# Performance of Low Impact Development Practices on Stormwater Pollutant Load Abatement

Minnesota Pollution Control Agency 319 project Final Report

By John S. Gulliver, Principal Investigator

September 22, 2011

# Work Plan Review

Objective A: Literature review and site selection.

Update previous USEPA and other recent literature reviews of LID BMP performance with an emphasis on infiltration/filtration practices in urban settings and their performance for water quantity reduction and suspended solids, phosphorus, pathogen, heavy metal and gasoline/diesel derivative pollutant removal. One to three watersheds representative of typical Twin Cities Metro urban areas will be selected from partnering local units of government who have existing LID monitoring efforts.

The literature review and site selection are complete. These will contribute to literature reviews for two project reports for objectives B and C.

Objective B: Infiltration capacity of LID practices (summary)

Infiltration capacity testing will be performed on several LID practices. Capacity testing will implement the modified Philip-Dunne infiltrometer as a low-effort, low- cost method to determine saturated hydraulic conductivity, a predictor of infiltration capacity. Simulated runoff testing is also to be performed on the LID practices to confirm the results of the capacity testing.

A final report on the infiltration studies is in press.

Objective C: Pollution retention and groundwater pollution caused by infiltration

A literature review will be undertaken to determine soil parameters relevant to pollutant retention and transport in rain gardens. Soil parameters include contaminant sorption capacities and degradation rates in soils typically used in LID infiltration practices. Batch and column studies will be performed on soils and compost typically used in rain gardens. The ability of the soils to remove phosphorus, nitrogen, cadmium, copper, and zinc will be studied and compared to field studies.

The column studies are complete and a final report is in press.

Objective D: TMDL demonstration study

The demonstration study is complete and a Project report has been submitted.

Objective E: Public Outreach / Public Participation and Deliverables

Task E.1. Outreach and Technical Advisory Panel meetings: Bi-annual technical Advisory Panel meetings were held and outreach to the professional community is on-going. Three UPDATES Newsletters have addressed the research topics and three workshops have been held, "LID Assessment and Maintenance," at the Minnehaha Creek Watershed District, 20 November 2009; "Stormwater Maintenance Strategies," in Blaine, MN, 3 November 2010; and "Bioretention Systems: The "Dirt" on Soils, Water, & Infiltration" at the Minnehaha Creek Watershed District, 9 August 2011.

Task E.2. Progress reports: Progress reports were completed and submitted on October 1, 2008 and every February 1 and August 1 for the remainder of the project.

Task E.3. Incorporation into education program: The project results are currently utilized in University of Minnesota coursework, particularly the Civil Engineering and Bioproducts and Biosystems Engineering

"capstone" design courses and a new course in the Civil Engineering Program, "Urban Hydrology and Land Development."

Task E.4. Final Report: Three project reports have been completed and submitted, or are in the submission process: SAFL Project Report No. 558, "Total Daily Maximum Daily Load Demonstration Study," SAFL Project Report No. 559, "Sorption and Release of Dissolved Pollutants Via Bioretention Media," and SAFL Project ReportNo. 560, "Infiltration capacity of LID practices." The research has been implemented into the on-line manual *Stormwater Treatment: Assessment and Maintenance*, as appropriate.

## **Grant Results**

### Measurements:

Measurements of infiltration in the field were made with the Modified Philip-Dunne Infiltrometer. All other measurements were performed in a laboratory setting, designed to investigate the retention and release of specific chemicals from bioretention media.

## **Products:**

Interim results of the project were communicated through three UPDATES newsletters, "Spatial Variation of Infiltration in LID practices," February 2011, "Recommendation for Bioretention Redesign," October 2010, and "Measuring and Estimating Infiltration Rate with the MPD Infiltrometer," May 2010. These newsletters are received by over 2400 subscribers across Minnesota and the United States. The newsletters are attached.

One interim literature review report is attached.

Three project reports, SAFL Report Nos. 558, 559 and 560 are also attached.

**Public outreach and education:** Due to demand, MPD Infiltrometers are currently being manufactured and sold to the public. Even though manufacturing started in June, 2011, we have already sold 50 MPD infiltrometers to date. The three UPDATES articles reached over 2400 subscribers each, for a total of 7200 subscribers. Finally, the three workshops had approximately 90 participants.

## **Long Term Results**

The results of this project will build capacity that can increase the likelihood of long-term outcomes, such as environmental problems identified or understood. These would include the ability of compost-enhanced media to remove toxic metals common to stormwater runoff and the phosphorus released by compost. Recommendations for a rain garden design when under-drains are installed have been made. We currently can remove dissolved phosphorus from rain garden discharges into underdrains, which has been implemented and will continue to be implemented in the future. In addition, the MPD infiltrometer has been utilized and proven as a technology that will provide an increased ability to solve infiltration questions and problems in the future.

The following activities have benefited from this project:

- 1. Installation of three rain gardens with a treatment train concept that combine compost enhanced sand with iron enhanced sand for dissolved phosphorus removal in the City of Maplewood.
- 2. Development of a protocol for MnDOT personnel to utilize the MPD infiltrometer to determine the infiltration capacity of their grassed swales.

The project has begun long-term research in the following areas:

1. Enhanced treatment to remove dissolved nitrogen. Dissolved phosphorus can be removed by iron, and toxic metals and oils can be removed by compost, but dissolved nitrogen removal has not been developed for stormwater practices.

- 2. Development of horizontal enhanced sand filters that will function in swales and other locations with limited head difference.
- 3. Use of the MPD Infiltrometer to specify infiltration of many urban practices.

# **Final Expenditures**

Final expenditures are documented in the attached charts.

# Attachments

# **UPDATES Newsletters**

# **Spatial Variation of Infiltration in LID practices**

# February 2011 (volume 6 - issue 2)

Contributed by <u>Farzana Ahmed</u>, St. Anthony Falls Laboratory, University of Minnesota (Advisors: John Gulliver, Department of Civil Engineering, and John Nieber, Department of Bioproducts and Biosystems Engineering.)

Funded by the <u>Minnesota Pollution Control Agency</u>, the <u>Minnesota Local Road Research</u> <u>Board</u> and <u>Minnesota Department of Transportation</u>.

Saturated hydraulic conductivity (Ksat) indicates the ease at which water moves through the pore space when the soil is in a saturated condition, and is used to determine the infiltration rate of low impact development (LID) practices. Measurements of the infiltration rate applied to a design storm are helpful to determine performance, schedule maintenance and meet regulatory requirements of LID practices. The most common devices used to determine the infiltration capacity of soil are the single and double ring infiltrometers. The drawback of using these devices is that they require constant head with the associated large volumes of water, which means that it is difficult to perform more than one test simultaneously. We have found, however, that infiltration rates have great spatial variation. A number of infiltration measurements are therefore required in the infiltration practice to get a representative mean value of saturated hydraulic conductivity and an uncertainty in that mean value.

The Modified Philip Dunne (MPD) Infiltrometer has been developed by St. Anthony Falls Laboratory to measure the infiltration rate of soil at up to 20 simultaneous locations at a site, sufficient to estimate a representative infiltration capacity. The MPD has been used on an infiltration basin, eight rain gardens, one swale and non-engineered soils. Since most of these infiltration practices are constructed by filling with engineered soil, a minor variation of Ksat within that infiltration practice was expected. Table 1 indicates that the converse is true; the variations in the engineered soil as shown by the coefficient of variation (COV) were found to be of the same order as that for non-engineered soil. Table 1: Statistics of Ksat measurements.

Location	Soil Type	Number of Infiltration Measurements	Arithmetic Mean of Ksat (cm/hr)	Geometric Mean of Ksat (cm/hr)	Coefficient of Variation
Stillwater Infiltration Basin		65	11.2	3.29	1.59
Burnsville Rain Garden		23	11.8	6.75	0.92
Cottage Grove Rain Garden	Engineered Soil	20	18.5	16	0.53
RWMWD Rain Garden		32	3.93	1.59	1.23
Thompson Lake Rain Garden		30	9.56	1.63	1.19
U of M Duluth Rain Garden		33	7.25	1.68	1.78
U of M St. Paul Rain Garden		40	2.76	0.833	1.21
Albertville Swale		9	25.2	1.16	1.3
French Regional Park		18	3.74	2.38	1.1
Maple Lake Park	Non- Engineered Soil	31	3.09	2.73	0.56
Lake Minnetonka Regional park		14	7.55	2.13	1.73
Minnetrista		138	5.09	0.712	2.28

Regardless of whether the soil is engineered or not, the COV of Ksat is, in most cases, relatively high. This indicates that one infiltration measurement at each site may not represent the infiltration rate of the whole area. Thus, roughly 10 measurements of infiltration rate are required to capture this high spatial variation of Ksat and compute the mean Ksat values. The Thompson Lake Rain Garden is one example, where 30 infiltration measurements of Ksat were made with the MPD infiltrometer, as shown in the following figure. Though this rain garden had engineered soil, the Ksat value varied from less than 10 to 194 cm/hr. One measurement of infiltration rate would likely not be representative of the infiltration in the Thompson Lake Rain Garden.



