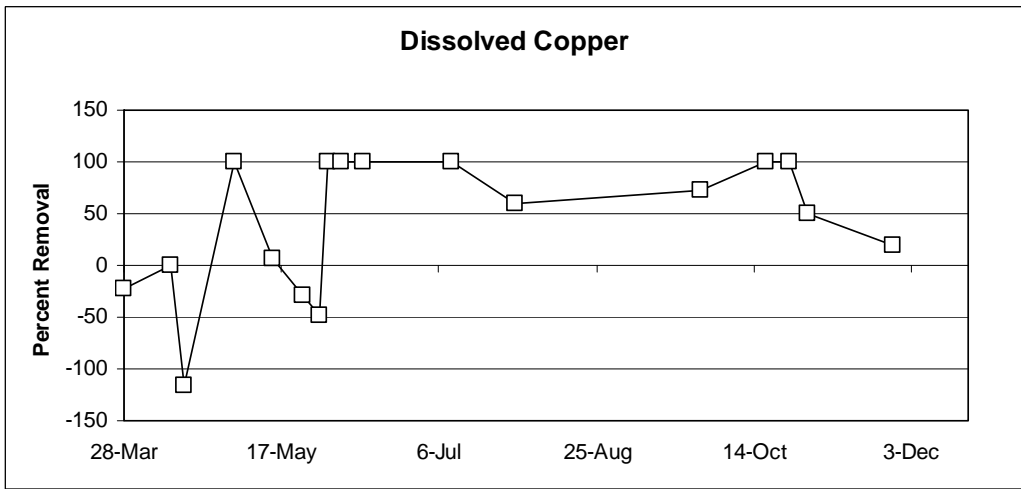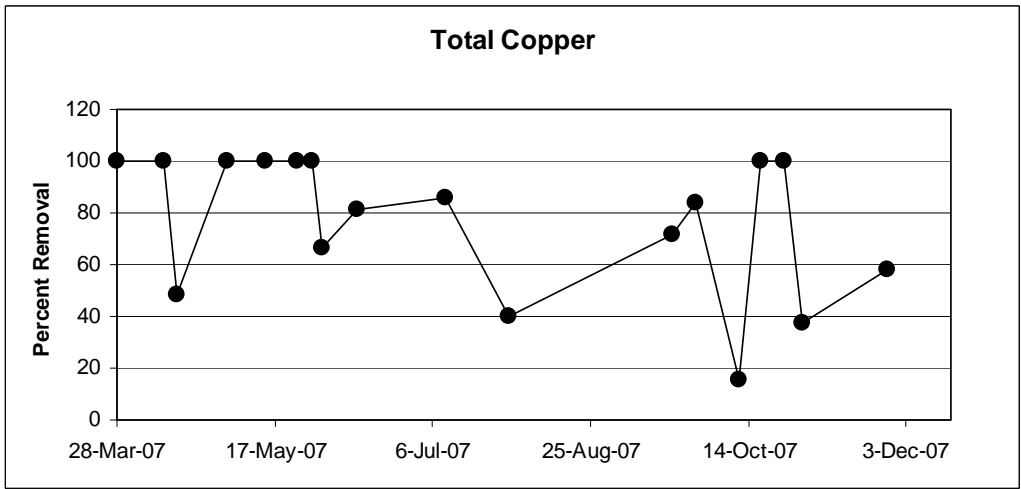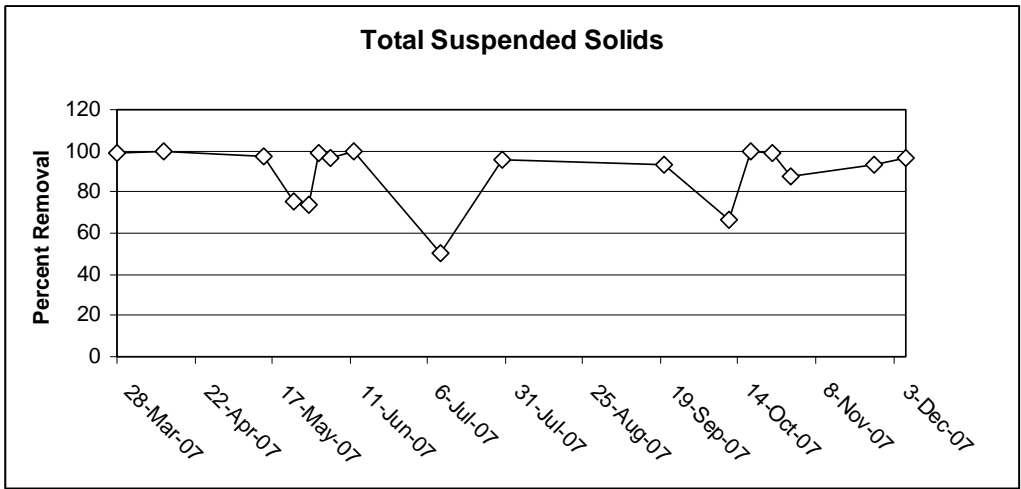
Figures 3. TSS and copper removal in the storm sewer and bioretention basin.