# **Thompson Lake Rain Garden**

Figure 1: (Image courtesy B. Asleson & R. Nestingen)

To meet requests and provide service to the industry, the St. Anthony Falls Laboratory has begun manufacturing the MPD infiltrometer for purchase. If interested, please contact <u>Bonnie Jean MacKay</u>.

## November 2010 (vol. 5, issue 6)

## **Recommendation for Bioretention Redesign**

Contributed by <u>Joel Morgan</u>, <u>John Gulliver</u>, St. Anthony Falls Laboratory, University of Minnesota and Ray Hozalski, Department of Civil Engineering, University of Minnesota.

## Funded by the Minnesota Pollutation Control Agency

Bioretention facilities, or rain gardens, are a useful and aesthetically appealing option for managing storm water runoff. Rain gardens have been placed alongside roadways or next to buildings to allow rainwater to infiltrate and decrease peak runoff discharges. Infiltration of the storm water runoff through the rain garden media may also remove oils and greases, suspended solids, and heavy metals. Typically, these facilities have been constructed using engineered soils or a combination of sand and compost. The ease of acquiring rain garden media and the relative small size of a rain garden make implementing this management practice attractive. Many municipalities and other groups have encouraged both local homeowners and other site developers to build rain gardens. For example, Kansas City, Kansas and Melbourne, Australia have started initiatives to build 10,000 rain gardens, respectively. Thus, the number of rain gardens in the U.S. is expected to grow rapidly in the coming years.

The effectiveness of organic, leaf-based compost at simultaneously removing heavy metals, such as cadmium, copper, and zinc, is currently being studied at the St Anthony Falls Laboratory (SAFL). A small amount of compost was mixed in a bottle with a synthetic storm water solution whose chemistry (e.g., pH) matches what one would find in storm water runoff. After initial kinetic studies (e.g., Figure 1), the dosage of compost was varied to obtain sorption isotherms. The sorption results were then used to determine an estimated life span of a typical rain garden.



Figure 1: Cadmium removed from 250 mL of synthetic stormwater by 1 gram of compost ( $C_{t=0} = 500 \mu g/L$ )

The top 6 inches of a rain garden, assuming a ratio of compost to sand of 30/70% by volume, can effectively remove cadmium for 80 years assuming typical precipitation levels for Minneapolis, MN and storm water cadmium concentrations reported in the literature. Likewise, the top 6 inches of a rain garden will last 145 years removing zinc from storm water runoff. Thus, the compost in rain gardens should be very effective at removing dissolved toxic metals. Other studies, including ongoing work in our laboratory, found that rain gardens can also remove petroleum hydrocarbons.

Unfortunately, the material used to construct rain gardens may not be suitable for removing all necessary storm water pollutants. For example, we also observed that compost may be a source of phosphorus, which is the target of many storm water management practices. A batch experiment was performed in which a small amount of organic, leaf-based compost was added to a synthetic stormwater and sampled over time. Figure 2 shows that phosphorus leaches off of compost and that the longer the compost is in contact with water, more phosphorus is released from the compost.



Figure 2: Phosphorus release from 1.0 g of compost added to 250 mL of synthetic stormwater.

So if compost leaches phosphorus, then there is a concern that the released phosphorous may eventually make its way into surface waters. Fortunately, there is a solution to the leaching of phosphorus. Work done at the St. Anthony Falls Laboratory by Andrew Erickson demonstrated that filtration with sand amended with iron filings is effective at removing phosphorus from stormwater. A sand filtration basin amended with 5% iron filings, by weight, may remove at least 80% of total phosphorus for up to 30 years of service under a hydraulic loading rate of 5.6 m/yr (Figure 3). There are other enhancements currently being tested, but so far iron has proved to be the most cost-effective solution.



It is thus possible to combine the results from both of these investigations into a hybrid bioretention system that removes both dissolved metals and phosphorus. Bioretention facilities can be designed as a two-stage system where the top layer is constructed of compost amended sand and the bottom layer is comprised of iron-enhanced sand (Figure 4). An appropriately sized layer of filter fabric may need to be placed between the two layers to minimize mixing of the two materials. Storm water runoff will infiltrate through the compost-amended sand, where the suspended solids and dissolved metals will be removed. The water will then infiltrate through the iron-enhanced sand where any phosphorus in the storm water runoff and any phosphorus that has leached off of the compost will be removed by the iron filings. Lastly, adequate oxygen is needed to continuously oxidize the iron filings to produce the Fe(III) required for phosphorus removal. If the dissolved oxygen in the stormwater reaching the iron-enhanced sand layer is inadequate, then an underdrain that is open to the air is needed.



Figure 4: Proposed design of a bioretention facility.

Rain gardens can be an effective best management practice for treating storm water runoff. When designed and built properly, they can be aesthetically appealing and long lasting. The proposed two-stage rain garden design can filter suspended solids, remove dissolved metals and hydrocarbons in the upper layer, and remove dissolved phosphorus in the lower layer. The key is proper media selection, installation, and maintenance so that rain garden will continue to infiltrate water quickly throughout the desired lifespan of the installation. Overall, rain gardens appear to be effective pollution prevention devices.

# May 2010 (vol. 5, issue 2)

## Measuring and Estimating Infiltration Rate with the MPD Infiltrometer

### Contributed by Farzana Ahmed

## Funded by Minnesota Pollution Control Agency

Infiltration is an essential process of many stormwater best management practices (BMPs). However, infiltration rates have great spatial variation, making quantification of infiltration rates challenging. In addition, accumulation of fine particles at the surface can limit the infiltration rate of these practices. Therefore, measurements of the infiltration rate are needed to determine performance, schedule maintenance, and meet regulatory requirements. The Modified Philip Dunne (MPD) Infiltrometer has been developed as a fast, simple, and inexpensive device to measure the infiltration rate of water into the soil at a number of locations in rain gardens, infiltration basins and trenches, swales, and filter strips. A person with minimal training can obtain the saturated hydraulic conductivity at a number of locations in an infiltration rates for a variety of storms. The MPD Infiltrometer is a falling head device. This infiltrometer is made of a hollow open-ended cylinder that is pounded two inches deep into the soil. Next, the device is filled with water to a predetermined height; a stopwatch is started when the water level starts to drop, and the water level is recorded over time. An MPD spreadsheet, developed for application in EXCEL, is then used to determine the saturated hydraulic conductivity (K<sub>sat</sub>) and soil suction (C) based on the water level vs. time data, dimensions of the MPD, and the initial and final moisture conditions.



Figure 2: Modified Philip Dunne Infiltrometer (Courtesy F. Ahmed)

The spreadsheet minimizes the root mean square (RMS) of the difference between the observed and predicted time increment ( $\Delta$ t), as well as the observed ad predicted head increment ( $\Delta$ H), by adjusting the saturated hydraulic conductivity (K<sub>sat</sub>) and soil suction (C). The MPD spreadsheet and a set of MPD infiltrometers will be available for purchase from St. Anthony Falls Laboratory in the summer of 2010.

# Adsorption of Dissolved Toxic Metals on Bioretention Media

# **An Interim Literature Report**

Joel Morgan, John Gulliver, Ray Hozalski St. Anthony Falls Laboratory University of Minnesota

Prepared for the Minnesota Pollution Control Agency Bruce C. Wilson, Project Manager

14 December 2011

### 1.0 Introduction

Effective management of urban stormwater runoff is an important goal of engineers, planners, and watershed managers. From hydrodynamic separators to rain gardens, there has been a search for best management practices that are low-cost, easy to install and maintain, and robust and effective at removing pollutants commonly found in stormwater. Bioretention facilities, or rain gardens, have become an increasingly viable option for managing stormwater runoff (Figure 1).



Figure 1 Diagram of a generic rain garden. Polluted stormwater runoff enters from a curb cut or gutter system and infiltrates through the media. Adapted from Davis et al. (2009)

Rain gardens are shallow depressions that have had native soil removed and replaced with a mixture of compost, sand, and soil (Minnesota Stormwater Manual). In Minnesota, compost used in rain gardens fits the Minnesota Department of Transportation (MnDOT) Grade 2 specification and is derived from leaf and yard waste. No household waste or manure is added to this mix. Additionally, a sandy loam or loamy sand soil and sand conforming to the AASHTO M-6 or the ASTM C-33 classification are combined with compost to form a uniform rain garden mix. Stormwater runoff is routed to rain gardens via curb cuts or gutter systems and infiltrates down through this rain garden mix. Commonly used as an aesthetic means to infiltrate stormwater runoff, rain gardens can also reduce stormwater runoff pollutants. Straining, filtration, and adsorption to organic and mineral materials in the rain garden media have the ability to remove pollutants.