Chapter 5

Preliminary Column Studies

Column Design

Deionized water was pumped from a storage jug to the top of each column at a rate of 1.2 mL/min. At the top, a perforated plastic disk and a mesh filter, below the disk, were installed to help distribute the water evenly across the top of the soil. The soil was extracted from the bioretention basin in the field and shaken through a 22 mm sieve. The screened soil in each column was approximately one-foot in depth and was suspended from the base of the column by another mesh filter. At the base, water exited the columns through a tube to another storage jug or to a fractional collector when samples were tested for copper concentrations (Figure 4).
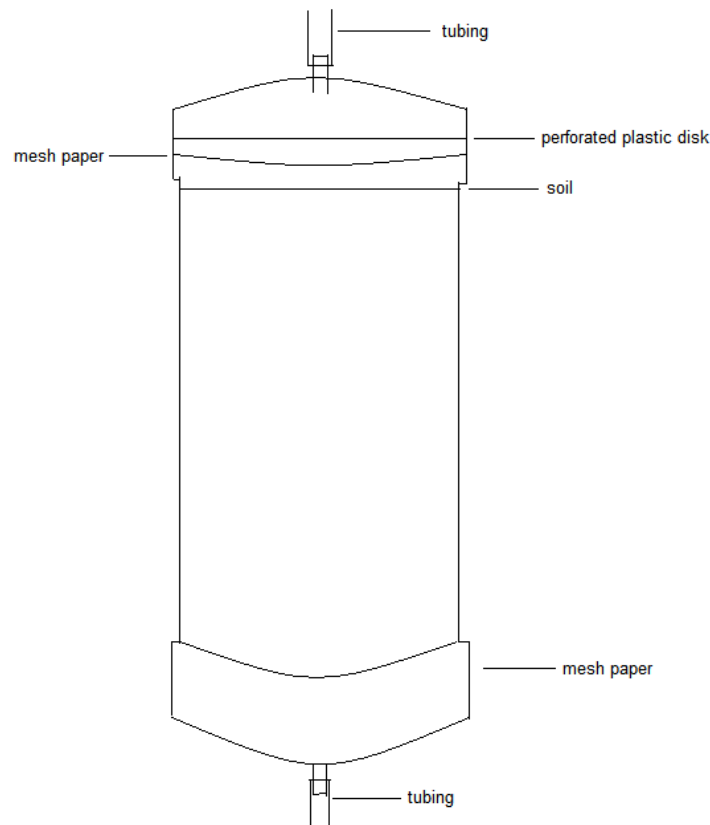

Figure 4. Drawing of laboratory soil column.

Methods

A tracer study was performed on the columns to examine water retention times. The columns were first saturated with deionized water, and then 0.1 M potassium chloride was pumped through the columns for thirty minutes. After the addition of KCl, deionized water was pumped through for approximately 24 hours. Column effluent was collected every 15 minutes in test tubes using a fractional collector. The test tubes were cleaned in 0.5 M sulfuric acid and rinsed with deionized water prior to use. Chloride concentrations were analyzed using a conductivity meter.

Dissolved copper mobilization was tested in both soil columns. The columns were saturated with deionized water and then received a 0.01 M copper nitrate solution for thirty minutes. Deionized water was restarted, and the columns were left running until a steady-state copper concentration was observed in the effluent. For the first two days, samples were collected in acid-washed test tubes every 15 minutes with a fractional collector. After two days, a sample was collected in the morning and another in the evening until steady-state was reached. All samples were preserved with 0.25 mL analytical grade nitric acid. Dissolved copper concentrations were determined through flame atomic absorption spectrometry.

Results

The results of the tracer study are depicted in Figure 5. The results for both columns are very similar regarding the pattern of chloride release in the effluent. In both columns, the effluent chloride concentration peaked after approximately 6.6 hours. Also, the chloride emerged in the effluent and the chloride concentration returned to the baseline concentration at similar times in both studies. The chloride began to show up in the effluent after approximately five hours, while the two columns returned to their baseline chloride concentrations after about 23 hours.
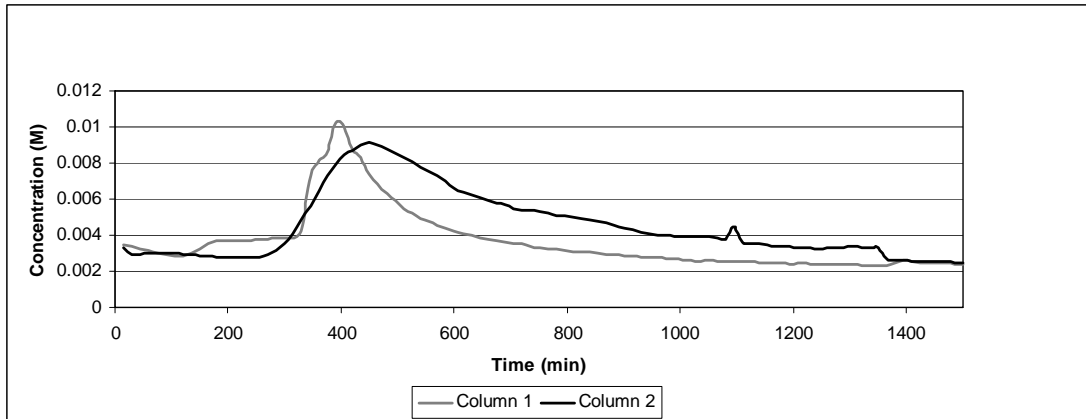
Figure 5. Chloride concentrations of samples collected every 15 minutes to test the water retention time through each column.

Copper retention tests were performed twice in each column using a 6.75 mg copper nitrate solution. In Column 1, the percentages of copper recovered in the column effluent in the initial and subsequent tests were 33 percent and 9 percent, respectively. In Column 2, the results were 12 percent and 6 percent. The initial runs in each column showed copper concentration peaks in the effluent samples after approximately 17 hours in Column 1 and 12.5 hours in Column 2. The effluent copper concentrations collected during the second runs were much more constant, showing no peaks and indicating improved copper retention. During the initial runs in both columns, the peak copper concentration in the effluent occurred after twice the length of time, or more, of when the peak chloride concentrations occurred in the tracer study. In both columns, short-term copper retention was successful and even improved during the second test. There is no way to tell if copper retained during the first test remained in the column during the second test because deionized water was almost continuously pumped through the columns between tests, and the effluent water was not tested for copper concentrations.