As with any best management practice, however, there is a potential for failure. Failure can be defined as anything from a slow infiltration rate to being a source of sediment or pollutants. Design, construction, and maintenance can factor how a rain garden might fail. For example, a slow infiltration rate can be caused by clogging of infiltration pathways by deposited sediment, which shows that the rain garden is capturing pollutants but needs maintenance, or by a high clay content in the rain garden soils, which is an example of poor design or construction. Routine maintenance, such as visual inspection, leaf and litter removal, and routine mowing, can often reveal conditions that may lead to future failure. The goal with maintenance is to eliminate the need for large-scale repairs or major maintenance (Figure 2).



Figure 2 Levels of Maintenance for Stormwater Treatment Practices (Gulliver et al. 2010)

Some modes of failure, though, are difficult to determine by visual inspection or by quick and easy field measurements. For example, adsorption of stormwater pollutants and subsequent exhaustion of the removal capacity is a mode of failure that is difficult to quantify without field-testing and laboratory analysis.

The objectives of this paper are to develop an understanding of the adsorption ability of commonly used bioretention media; determine fate and transport of various pollutants; use this knowledge to develop a life-cycle analysis of rain garden media; and to provide suggestions for preventative and non-routine maintenance to extend the life span of a rain garden.

#### 2.0 Background

The scope of this literature review began with a look into infiltration practice filter media and conventional stormwater pollutants, which include suspended solids, total and dissolved phosphorus, toxic metals, petroleum hydrocarbons, and pathogens. Phone interviews with two local landscape architects (Kurt Leuthold and Rusty Schmidt), the filtration media was narrowed down to native soil, compost, and sand. Both landscape architects discussed the elimination of native soil as a filtration media due to the lack of consistent quality in native soil. Some soil may contain clay which can inhibit infiltration and cause hydraulic failure of the infiltration practice. Other soils may not contain much clay. The lack of knowledge about soil composition has led area infiltration practice designers to eliminate soil as filter media.

The pollutant of choice was narrowed down to toxic metals because similar research has been performed recently by University of Minnesota scientists on phosphorus and petroleum hydrocarbons. Furthermore, pathogens were eliminated as a pollutant of concern for the experimental portion of this project because of health concerns over materials handling.

### 2.1 Stormwater Pollutants

One set of pollutants in stormwater runoff that are of particular concern is dissolved metals. Pollutants such as these can come from a variety of sources. The primary source for cadmium, copper, and zinc is wear and tear on vehicles, such as brake nads and tires (

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	Brakes	Tiros	Frame &	Fuels &	Concrete	Asphalt	De-Icing	littor	
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Cadmium									
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Copper									
Iron									
Lead									
Nickel									
Vanadium									
Zinc									
Chlorides									
Organic Solids									
Inorganic Soilds									
PAHs									
Phenols									
Legend: Primary Source ////////////////////////////////////							y Source		

Figure 3). Other sources include industrial runoff and zinc coated roofs (Duncan 1999).

	Brakes	Tiroc	Frame &	Fuels &	Concrete	Asphalt	De-Icing	littor
	Diakes	Tiles	Body	Oil	Pavement	Pavement	Slats	Litter
Cadmium								
Chromium								
Copper								
Iron								
Lead								
Nickel								
Vanadium								
Zinc								
Chlorides								
Organic Solids								
Inorganic Soilds								
PAHs								
Phenols								
		Legend:		= Primary S	Source		= Secondar	y Source

Figure 3 Sources of stormwater runoff pollutants (Sansalone and Buchberger 1997)

The concentrations of these metals in actual stormwater runoff were determined in a study done on NPDES MS4 permit holders (Pitt 2005). Runoff grab samples were collected and analyzed for various characteristics, including: pH, hardness, total and dissolved pollutant concentrations, and nutrient concentrations (Table 1).

	nH	Cadmium		Copper		Lead		Zinc	
	рп	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved
Median (ug/L)	7.4	1	0.5	16	8	15.9	3	112	51
Dango	3.4	0.04	0.1	0.17	0.09	.049	0.5	0.37	3.1
Range	10.7	334	5.7	1360	195	1200	130	22500	13900

**Table 1 Select Pollutant Concentrations in Stormwater Runoff** 

(Maestre and Pitt 2005)

This paper focuses on the ability of a rain garden to remove cadmium, copper, and zinc from infiltrating water. Excessive concentrations of cadmium and copper can cause kidney or liver damage and excessive zinc can cause aesthetic concerns in water. These metals are regulated by the states. For example, the Minnesota Pollution Control Agency specifies water quality standards of 3.9, 18, 82, and 117  $\mu$ g/L for Cd, Cu, Pb, and Zn, respectively (MPCA 2009) for Class 2 (fishing and recreational use) waters with a total hardness of 100 mg/L. The final acute concentration for each of these pollutants is two times the values listed above. This acute value will kill about half the exposed individuals in a sensitive species (MPCA 2009). Additionally, bioaccumulation of metals may eventually lead to neurological, gastrointestinal, or other maladies in higher-order organisms that may not be affected by current runoff concentrations. Removal of these pollutants from stormwater runoff is vital to maintaining a healthy ecosystem.

#### 2.2 **Sorbent Materials**

One goal of this research is to investigate sorption ability of materials commonly used in bioretention facilities. The materials include soil, sand, and compost conforming to the requirements listed in the Minnesota Stormwater Manual. Compost used in this research fits the Minnesota Department of Transportation (MnDOT) Grade 2 specification and is derived from leaf and yard waste (Table 2).

		1	able 2 marys	is of Compose		
Sample	Water	Ammonia-	Total	Total	Saturation	Moistur
	рН	N* (ppm)	Carbon	Nitrogen	Extract	(%)*
			(%)**	(%)**	(mmhos/cm)	
1	6.9/6.8	292.5/282.3	12.1/11.3	1.18/1.19	11.9	8.1/8.2
2	6.9/6.8	36.5/39.6	9.92/9.49	1.13/1.12	10.6/10.7	< 0.1

Table 2 Analysis of Composi

e

\* Expressed on an 'as received' basis

\*\* Expressed on a dry weight basis

This is a leaf based compost with no manure added to the mix. Prior to analysis, the samples were either air-dried (#1) or oven-dried (#2). This accounts for the relatively low moisture content and difference in the Ammonia-N values. Two values per category represent duplicate tests on the same material. Additionally, a sample of compost was ashed and analyzed to determine the background concentrations of metals on the compost (Table 3).

	Cadmium	Copper	Zinc
Sample 1	0.273	13.962	63.422
Duplicate	0.341	13.877	57.931

Table 3 Background Analysis of Metals Concentration on Compost. Units - mg/kg

The background concentration of these metals on compost is larger than what one would find in stormwater runoff (See Table 1). However, without acid digestion, the majority of these metals stay attached to the compost material and do not desorb. Additionally, the compost sample includes aluminum (2,800 mg/kg), calcium (20,000 mg/kg), iron (3,300 mg/kg), potassium (4,200 mg/kg), and magnesium (4,600 mg/kg). The relatively high concentrations of these suggests that cation exchange may be available as a specific retention mechanism for removing cadmium, copper, and zinc.

The Minnesota Stormwater Manual requires that the top soil used be classified as either a sandy loam or loamy sand with less than 5% clay content. Lastly, sand must conform to either AASHTO M-6 or the ASTM C-33 designation and have a grain size of 0.02 to 0.04 inches. Each material was sieved using a #10 sieve (2 mm opening size) to remove large pieces and develop a more uniform size. Materials were provided by Minnesota Mulch and Soil company and The Mulch Store.

### 3.0 Literature Review

### 3.1 Chemistry

Rain garden soils are thought to be a viable option for removing metals because the soil and compost has the ability to adsorb and hold onto the pollutants. Dissolved cadmium, copper, and zinc are removed from the bulk fluid by adsorbing to the surface of the rain garden mix. Adsorption, or movement of a solute from the bulk fluid onto a solid surface, is a chemical process typically used in drinking water treatment (Crittenden et al. 2005) for removal of taste and odor compounds and removal of synthetic organic chemicals. Several specific mechanisms are attributed to adsorption in water treatment applications: ligand exchange, cation exchange, and hydrophobic bonding (Schlautman et al. 1994). In Schlautman et al (1994), aluminum oxide particles were used to remove organic material, specifically aquatic humic substances. Adsorption in rain gardens occurs in a similar manner by using these processes to remove dissolved metals by organic and inorganic material.

The specific adsorption process varies based on the specific constituent – that is to say, surface reactivity is different between compost, soil, and sand. The amount of inorganic or organic functional groups, polarity, composition, and surface area all play a role in determining sorption capacity and which adsorption process controls (Essington 2004).

While it is hard to quantify the exact constituents of soil, we do know it contains both organic and inorganic materials. Aside from anthropogenic forms of detritus, the inorganic materials in soil are minerals. Silicates are the most common minerals in soil with phyllosilicates controlling the majority of soil characteristics. Kaolinite, mica, vermiculite, montmorilonite, and talc are examples of layered, crystalline phyllosilicates (Essington 2004). Phyllosilicates adsorb dissolved metals because of the interplay between surface charge, cation exchange, and isomorphic substitution.

Essington (2004) describes the basic formula for a 2:1 layered phyllosilicate as {Interlayer cation}{Octohedral Layer}{Tetrahedral Layer} $O_{10}(OH)_2$ . The 2:1 layering just refers to the ratio of tetrahedral base layers to octahedral base layers. For example, vermiculite is a 2:1 layered phyllosilicate whereas kaolinite is layered in a 1:1 ratio. The

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terms octahedral and tetrahedral refer to the individual crystal structure of specific compounds. An example of the basic structural formula for a 2:1 dioctahedral mineral is: (K, Ca, Na)(Fe, Mg, Al)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> where iron, magnesium, and aluminum are in the +3 valence state. Potassium, calcium, or sodium is the interlayer cation and aluminum, magnesium, or iron hydroxides form the octahedral layer, and silicates form the tetrahedral layers. In nature, the structure of phyllosilicates varies based on weathering of the mineral (Figure 4).



Figure 4 Structural Characteristics of various 2:1 phyllosilicates (Essington 2004).

In the structural formulas shown in Figure 4, isomorphic substitution has occurred in either the octahedral layer or it has occurred in the tetrahedral layer. In the tetrahedral layer for beidellite, there should be four Si<sup>+4</sup> ions per ½ unit cell, but an Al<sup>+3</sup> has replaced a silicon in a portion of the mineral. This creates a charge imbalance which is balanced by changing the amount of the interlayer cation. For beidellite, the ideal structural formula is Na<sub>0.4</sub>Al<sub>2</sub>(Si<sub>3.6</sub>Al<sub>0.4</sub>)O<sub>10</sub>(OH)<sub>2</sub>. The charge imbalance caused by the addition of the Al<sup>+3</sup> ion is

neutralized by decreasing the amount of the interlayer cation, Na<sup>+</sup>. Likewise, according to Figure 4, montmorillonite has had isomorphic substitution in the octahedral layer. Mg<sup>+2</sup> has replaced a portion of the Al<sup>+3</sup> and this imbalance is corrected by the interlayer cation (Essington 2004).

Isomorphic substitution alone is not a viable option for adsorption of stormwater pollutants, however, it does produce a permanent surface charge change in the mineral (Essington 2004) which enables the material to adsorb some stormwater pollutants. Depending on which ion is replaced in the crystal structure, a positive charge or a negative charge can be formed. According to Essington (2004), the location of the isomorphic substitution, whether in the octahedral or tetrahedral layer, changes the orientation of the proton on a structural OH. The proton will either point towards or away from the interlayer cation and this changes this internal attraction or repulsion. The interlayer cation, may or may not be held strongly due to the structural OH orientation, can be replaced to balance this permanent surface charge change. When a phyllosilicate is in solution with dissolved metals, the interlayer cation can be removed and exchanged for a metal that is in solution. Isomorphic substitution produces a permanent surface charge and this permanent surface charge can lead to adsorption of dissolved metals by cation exchange of the interlayer cation in a phyllosilicate structure.

Sorption to organic material in soil, such as compost, is highly dependent on surface functional groups. There is a potential for cation exchange and it occurs because of pH dependent surface charges and exchangeable cations. Examples of functional groups in soil organic matter include: carboxyl, phenolic-OH, carbonyl, sulfonic, amine, and imide functional groups (Essington 2004). The preference that a particular metal has for a

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specific ligand group may change, but X-ray absorption spectroscopy studies have indicated that cadmium may bind primarily to the carboxyl group of saltbrush biomass (Sawalha et al. 2008). The sorption ability of these groups depends on functional group pK value, the molecules to which they are attached, and solution pH. Metals ions, like Cd<sup>2+</sup> or metal hydroxides, like CdOH, for example, bind to negatively charged sorbent surfaces. The pH of stormwater runoff is roughly neutral (Maestre and Pitt 2005) and so phenolic-OH, for example, whose pKa value is 9.98, does not have a negative charge in typical soil and infiltration situations (Essington 2004). When bonded to certain molecules, however, the pK<sub>a</sub> of phenolic-OH can decrease and the surface charge may change to be more negative or positive. On the other hand, carboxyl groups are typically negatively charged at natural pH values and therefore can attract cations under neutral pH soil conditions. At pH values similar to what we find in nature, organic matter, which is a combination of these different functional groups, typically has an overall net negative charge.

Harmita et al. (2009) used a wet-chemistry method to determine the amount of each functional group on softwood and hardwood lignins by adding a small amount of each sorbent to sodium ethoxide (NAOC<sub>2</sub>H<sub>5</sub>), NaOH, or NaHCO<sub>3</sub>. The amount of each functional group was calculated assuming that the NaHCO<sub>3</sub> neutralizes only the carboxylic group, NaOH reacts with carboxylic and phenolic groups, and sodium ethoxide titrates the carboxyl, phenol, and carbonyl groups. The authors compared the sorption of copper and cadmium to the amount of each functional group and found increased sorption capacity with increasing carboxyl and phenol groups. Other papers have reported the carboxyl and phenolic groups as primary sources for sorption (Schiewer & Volesky 1999; Toles et al. 1999). In comparing the role of organic material in metals sorption, studies have shown

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that removal of organic material from soils decreases the sorption capacity of the soils (Elliott et al. 1986; Grimes et al. 1999).

Specific retention mechanisms for organic matter are discussed in depth in Schlautman et al. (1994). These mechanisms include hydrophobic bonding, ligand exchange, and water bridging or cation bridging. Ligand exchange occurs when a direct bond forms between the carboxyl group on organic matter and the surface hydroxyl group on the metal species. Ligand exchange predicts that sorption will decrease as protonation of the surface decreases. In other words, adsorption decreases as pH increases because this reaction consumes protons (H<sup>+</sup>).

Hydrophobic bonding, or Van Der Waal's forces, occurs when the ionic strength of the solution is relatively high. The high ionic strength shields negatively charged functional groups on the organic material and allows hydrophobic compounds to bind together. Schlautman et al. (1994) found that their sample of humic acid adsorbed more strongly to alumina oxides particles that fulvic acid because it is more hydrophobic.

Lastly, cation or water bridging occurs when the carboxylate group on the organic matter bonds in an inner-sphere complex with cations on the metal species. Cation bridging is important for minerals that are 2:1 phyllosilicates with isomorphic substitution and may be important for hydrous metal oxides when the solution pH is greater than the oxides pH of zero net charge. As ionic strength increases, so does the propensity for cation bridging. However, this may also induce hydrophobic bonding. The specific retention mechanism depends on solution chemistry and adsorbate and adsorbent properties (Essington 2004). It should be noted that high degree of variability in the compost and soil used in the research described in this paper leads to some uncertainty in determining the exact retention mechanism.

Research has been done to show how changes in solution pH affect sorption of dissolved metals onto soil, sand, compost, or mulch (Davis et al. 2001; Elliott et al. 1986; Grimes et al. 1999; Harmita et al. 2009). Davis et al. (2001) studied mulch, top soil, and sand for removal of copper, lead, zinc, phosphorus, and nitrates. A batch study was performed on sandy loam soil at varying pH values to determine how removal efficiency is affected by pH (Figure 5). The initial solution pH was varied from approximately 3 to 9.



Figure 5 Metal Sorption to Sandy Loam soil (2 g/L) Initial metal concentrations: Cu-106 µg/L, Pb-72 µg/L, Zn-600 µg/L (Davis et al. 2001)

Metals removal peaks at pH values that are near neutral (pH 6-8). Stormwater runoff, as seen in Table 1, varies from 3.4 to 10.7 with a median value of 7.4, so one may expect reasonably good removal for metals infiltrating through top soil. It is noted that at low pH values (<4), very little sorption occurs and even some metals leached off the soil at low pH values.

The research shows that as pH increases, adsorption increases as well. As pH increases, there are fewer protons in solution and sorbent material starts to deprotonate to maintain equilibrium with the solution. Deprotonation of functional groups will change the sorbent material surface charge from positive to negative and increase the likelihood of adsorption. Likewise, metals can hydrolyze at high pH values (Elliott et al. 1986; Schlautman 1994), yielding a more negative charge. Depending on the extent of hydrolysis, metal adsorption can be affected. Elliott et al. (1986) found that sorption is greater for metals with only one level of hydrolysis, CdOH<sup>+</sup>, for example, than for the metal ion alone, Cd<sup>+2</sup>.