Future Studies

The preliminary tests completed in the columns linked the field work to more controlled studies in the laboratory which could analyze specific aspects of the

bioretention basin, such as dissolved metal retention in the soil layer. These pilot studies also helped to create methods for additional future studies. Future column studies should investigate the relationship between mulch type and metal retention. One possible study might be to compare the metal retention capacity in two columns, each having a unique mulch layer. The actual wood chip mulch layer from the field basin could be used in one column, and fresh bark or shredded mulch, as suggested by Winogradoff (2002), could be used in the second column. In order to investigate both total and dissolved metal retention for numerous metals, highway runoff collected from the field could be used as the column influent instead of a synthetic runoff solution containing only dissolved metals.

Future column studies could also test the role deicing salts play in the retention of heavy metals on adsorbing surfaces in the mulch and soil layers. One study could focus on how changes to the salinity level in highway runoff affect the solubility of heavy metal-organic matter complexes. One column could receive a low concentration of deicing salts, typical of salt concentrations found in highway runoff during summer and fall months. The second column could receive an elevated concentration of deicing salts comparable to that found in highway runoff during the winter months. Another study could further investigate the role different types of road salts have on heavy metal retention. Two influent solutions with similar salinity levels, containing both heavy metals and a deicing salt, could be pumped through the columns. One column could receive calcium magnesium acetate, and the other column could receive calcium or sodium chloride.

Chapter 6

Conclusions and Recommendations

Field Study

Stormwater runoff collected from Mize Boulevard contains elevated levels of heavy metals associated with automobile use and road surfaces as well as seasonally-associated, dissolved products of deicing salts. Greater total copper concentrations in sewer samples compared to dissolved copper concentrations aligns with findings in other studies that suggest that the majority of copper found in runoff from roads and parking lots is in the particulate form. The bioretention basin effectively removed TSS and solid-associated, metal pollutants from the stormwater runoff at removal rates that are within typical performance levels for bioretention systems in the published literature. It is apparent, however, that the majority of solids were captured in the mesh trap as the runoff passed through the storm sewer entrance.

Removal rates of dissolved copper were low or nominally negative in the bioretention basin. These rates were calculated based on concentration and were not adjusted for any changes in water volume due to evaporation and/or transpiration within the bioretention basin. Contaminant removal could be more accurately measured by comparing the total loadings of contaminants in influent and effluent samples on a mass basis after determination of the total water volume and the average contaminant concentration for a particular storm event. Mass loadings leaving the bioretention basin were not determined during this study because of insufficient hydrological data on the basin.

Although the dissolved metal concentrations in runoff samples, in many cases, were near or below detection limits, the low removal rates of dissolved metals may have been hindered by two components of the bioretention basin, the mulch layer and the age of the basin. The mulch was inappropriate for bioretention in regards to both its size and type. According to Winogradoff (2002), fresh bark or shredded mulch

should be used instead of mulch chips, which were used at the field site. The chip variety cannot effectively promote the decomposition of organic material or provide surfaces for the adsorption and bonding of heavy metals. In addition, the soil matrix was less than a year old when samples were collected, and organic matter and mineral oxides had not had a chance to accumulate and provide numerous surfaces where adsorption and complexation could readily occur. Future studies should investigate dissolved metal removal as it relates to basin age and the development of adsorbing surfaces.

Column Study

Although the column study was a preliminary investigation, the soil column design was successful on the basis of short-term copper retention. As previously mentioned, the soil layer from the bioretention basin was used in both columns; however, the mulch layer was not used in the columns because of the size of the wood chips. Copper retention in the columns may have been greater had a mulch layer been incorporated in the design of the columns because mulch would provide additional surfaces for the adsorption and complexation of copper cations.

Although long-term dissolved copper retention did not occur during this study, changes could be made to the design of the columns and their operation that would allow them to more closely mimic what occurs in a bioretention basin and possibly retain copper more successfully. For example, storm events could be better simulated by turning the water pumps on for lengths of time similar to the duration of an average storm instead of operating the pumps continuously. This would allow the soil to experience the wet/dry cycles that occur in bioretention basins.