The pK values for cadmium, copper, and zinc between the metal ion and the first level of hydrolysis are 10.1, 8.96, and 7.7, respectively (Elliott 1986; Essington 2004). At pH values that are near neutral, Figure 6 shows that cadmium exists as the single metal ion, Cd<sup>+2</sup>, and is therefore readily available for sorption.



Figure 6 Cadmium Hydrolysis as a function of pH (MINEQL)



Figure 7 Copper Hydrolysis (MINEQL)

Figure 7 shows that copper precipitates as tenorite at pH values that are commonly found in stormwater runoff. This has implications for the adsorption of copper. Depending on the size of the precipates, they may be removed by filtration or they may pass completely through the filter media.



Figure 8 Zinc Hydrolysis (MINEQL)

There is a balance between deprotonating the surface functional groups on the organic and inorganic material and hydrolysis of metals and this balance is dependent on the pK values for each individual constituent. Furthermore, at very low pH one may expect negligible removal of metals because of the abundance of protons. At low pH, adsorption competition occurs and surface functional groups preferentially protonate rather than adsorb metals.

#### 3.2 Adsorption Modeling

Table top jar tests are typically performed to determine the relative affinity for sorption and the maximum sorption capacity. Generally, a fixed initial pollutant concentration is mixed in bottles that contain varying masses of the sorbent. Solution characteristics such as ionic strength, pH, and temperature are held constant. After mixing, a portion of the liquid is removed and analyzed for pollutant concentrations. The amount of pollutant sorbed is equal to

$$q = \frac{V * (C_i - C_{eq})}{m} \tag{1}$$

where *V* is equal to the volume of the liquid (L),  $C_i$  is the initial pollutant concentration (mg/L),  $C_{eq}$  is the equilibrium pollutant concentration after mixing (mg/L), *m* is the mass of the sorbent (g), and *q* is the mass of pollutant sorbed per mass of sorbent (mg/g). Varying mass yields varying *q* values and a sorption isotherm curve is generated. Both sorption kinetic data and equilibrium data are generally collected and modeled.

Sorption kinetics, or how fast the pollutant will adsorb to the media, is important to determine as it can help develop an understanding of reaction mechanisms and pathways. A Lagergren Pseudo-Second order equation is typically used to model sorption kinetics (Ho and McKay 1999). The kinetic equation,

$$\frac{dq}{dt} = k(q_e - q)^2 \tag{2}$$

where q is the amount of solute sorbed per mass of sorbent (mg/g), k is the rate constant (g/mg\*time), and  $q_e$  is the equilibrium sorption amount (mg/g). This equation can be solved and linearized to find the rate constant and equilibrium sorption amount, as follows:

Substititute,

$$\hat{q} = q_e - q$$
  
 $d\hat{q} = -dq$ 

So,

$$\frac{d\hat{q}}{dt} = -k\hat{q}^2$$

Separate variables and then integrate:

$$\begin{split} \int_{q_e}^{\hat{q}} \frac{d\hat{q}}{q^2} &= -\int_{0}^{t} kdt \\ &\quad \left. \frac{-1}{\hat{q}} \right|_{q_e}^{\hat{q}} = -kt \\ &\quad \left. \frac{1}{\hat{q}_e} - \frac{1}{q_e - q} = -kt \\ &\quad \left. \frac{1}{q_e} - \frac{1}{q_e - q} = \frac{q_e - q - q_e}{q_e(q_e - q)} = \frac{q}{q_e q - q_e^2} = \frac{1}{q_e - \frac{q_e^2}{q_e^2}} \\ &\quad kt \left( \frac{q_e^2}{q} - q_e \right) = 1 \\ &\quad 1 + q_e kt = kt \frac{q_e^2}{q} \end{split}$$

The final form of the Lagergren Pseudo-Second order equation is:

$$q = \frac{ktq_e^2}{1+ktq_e} \tag{3}$$

This can be linearized as folows:

$$\frac{t}{q} = \frac{1}{k \cdot q_e^2} + \frac{t}{q_e} \tag{4}$$

Plotting this linearized form will give a y-intercept of  $1/k^*q_e^2$  and a slope of the line equal to  $1/q_e$ . These values can be used in the final form of the kinetic equation (Equation 12) to plot a model fit.

Sorption capacity modeling can be done in a similar manner. Equilibrium data can be fit to either the Langmuir or Freundlich isotherm models to determine the sorption capacity and the relative affinity for sorption. The Langmuir equation is:

$$q = \frac{q_m * K_L * C_{eq}}{1 + K_L * C_{eq}} \tag{5}$$

where  $q_m$  is the maximum sorption capacity of the sorbent (mg/g) and  $K_L$  is the sorption isotherm constant (L/mg pollutant). As  $q_m$  increases, the amount of pollutant that a sorbent may remove increases as well. Likewise, as  $K_L$  increases, the sorbent has a greater affinity for sorption of a particular pollutant. The Langmuir isotherm was originally a theoretically derived equation for gas adsorption by solid surfaces (Essington 2004). It assumes the following: site specific sorption on media; sorption surface is homogenous (all sites are equal); sorption occurs in a monolayer; and adsorbed species do not interact. The equation is based on the equilibrium concentration and empirically derived constants.

The Freundlich isotherm, on the other hand, is just a power law curve that is fit to data, relating sorption capacity to equilibrium concentration. It does not make the same assumptions as the Langmuir isotherm. The Freundlich equation is:

$$q = K_f C_{eq}^{1/n} \tag{6}$$

where  $K_f$  is the Freundlich isotherm constant (L/g sorbent), and *n* refers to the intensity of sorption (unitless). When modeling sorption data, both equations are fit to the data and model that correlates closest is typically used for any subsequent work.

### 4.0 **Previous Research**

In the field of environmental engineering, sorption studies have more commonly been used for water and wastewater treatment. However, with a new emphasis on treating stormwater, more research has been done recently to find low cost and robust sorbents.

### 4.1 Batch Sorption Studies

Batch studies have been done to look at cadmium, copper, and zinc removal by both organic and inorganic, such as tree leaves, soil, or zeolites, and natural and man-made materials, such as compost, granular activated carbon (GAC), iron oxide coated sand, or fly-ash, which is a by-product of coal power plants. In general, these materials have provided satisfactory removal of dissolved metals. Comparison between sorbent materials can be done by understanding the material's maximum sorption capacity and the relative affinity for sorption, or how quickly the material reaches its maximum sorption capacity.

For cadmium removal, Langmuir maximum sorption capacities vary from 6 mg/g to 80 mg/g for various bio-based sorbents (Table 4). A range of initial sorbent masses and metal concentration were tested under a range of initial pH values.

		Lang	muir	Freur	alich	
Paper	Sorbent	q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	K <sub>f</sub> (L/g)	n	Conditions
	Fly Ash	374.3	1.14E-03	-	-	Raw
	Fly Ash	223.2	1.17E-03	-	-	Washed
Apply at al. $(1008)$	Fly Ash	217.2	6.07E-03	-	-	Acid Treated
Apak et al. (1990)	Red Mud	113.7	5.70E-04	-	-	Raw Material
	Red Mud	107.5	1.10E-04	-	-	Acid Treated
	Red Mud	112.0	6.50E-04	-	-	Heat Treated
Saeed & Iqbal (2003)	Black Gram Husk	38.76	0.38	-	-	
	Activated Carbon	11.27	0.02	0.61	0.53	pH=6.0, Single ion
Ulmanu ot al (2002)	Kaolin	3.04	0.07	0.78	0.28	pH=6.0, Single ion
offianti et al (2003)	Compost	9.34	0.68	3.79	0.33	pH=6.0, Single ion
	Cellulose Pulp Waste	5.82	0.05	0.9	0.37	pH=6.0, Single ion
Ulmanu ot al (2002)	Compost	5.36	0.76	2.76	0.19	pH=6.0, Co-ion
Offianu et al (2005)	Cellulose Pulp Waste	1.82	0.39	1.38	0.06	pH=6.0, Co-ion
Min et al (2004)	Juniper fibers	29.54	1.00E-05	950	1.72	pH=4.2
	Coffee	6.47	0.49	1.06E-03	2.78	pH=6.7
Minamisawa at al. (2004)	Green Tea	6.37	0.26	3.33E-03	2.13	pH=6.7
willianiisawa et al. (2004)	Activated Carbon	6.22	0.40	1.31E-03	2.50	pH=6.7
	Zeolites	5.20	0.55	3.62E-03	3.70	pH=6.7
	Organoclay/anthracite	1.43	3.00E-09	-	-	
Tillman at al (2005)	Organoclay	5.00	3.00E-09	-	-	
fillinali et al (2005)	Zeolite	25.00	1.50E-08	-	-	
	Bone Char	60.00	2.00E-07	-	-	
Conc Eubrman at al	Bark	-	-	260	1.15	pH=6.5, IS=10mM
	Fly Ash	-	-	5010	0.64	pH=6.5, IS=10mM
(2007)	Sand	-	-	420	3.57	pH=6.5, IS=10mM
Sangi at al (2008)	Fraxinus Tree leaf	67.2	-	-	-	pH=5.0
Jangi et al (2008)	Ulmus tree leaf	80.0	-	-	-	pH=5.0

# Table 4 Sorption model coefficients for sorption of cadmium onto various materials Langmuir

There is also quite a range for the Freundlich coefficients for cadmium removal. Likewise, the Langmuir and Freundlich coefficients have a wide range for sorption of copper (Table 5).

Paper	Sorbent	q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	K <sub>f</sub> (L/g)	n	Conditions
	Fly Ash	335.2	9.4E-04	-	-	Raw
	Fly Ash	328.2	7.5E-04	-	-	Washed
Amelia et al. (1000)	Fly Ash	283.9	7.3E-04	-	-	Acid Treated
Apak et al (1998)	Red Mud	90.0	9.6E-04	-	-	Raw Material
	Red Mud	65.4	1.0E-03	-	-	Acid Treated
	Red Mud	87.8	7.9E-04	-	-	Heat Treated
Davis et al (2001)	Sandy Loam soil	-	-	2.5	1	pH=7.0
	Activated Carbon	6.61	0.06	0.81	0.45	pH=6.0, Single ion
(January 1, 1, 1, 2002)	Kaolin	4.47	0.15	1.46	0.24	pH=6.0, Single ion
Olmanu et al (2003)	Compost	12.77	0.35	3.51	0.48	pH=6.0, Single ion
	Cellulose Pulp Waste	4.98	0.20	1.92	0.22	pH=6.0, Single ion
	Activated Carbon	4.77	0.20	1.99	0.19	pH=6.0, Co-ion
	Kaolin	4.36	0.17	2.74	0.09	pH=6.0, Co-ion
Ulmanu et al (2003)	Compost	8.90	0.64	3.7	0.29	pH=6.0, Co-ion
	Cellulose Pulp Waste	4.55	0.13	1.55	0.23	pH=6.0, Co-ion
	Hardwood Mulch	20.59	0.11	0.325	2.42	pH=5.0, single metal
lang et al (2005)	Hardwood Mulch	22.81	0.12	0.379	2.30	pH=6.0, single metal
Jang et al (2005)	Hardwood Mulch	6.588	-	-	-	pH=5.0, Co-ion
	Hardwood Mulch	6.388	-	-	-	pH=6.0, Co-ion
	Organoclay/anthracite	2.50	1.30E-08	-	-	, , , , , , , , , , , , , , , , , , , ,
	Organoclay	3.33	3.30E-07	-	-	
Tillman et al (2005)	Zeolite	20.00	3.00F-08	-	-	
	Bone Char	50.00	2 00F-07	-	-	
	bone chui	57.47	2.00E-03	0.235	1 28	nH = 3.0
		71 43	2.00E-03	0.255	1.20	pH = 3.5
		96.15	2.20E-03	0.501	1.35	pH = 4.0
Vijayaraghavan et al	Turbinaria Ornata	104 17	2.80E-03	0.787	1.00	pH = 4.5
(2005)	Biomass	119.05	2.00E-03	0.947	1.41	pH = 5.0
		125.00	3 40F-03	1 266	1.10	pH = 5.5
		147.06	4 30F-03	2.287	1.64	pH = 6.0
	Compost	-	-	0.56	1.01	pH=5, particle size=2360-4750 µm
	Compost	-	-	0.67	1.43	pH=5, particle size=1181-2360 um
Seelsaen et al (2006)	Compost	-	-	0.71	1.15	pH=5, particle size=601-1180 um
	Compost	-	-	0.96	1.10	pH=5, particle size=151-600 um
	Compost	-	-	1.24	1.02	pH=5, particle size=<150 um
	Bark	-	-	90	-0.42	
Genc Fuhrman et al (2007)	Fly Ash	-	-	100	0.46	
Genc Fuhrman et al (2007)	Sand	-	-	100	1.57	
Amarasinghe (2008)	Black Tea waste	48.0	0.0076	0.7012	1.35	pH=5.5
	Compost	29.8	0.016	-	-	No pH set
	Green Waste Cmpst	30.2	0.022	-	-	No pH set
Nwachukwu et al (2008)	Peat	11.8	0.034	-	-	No pH set
	Wood Bark	17.1	0.034	-	-	No pH set
	Fraxinus Tree leaf	33.1	-	-	-	pH=5.0
Sangi et al (2008)	Ulmus tree leaf	69.5	-	-	-	pH=5.0
	Na-Montmorillonite	33.3	-	-	-	pH=5.6, IS=1mM
	Fly Ash	18.8	-	-	-	pH=5.6. IS=1mM
	Fly Ash	126.7	-	-	-	pH=8.7, IS=1mM
	Goethite powder	10.3	-	-	-	pH=5.6, IS=1mM
xiao et al (2009)	Camellia tree leaf	47.6	-	-	-	pH=5.6, IS=1mM
	Primary sludge	41.7	-	-	-	pH=5.6, IS=1mM
	Pinewood sawdust	22.6	-	-	-	pH=5.6, IS=1mM
	Fraxinus Tree leaf	33.1	-	-	-	pH=5.0

# Table 5 Sorption model coefficients for sorption of copper onto various materials Langmuir Freundlich

The Langmuir maximum sorption capacity varies from 11.8 mg/g for sorption to peat to 69.5 mg/g for sorption to Ulmus tree leaves. The Freundlich coefficient, K<sub>f</sub>, varies from 0.38 L/g for to 90 L/g for hardwood mulch and bark, respectively. Table 2 shows the high degree of variability in using different sorbent materials and highlights the need for simple batch tests prior to calculating the life cycle of a rain garden that may be using these materials. Like cadmium and copper, zinc removal has also been studied and shown to have

#### varying degrees of sorption (

		Lang	gmuir	Freu	ndlich	
Paper	Sorbent	q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	K <sub>f</sub> (L/g)	n	Conditions
Davis et al (2001)	Sandy Loam soil	-	-	0.15	1	pH=7.0
	Hardwood Mulch	12.10	0.37	0.196	4.22	pH=5.0, single metal
lang at al $(2005)$	Hardwood Mulch	12.23	0.41	0.200	4.43	pH=6.0, single metal
	Hardwood Mulch	1.210	-	-	-	pH=5.0, Co-ion
	Hardwood Mulch	0.978	-	-	-	pH=6.0, Co-ion
	Organoclay/anthracite	0.83	2.30E-08	-	-	
Tillman at al (2005)	Organoclay	5.00	2.00E-09	-	-	
fillinali et al (2005)	Zeolite	16.67	4.00E-08	-	-	
	Bone Char	43.00	1.00E-07	-	-	
Soolsoon (2006)	Compost	11.2	3.16E-02	-	-	
Seelsaeli (2000)	Zeolites	4.25	6.92E-03	-	-	
	Bark	-	-	1	0.63	
Genc Fuhrman et al (2007)	Fly Ash	-	-	40	0.42	
	Sand	-	-	30	1.37	
	Compost	13.4	0.093	-	-	No pH set
Nwachukwu at al (2008)	Green Waste	13.9	0.098	-	-	No pH set
NWACHUKWU EL AI (2008)	Peat	4.2	0.041	-	-	No pH set
	Wood Bark	11.0	0.022	-	-	No pH set

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 Table 6 Sorption model coefficients for sorption of zinc onto various materials

		Lang	muir	Freur	nalich	
Paper	Sorbent	q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	K <sub>f</sub> (L/g)	n	Conditions
Davis et al (2001)	Sandy Loam soil	-	-	0.15	1	pH=7.0
	Hardwood Mulch	12.10	0.37	0.196	4.22	pH=5.0, single metal
lang at al (200E)	Hardwood Mulch	12.23	0.41	0.200	4.43	pH=6.0, single metal
Jang et al (2005)	Hardwood Mulch	1.210	-	-	-	pH=5.0, Co-ion
	Hardwood Mulch	0.978	-	-	-	pH=6.0, Co-ion
	Organoclay/anthracite	0.83	2.30E-08	-	-	
Tillman at al (2005)	Organoclay	5.00	2.00E-09	-	-	
fillinali et al (2005)	Zeolite	16.67	4.00E-08	-	-	
	Bone Char	43.00	1.00E-07	-	-	
Soolsoon (2006)	Compost	11.2	3.16E-02	-	-	
Seelsaell (2000)	Zeolites	4.25	6.92E-03	-	-	
	Bark	-	-	1	0.63	
Genc Fuhrman et al (2007)	Fly Ash	-	-	40	0.42	
	Sand	-	-	30	1.37	
	Compost	13.4	0.093	-	-	No pH set
Nwashukuwu at al (2008)	Green Waste	13.9	0.098	-	-	No pH set
wachukwu et al (2008)	Peat	4.2	0.041	-	-	No pH set
	Wood Bark	11.0	0.022	-	-	No pH set

Elliott (1986) showed that competition exists between different metals for sorption sites. The relative order of sorption preference is Pb > Cu > Zn > Cd and the competition effect has been observed in other studies (Al-Asheh et al. 1997; Al-Asheh et al. 2008; Jang et al. 2005; Nwachukwu et al. 2008). Comparing similar materials in Table 4 through Table 7

shows that lead has the highest affinity for sorption, followed by copper, zinc, and cadmium.