References

Amrhein, C., Strong, J. E., & Mosher, P. A. (1992). Effect of deicing salts on metal and organic matter mobilization in roadside soils. Environmental Science & Technology, 26, 703-709.

Åsteböl, S. O., Pedersen, P. A., Röhr, P. K., Fostad, O., & Soldal, O. (1996). Effects of De-Icing Salts on Soil, Water, and Vegetation (Report MITRA 05/96). Oslo, Norway: Norwegian National Road Administration.

Bhaduri, B., Harbor, J., Engel, B., & Grove M. (2000). Assessing watershed-scale long-term hydrological impacts of land-use change using a GIS-NPS model. Environmental Management, 26, 643-658.

Burges, S. J., Wigmosta, M. S., & Meena, J. M. (1998). Hydrological effects of land-use change in a zero-order catchment. Journal of Hydrological Engineering, 3, 86-97.

Casey, R. E., Shaw, A. N., Massal, L. R., & Snodgrass, J. W. (2005). Multimedia evaluation of trace metal distribution within stormwater retention ponds in suburban Maryland, USA. Bulletin of Environmental Contamination and Toxicology, 74, 273-280.

Celis, R., Carmenhermosian, M., & Cornejo, J. (2000). Heavy metal adsorption on functionalized clays. Environmental Science & Technology, 34, 4593-4599.

Clesceri, L. S., Greenberg, A. E., & Eaton, A. D. (2005) Standard Methods for the Examination of Water and Wastewater. American Public Health Association, American Water Works Association, & Water Environment Federation.

Davis, A. P. (2007). Field Performance of Bioretention: Water Quality. Environmental Engineering Science, 24, 1048-1064.

Davis, A. P., Shokouhian, M., Sharma, H., & Minami, C. (2001). Laboratory study of biological retention for urban stormwater management. Water Environment Research, 73, 5-14.

Davis, A. P., Shokouhian, M., Sharma, H., Minami, C., & Winogradoff, D. (2003). Water quality improvement through bioretention: lead, copper, and zinc removal. Water Environment Research, 75, 73-82.

Dean, C. M., Sansalone, J. J., Cartledge, F. K., & Pardue, J. H. (2005). Influence of hydrology on rainfall-runoff metal element speciation. Journal of Environmental Engineering, 131, 632-642.

Durand, C., Ruban, V., & Ambles, A. (2004). Mobility of trace metals in retention pond sediments. Environmental Technology, 25, 881-888.

Ellis, J. B., Revitt, D. M., Harrop, D. O., & Beckwith, P. R. (1987). The Contribution of Highway Surfaces to Urban Stormwater Sediments and Metal Loadings. Science of the Total Environment, 59, 339-349.

Gier, S., & Johns, W. D. (2000). Heavy metal-adsorption on micas and clay minerals studied by X-ray photoelectron spectroscopy. Applied Clay Science, 16, 289-299.

Glenn III, D. W., & Sansalone, J. J. (2002). Accretion and partitioning of heavy metals associated with snow exposed to urban traffic and winter storm maintenance activities. II. Journal of Environmental Engineering, 128, 167-185.

Goldman, C. R., & Hoffman, R. S. (1975). A study of the influence of highway deicing agents on the aquatic environment in Lake Tahoe Basin and drainage along Interstate 80. Sacramento, CA: California Department of Transportation.

Hsieh, C., & Davis, A. P. (2005). Evaluation and optimization of bioretention media for treatment of urban storm water runoff. <u>Journal of Environmental Engineering, 131,</u> 1521-1531.

Kayhanian, M., Suverkropp, C., Ruby, A., & Tsay, K., (2007). Characterization and prediction of highway runoff constituent event mean concentration. <u>Journal of Environmental Management, 85,</u> 275-295.

Kobriger, N. P., & Geinopoles, A., (1984). Sources and mitigation of highway runoff pollutants.