		Lang	muir	Freur	ndlich	
Paper	Sorbent	q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	K <sub>f</sub> (L/g)	n	Conditions
	Fly Ash	526.0	1.1E-03	-	-	Raw
	Fly Ash	490.7	1.1E-03	-	-	Washed
Analyst at $al(1008)$	Fly Ash	483.0	8.4E-04	-	-	Acid Treated
Apak et al (1990)	Red Mud	158.9	6.6E-04	-	-	Raw Material
	Red Mud	118.5	1.6E-03	-	-	Acid Treated
	Red Mud	137.2	1.2E-03	-	-	Heat Treated
Davis et al (2001)	Sandy Loam soil	-	-	4.5	1	pH=7.0
	Coffee	16.5	0.20	7.5E-03	1.89	pH=4.0
Minamisawa at al (2004)	Green Tea	24.0	0.29	3.8E-03	2.38	pH=4.0
Williamisawa et al (2004)	Activated Carbon	21.34	0.20	1.7E-03	2.63	pH=4.0
	Zeolites	206.4	0.03	5.8E-03	1.64	pH=4.0
	Hardwood Mulch	63.40	0.23	0.35	4.51	pH=5.0, single metal
lang of al $(2005)$	Hardwood Mulch	72.52	0.26	0.43	4.03	pH=6.0, single metal
	Hardwood Mulch	31.70	-	-	-	pH=5.0, Co-ion
	Hardwood Mulch	34.81	-	-	-	pH=6.0, Co-ion
Amarasinghe (2008)	Black Tea waste	65.0	0.049	9.65	2.57	pH=5.5
	Compost	58.9	0.030	-	-	No pH set
Nwachukwu et al (2008)	Green Waste Cmpst	86.5	0.044	-	-	No pH set
Nwachukwu et al (2008)	Peat	47.8	0.021	-	-	No pH set
	Wood Bark	75.3	0.011	-	-	No pH set
Sangi et al (2008)	Fraxinus Tree leaf	172.0	-	-	-	pH=5.0
Jaligi et al (2000)	Ulmus tree leaf	201.1	-	-	-	pH=5.0

 Table 7 Sorption model coefficients for sorption of lead onto various materials

Jang et al. (2005) studied the competition effect for copper, lead, and zinc. At pH 5.0 and in the presence of other metal ions, the maximum sorption capacity for copper decreased from 20.6 to 6.6 mg/g. Zinc decreased from 12.1 to 1.2 mg/g under similar conditions and lead decreased from 63.4 to 31.7 mg/g (Jang et al. 2005). The sorption capacities found during experiments using multiple metals may be a more realistic expectation for the ideal capacity of a material. The study described herein seeks to maintain a realistic stormwater pollutant mixture and so a combination of the metals is used.

## 4.2 Column Study research

Fixed bed, flow through columns are a valuable tool for studying sorption because they are typically cheaper, quicker, and more controlled than field monitoring in an actual rain garden. Additionally, column studies allow a much larger representative sample of the sorbent material and a wider variety of experimental conditions that mimic realistic conditions better than a batch study. Examples of the variation in column studies include alternating wet and dry periods (Hatt et al. 2007a), competitive heavy metal transport (Kratochvil & Volesky 2000; Tsang & Lo 2006) or testing various unconventional sorbents. The ultimate goal behind studying sorption in a column is to develop a breakthrough curve for a particular pollutant.

Several papers report breakthrough times as a function of bed volumes. Bed volumes are not directly comparable from paper to another because of varying column and fill media characteristics. The data in several papers has been compiled and normalized to report the results as depth of water treated at breakthrough, rather than bed volumes to breakthrough (Table 8).

			Definiti	on of	Depth of Wa	ater Treated	q at BT	q at Exh	Lifespan
Paper	Metal	Sorbent	Breakthrough	Exhaustion	at BT (m)	at Exh (m)	(mg/g)	(mg/g)	(yrs)
	Cu	Tea Waste	$C/C_{0} = 0.2$	$C/C_{0} = 1.0$	1.56	2.69	6	13	0.24
Americanaha (2007)	cu	GAC	$C/C_{0} = 0.2$	$C/C_{0} = 1.0$	1.56	3.54	3	8	0.24
Paper Amarasinghe (2007) Davis et al (2001) Genc-Fuhrman et al (2008) Liu et al (2005) Saeed & Iqbal (2003) Tillman et al (2005) Zhang et al (2008)	DI.	Tea Waste	$C/C_0 = 0.2$	$C/C_0 = 1.0$	7.07	9.90	33	46	1.10
Paper Amarasinghe (2007) Davis et al (2001) Genc-Fuhrman et al (2008) Liu et al (2005) Saeed & Iqbal (2003)	PD	GAC	$C/C_{0} = 0.2$	$C/C_{0} = 1.0$	3.96	8.49	8	19	0.61
	Cu	Sandy Loam soil	-	$C/C_0 = 1.0$			> 0.05	-	58
	Pb	Sandy Loam soil	-	$C/C_0 = 1.0$			> 0.016	-	> 58
	Zn	Sandy Loam soil	-	$C/C_0 = 1.0$	No breakthi	ough found	> 0.300	-	> 58
Davis et al (2001)	Сп	Shredded mulch	-	$C/C_{0} = 1.0$	at a depth	treated of	> 0 10	-	-
	Ph	Shredded mulch	_	$C/C_{2} = 1.0$	13.2	24 m	> 0 039	-	_
	7 n	Shredded mulch		C/C = 1.0			> 0.037		
	Cd	Silleudeu muich	-	$C/C_0 = 1.0$	200.1/	041.04	> 0.09	-	-
Genc-Fuhrman et al	Cu	Ferrosorp (from sorbent)	$C/C_0 = 0.010$	$C = C_0$	208.10	841.84	0.34	1.39	32.32
(2008)	Cu	Ferrosorp (Iron sorbent)	$C/C_0 = 0.07$	$C = C_0$	130.10	637.73	0.17	0.82	20.20
	Zn	Ferrosorp (iron sorbent)	$C/C_{0} = 0.60$	$C = C_0$	267.09	663.29	0.17	0.72	41.47
		Sand	$C/C_0 = 0.1$	$C/C_0 = 0.9$	4.98	-	<0.001	<0.001	0.77
	7n	GAC	$C/C_{0} = 0.1$	$C/C_{0} = 0.9$	22.40	-	0.4	1.63	3.48
	211	Iron Oxide Coated Sand	$C/C_{0} = 0.1$	$C/C_{0} = 0.9$	4.98	-	0.013	0.019	0.77
		Mn Oxide Coated Sand	$C/C_{0} = 0.1$	$C/C_{0} = 0.9$	13.76	-	<0.001	<0.001	2.14
		Sand	$C/C_{0} = 0.1$	$C/C_{0} = 0.9$	4.98	-	<0.001	0.0016	0.77
	Cu	GAC	$C/C_{0} = 0.1$	$C/C_{0} = 0.9$	149.36	-	3.51	4.1	23.19
Liu et al (2005)		Iron Oxide Coated Sand	$C/C_0 = 0.1$	$C/C_0 = 0.9$	4.98	-	0.006	0.122	0.77
		Mn Oxide Coated Sand	$C/C_0 = 0.1$	$C/C_0 = 0.9$	137.55	-	0.028	0.15	21.36
		Sand	$C/C_0 = 0.1$	$C/C_0 = 0.9$	4.98	-	<0.001	<0.001	0.77
		GAC	$C/C_{0} = 0.1$	$C/C_{0} = 0.9$	7 47		0.02	1 11	1 16
	Cd	Iron Ovide Coated Sand	C/C = 0.1	C/C = 0.0	/ 08		0.02	0.017	0.77
		Mn Oxide Coated Sand	C/C = 0.1	$C/C_0 = 0.7$	12 76		<0.013	<0.017	2.14
Sacad & Jahal (2002)	Cd		$C/C_0 = 0.1$	$C/C_0 = 0.9$	15.70	-	<0.001	<0.001	2.14
Saeeu & Iquai (2003)	Cu	Black grann nusk	$C/C_0 = 0.01$	$C/C_0 = 1.0$	100.40	202.14	49.74		24.29
		Organociay/anthracite	$U/U_0 = 0.95$	-	2.50	-	0.78	-	0.39
	Cd	Organoclay	$C/C_0 = 0.95$	-	4.45	-	1.84	-	0.69
		Zeolite	C/C <sub>o</sub> = 0.95	-	61.72	-	25.98	-	9.58
		Bone Char	$C/C_0 = 0.95$	-	112.78	-	63.91	-	17.51
		Organoclay/anthracite	$C/C_0 = 0.95$	-	2.77	-	0.59	-	0.43
Tillman et al (2005)	Cu	Organoclay	$C/C_{o} = 0.95$	-	9.88	-	1.23	-	1.53
	cu	Zeolite	$C/C_{o} = 0.95$	-	76.69	-	16.37	-	11.91
		Bone Char	$C/C_{0} = 0.95$	-	99.85	-	42.45	-	15.51
		Organoclay/anthracite	$C/C_0 = 0.95$	-	3.27	-	0.68	-	0.51
	-	Organoclay	$C/C_0 = 0.95$	-	3.78	-	0.95	-	0.59
	Zn	Zeolite	$C/C_0 = 0.95$	-	35.23	-	8.96	-	5.47
		Bone Char	$C/C_0 = 0.95$	-	71.32		28.72	-	11.08
		Sand	C/Co = 0.01	-	268		-	-	41.61
	Cu	Sand + 2.5% Fly Ash	C/Co = 0.01	-	1135	-	-	-	176.24
		Sand + 5% Fly Ash	C/Co = 0.01	-	13115	-	-	-	2036.49
		Sand	C/Co = 0.01	-	574	-	-	-	89.13
Zhang et al (2008)	Pb	Sand + 2.5% Fly Ash	C/Co = 0.01	-	1204		-	-	186.96
		Sand + 5% Fly Ash	C/Co = 0.01	-	21960		-	-	3409.94
	7n	Sand L 2 5% Ely Ach	C/CO = 0.01	-	3/0		-	-	18.48
	211	Sand + 5% Fly Ash	C/CO = 0.01 C/CO = 0.01	-	10919		-	-	1695.50

## Table 8 Column study results for various metals and sorbents

In Table 8, the depth of water treated was calculated using several different methods based on the information given in each paper. The depth of water treated was chosen as a consistent method of normalizing the data across a variety of column geometries so that the results from each column study may be compared. One method to determine the depth of water is:

$$D_w = \frac{t * Q}{Area} \tag{7}$$

where *t* is the time elapsed to breakthrough or exhaustion, *Q* is the flow rate of water through each column, *Area* is the inside cross-sectional area of the column, and  $D_w$  is the depth of water treated. Another method for determining the depth of water treated is:

$$D_w = \frac{N * V_p}{\eta * Area} \tag{8}$$

where *N* is the number of pore volumes to breakthrough or exhaustion,  $V_p$  is the column pore column,  $\eta$  is the porosity of the filter media, and *Area* is the inside cross-sectional area of the column. Alternatively, one may calculate  $D_w$  as:

$$D_w = N * L \tag{9}$$

where *L* is the depth of the filter media. A fourth method to determine  $D_w$  is:

$$D_w = \frac{V_w}{Area} \tag{10}$$

 $V_w$  is the volume of water passed at breakthrough or exhaustion. The life span of the media is found by dividing the depth of water treated by annual runoff per year. Rain gardens are designed to infiltrate the first  $\frac{1}{2}$  inch (0.0127 m) of runoff, with the excess routed to other drainage systems.

$$D_R = \frac{\sum \min(C * R_d, 0.0127m)}{k * f}$$
(11)

where  $D_R$  is the annual depth of runoff (m/yr), *C* is a runoff coefficient  $R_d$  is the daily rainfall amount, *0.0127 m* is the first  $\frac{1}{2}$  inch of runoff, *k* is the number of years in the precipitation record, and *f* is the ratio of rain garden area to drainage area. The runoff coefficient is assumed to be 0.5 and the rain garden area is assumed to be 5% of the drainage area; *f* equals 0.05 The precipitation record for the Minneapolis/St. Paul area from 2000-2009 was used in this calculation and the annual depth of runoff treated was found to be 6.44 m/yr.

Several other papers did not report breakthrough data, yet still provide pertinent information for discussion. Hatt et al. (2007) studied the impact of variable wet and dry periods on removal of heavy metal (Cu, Pb, Zn), phosphorus, nitrogen, and sediments using fixed bed columns made with sandy loam soil and various supplementary materials, such as sand, compost, vermiculite, mulch, or charcoal. This paper found that alternating wet and dry periods did not impact metals, phosphorus, or sediments removal. However, nitrogen removal was impacted because of the creation or elimination of an anaerobic zone. Anaerobic or aerobic conditions will not effect metals removal in typical stormwater conditions. In a companion paper, Hatt et al. (2008) reports the performance of the different materials used in the column studies. Mean concentration for 6 different media combinations are reported along with soil standards for metals and years of operation before pollutant levels in the soil exceed the standard. As reported, the years until the standards are exceeded are 6, 37, 4, 4 for copper, manganese, lead, and zinc, respectively, for the top 5 centimeters of filter media. The author also reports that the soils used appear to be a source of nutrients, rather than a sink (Hatt et al. 2008)

Gong and Donahoe (1997) studied removal of various heavy metals by two different types of sandy loam soil. Using columns with an approximate bed volume of 40 mL, this paper found that cadmium, copper, and zinc were initially removed, followed by a period of leaching, where the effluent concentration exceeded the initial concentration, and then lastly, an effluent concentration that equals the initial metals concentration (Figure 9). K, Ca, and Mg were released, indicating that cation exchange may play a role in removal of the metals.



Figure 9 Cd, Cu, and Zn removal by a sandy loam soil. Cd, Cu, Zn C<sub>0</sub> ~ 9 mg/L

Furthermore, analysis by scanning electron microscope indicates that specific adsorption to iron, aluminum, or manganese hydrous oxides also is a dominant removal mechanism. A simulated acid rain test was performed on these sample as well. The pH was approximately 4.4 Results indicate that all sorbed metals were released, including metals that originated on the soil itself (Gong and Donahoe 1997).

Simultaneous sorption of metals was studied using sandy loam soil in columns (Tsang and Lo 2006). The authors found that a binary solution of copper and cadmium reduced the total amount of metals sorbed when compared to the sum of metals removed from columns tested with only a single metal. In the binary metals columns, cadmium reached equilibrium first, followed by copper. The authors found that cadmium leached from the column after initially adsorbing to the soil surface because copper displaced the adsorbed cadmium after initial copper breakthrough. Similar results indicating competition between metals were found in other studies (Kratochvil and Volesky 2000; Syring et al. 2009). Lee and Davis (2001) found that competition effects in adsorption to soil were minimized in a solution of cadmium and copper, each at a concentration of 10<sup>-4</sup> M. In a solution of 1 mM cadmium and copper, sorption of cadmium was reduced by 30% because copper has a higher affinity for sorption to soil than cadmium.

Fixed bed columns provide the researcher with an experimental model that more closely resembles actual rain garden performance for both hydraulics and pollutant than batch studies. The results column studies can then be converted to determine a life span of the rain garden. For the materials listed in Table 8, the life span may range from 0.25 to over 3,000 years of service depending on the sorbent material, the ratio of desired effluent concentration to influent concentration, and hydraulics.

### 5.0 Discussion and Conclusions

There has been some research performed on the use of adsorption as a means of cleaning stormwater runoff, yet there are still some questions that should be researched. As one can see, the high degree of variability in sorptive materials lends importance to choosing rain garden materials wisely. Sand based materials have a low expected life span, but will not adversely affect the hydraulics or chemical characteristics of the effluent. Native soil, while it may have a greater sorption capacity, may also negatively impact infiltration. The effect of soil amendments, such as fly ash, GAC, or zeolites, on the soil should be studied. It is conceivable that changes in pH and ionic strength or leaching of other sorbed species, such as nutrients, could have a negative impact on the downstream ecosystem. Natural materials such as compost, woody debris, and different types of soil should continue to be studied and a cost analysis should be done to compare the relative effectiveness of a less costly alternative. Lastly, research is needed on media configuration, specifically with the goal of reducing dissolved metals and nutrients at the same time. Removal for nutrients differs from the specific chemistry used to remove dissolved metals. It may be possible to combine two technologies to effectively reduce both dissolved metals and nutrients.

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