Lee, J., Lee, B., Luoma, S. N., Choi, H. J., Koh, C., & Brown, C. L. (2000). Influence of acid volatile sulfides and metal concentrations on metal partitioning in contaminated sediments. <u>Environmental Science & Technology, 34,</u> 4511- 4516.

Liebens, J. (2001). Heavy metal contamination of sediments in stormwater management systems: the effect of land use, particle size, and age. <u>Environmental Geology, 41,</u> 341-351.

Mid-America Regional Council and the Kansas City Metropolitan Chapter of the American Public Works Association. (2008). <u>Manual of best management practices for stormwater quality.</u>

Marsalek, J. M., & Marsalek, P. M. (1997). Characteristics of sediments from a stormwater management pond. <u>Water Science and Technology, 36,</u> 117-122.

McBride, M., Sauve, S., & Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. <u>European Journal of Soil Science, 48,</u> 337-346.

Mungur, A. S., Shutes, R. B. E., Revitt, D. M., & House, M. A. (1995). An assessment of metal removal from highway runoff by a natural wetland. <u>Water Science and Technology, 32,</u> 169-175.

Muthanna, T. M., Viklander, M., Blecken, G., & Thorolfsson, S. T. (2007a). Snowmelt pollutant removal in bioretention areas. Water Research, 41, 4061-4072.

Muthanna, T. M., Viklander, M., Gjesdahl, N., & Thorolfsson, S.T. (2007b). Heavy Metal Removal in Cold Climate Bioretention. Water, Air, and Soil Pollution, 183, 391-402.

Norrstrom, A.C., & Bergstedt, E. (2001). The Impact of Road De-icing Salts (NaCl) on Colloid Dispersion and Base Cation Pools in Roadside Soils. Water, Air, and Soil Pollution, 127, 281-299.

Novotny, V., & Olem, H. (1994). Water Quality: Prevention, identification, and management of diffuse pollution, New York: Wiley.

Nriagu, J. O., & Coker, R. D. (1980). Trace metals in humic and fulvic acids from Lake Ontario sediments. American Chemical Society, 14, 443-446.

Paddock, T., & Lister, C. (1990). De-icing salt is here to stay, but can be used more wisely. Philadelphia, PA: The Academy of Natural Sciences.

Peltier, E., Young, B., and Lacy, S. (2008). Minimizing contaminant impact from road and parking lot runoff. University of Kansas Transportation Research Institute.

Römkens, P. F. (1993). Cu mobility in agricultural soils: effect of pH, Ca, and DOC. Madison, WI: American Society of Agronomy.

Sansalone, J. J., & Buchberger, S. G. (1995). An infiltration device as a best management practice for immobilizing heavy metals in urban highway runoff. Water Science and Technology, 32, 119-125.

Sansalone, J. J., & Buchberger, S. G. (1996). Characterization of metals and solids in urban highway snow and rainfall-runoff. Transportation Research Record, 1523, 147-159.

Sansalone, J. J., & Buchberger, S. G. (1997). Partitioning and first flush of metals in urban roadway storm water. Journal of Environmental Engineering, 123, 134-143.

Sansalone, J. J., & Glenn III, D. W. (2002). Accretion of pollutants in snow exposed to urban traffic and winter storm maintenance activities. I. Journal of Environmental Engineering, 128, 151-166.

Schlesinger, W. H. (1997). Biogeochemistry: an analysis of global change. San Diego, CA: Academic Press.

Schmitt, D., Taylor, H. E., Aiken, G. R., Roth, D. A., & Frimmel, F. H. (2002). Influence of natural organic matter on the adsorption of metal ions onto clay minerals. Environmental Science & Technology, 36, 2932-2938.

Schueler, T. R. (1987). Controlling urban runoff: A practical manual for planning designing urban BMPs. Washington, DC: Metropolitan Washington Council of Governments.

Scott, W. S., & Wylie, N. P. (1980). The environmental effects of snow dumping: a literature review. Journal of Environmental Management, 10, 219-240.

Spinello, A. G., & Simmons, D. L. (1992). Base flow of 10 south-shore systems, Long Island, New York, 1976-85, and the effects of urbanization on base flow and flow duration. United States Geological Survey.

Swift, R. S., & McLaren, R. G. (1991). Micronutrient adsorption by soils and soil colloids. Interactions at the Soil Colloid-Soil Solution Interface, 257-292.

U.S. Department of Transportation, Office of Infrastructure. (1999). Is highway runoff a serious problem (FHWA Environmental Technology Brief)? McLean, VA: Federal Highway Administration.

United States Environmental Protection Agency. (1983). <u>Results of the Nationwide Urban Runoff Program</u>. Washington, DC: USEPA, Water Planning Division.

United States Environmental Protection Agency. (2000). <u>Stormwater Phase II Final Rule: An Overview</u>. Washington, DC: USEPA, Office of Water.

Winogradoff, D.A. (2002). <u>The Bioretention Manual</u>. Prince George's County, MA: Department of Environmental Resources.

Weiss, J. D., Hondzo, M., & Semmens, M. (2006). Storm water detention ponds: Modeling heavy metal removal by plant species and sediments. <u>Journal of Environmental Engineering, 132,</u> 1034-1042.

Zachara, J. M., Smith, S. C., Resch, C. T., & Cowan, C. E. (1992). Cadmium sorption to soil separates containing layer silicates and iron and aluminum oxides. <u>Soil Science Society of America, 56,</u> 1074-1084.

Appendix I

Table 2: TSS Concentrations (mg/L) and Dissolved and Total Cu Concentrations (ppb) in All Collected Field Samples.

	Sewer			Auto-Sampler			Drain Pipe		
Date	TSS	Total	Dissolved	TSS	Total	Dissolved	TSS	Total	Dissolved
3-28-07	1.36	57.8	0.9		-	-	0.012	0	1.1
4-2-07	-	-	-		-	-	0.004	0	0.8
4-12-07	0.804	42.3	0.8	0.004	-	-	0	9	1.3
4-16-07	0	17.5	0.6	-	-	-	0.24	0	0
5-2-07	1.272	0	0.5	-	-	-	-	-	-
5-14-07	0.716	22.8	1.5	-	-	-	0.02	0	1.4
5-24-07	0.048	11.3	1.4	-	-	-	0.012	0	1.8
5-29-07	0.0136	0	2.3	-	-	-	0.036	0	3.4
6-1-07	0.116	64.2	48.9	0.04	25.0	0.89	0.001	21.4	0
6-5-07	0.608	0	0	0	21.0	13.2	0.02	14.6	0
6-12-07	1.312	147	22.2	0.092	82.5	54.5	0.004	28.0	0
6-21-07	-	-	-	0.02	32.5	0	0.008	30.8	0
7-3-07	-	-	-	0.072	31.2	0	0.028	14.6	0
7-10-07	0.048	93.1	74.1	0.044	61.8	55.8	0.024	13.3	0
7-30-07	0.2	64.9	18.8	0.124	53.0	3.50	0.008	39.0	7.46
8-29-07	0.184	89.6	21.9	-	-	-	-	-	-
9-20-07	0.614	105	0.65	0.002	20.1	9.43	0.04	29.9	20.0
9-27-07	0.017	48.4	16.9	-	-	-	0.087	7.73	4.70
10-4-07	0.014	32.5	19.5	0.007	17.3	5.48	-	-	-
10-11-07	0.003	24.2	0	-	-	-	0.001	20.5	8.52
10-18-07	1.969	293	5.96	0.004	17.0	6.91	0	0	0
10-25-07	0.102	31.6	0	-	124	0	0.001	0	0
10-31-07	0.016	37.6	15.5	-	23.5	15.3	0.002	23.6	7.62
11-27-07	0.119	38.7	8.25	0.013	12.4	10.9	0.008	16.3	6.71
12-7-07	0.084	-	-	0	-	-	0.003	-	-