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Sorption and Release of Dissolved Pollutants Via Bioretention Media

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Abstract

The removal and retention of cadmium, copper, and zinc is investigated with batch and column experiments of compost and sand using synthetic stormwater. The maximum sorption capacities found using the Langmuir isotherm equation for Cd and Zn are 2.13 mg/g and 3.82 mg/g for compost and 0.02 and 0.07 mg/g for sand. Copper precipitates at the solution pH and could not be modeled. Column studies using three different ratios of compost (50, 30, 10, and 0%, by bulk volume) in sand were conducted to develop breakthrough curves. The sorption capacities for 15 cm of filter media found using the Thomas Model are 0.78, 0.37, 0.23, and 0.07 mg Cd/g for 50%, 30%, 10% and 0% compost, respectively. The column study results were used to predict bioretention lifespan. At stormwater concentrations, 15 cm of filter media composed of 30% compost and 70% sand will last 95 years until breakthrough, when the effluent concentration is 10% of the influent concentration. In both batch and column studies, effluent concentrations of phosphorus exceeded the influent concentrations indicating phosphorus export from the filter media to receiving waters. The release of phosphorus was initially high, but then decreased to a steady state value of 0.29 mg/L (C_0=0.13 mg/L) and remained constant throughout the test. The total yearly load exported from a typical bioretention practice containing 30% compost is estimated at 347 mg dissolved phosphorus per year. Lastly, the results are discussed in relation to stormwater management operation and maintenance. Over time, toxic metals will continue to migrate down through the filter media. Influxes of new toxic metals and the release of toxic metals by degrading compost will cause the concentration in the filter media to increase. The removal of phosphorus is dependent on the background level of phosphorus on the chosen filter media and, based on the column study results, may continue to release from the filter media at a constant rate. Bioretention practices composed of MNDOT Grade 2 compost and C-33 sand may be a source of phosphorus to receiving waters. Thus, a novel recommendation for bioretention redesign is made that will enable us to better design infiltration practices for protection of receiving ground and surface waters by retaining both dissolved toxic metals and phosphorus.

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Executive Summary

This report reviews the literature on the concentrations, sources, and effects of dissolved toxic metals found in stormwater runoff. The review also discusses relevant management practices and parameters related to the removal of toxic metals using materials commonly found in bioretention practices, such as MNDOT Grade 2 compost and C-33 sand. The review also explores literature that indicates bioretention practices may be a source of phosphorus. A more comprehensive literature review on the concentration and effect of all stormwater pollutants on the contamination of soil and groundwater due to stormwater infiltration practices was previously completed (Weiss et al., 2008).

The removal and retention of cadmium, copper, and zinc was then investigated with batch and column experiments of compost and sand using synthetic stormwater. Sorption kinetics and equilibrium for compost were studied with 0.5 mg/L each of Cd^{2+}, Cu^{2+}, and Zn^{2+} at a solution pH of 7.2 in batch studies. The maximum sorption capacities found using the Langmuir isotherm equation for Cd and Zn are 2.13 mg/g and 3.82 mg/g for compost and 0.02 and 0.07 mg/g for sand. Copper precipitates at the solution pH and could not be modeled. Column studies using three different ratios of compost (50, 30, 10, and 0%, by bulk volume) in sand were conducted to develop breakthrough curves. The sorption capacities for 15 cm of filter media found using the Thomas Model are 0.78, 0.37, 0.23, and 0.07 mg Cd/g for 50%, 30%, 10% and 0% compost, respectively, with the sorption capacities close to constant for varying bed depths. These sorption capacities, when adjusted for mass of sand and compost, are consistent with the sorption capacities found using the batch studies. The column study results were used to predict bioretention lifespan. At stormwater concentrations, 15 cm of filter media composed of 30% compost and 70% sand will last 95 years until breakthrough, when the effluent concentration is 10% of the influent concentration.

In both batch and column studies, effluent concentrations of phosphorus exceeded the influent concentrations indicating possible phosphorus export from the filter media to receiving waters. The release of phosphorus was initially high, but then decreased to a steady state value of 0.29 mg/L (C_0=0.13 mg/L) and remained constant throughout the

test. The total yearly load exported from a bioretention practice containing 30% compost is 347 mg dissolved phosphorus per year.

Lastly, the results are discussed in relation to stormwater management operation and maintenance. Over time, toxic metals will continue to migrate down through the filter media. Influxes of new toxic metals and the release of toxic metals by degrading compost will cause the concentration in the filter media to increase. The removal of phosphorus is dependent on the background level of phosphorus on the chosen filter media and, based on the column study results, may continue to release from the filter media at a constant rate. Bioretention practices composed of MNDOT Grade 2 compost and C-33 sand may be a source of phosphorus to receiving waters. Thus, a novel recommendation for bioretention redesign is made that will enable us to better design infiltration practices for protection of receiving ground and surface waters by retaining both dissolved toxic metals and phosphorus.

1.0 Introduction

Modern wastewater treatment practice has effectively reduced much of the load coming from point sources of pollution, yet our lakes and rivers continue to suffer from water quality impairments. The focus on water quality has shifted to non-point sources such as stormwater runoff from urban and agricultural activities. To manage stormwater, the degree of impairment on the water body caused by influx of pollutants must be considered. The Clean Water Act of 1972 required (in the United States) that a total maximum daily load (TMDL) be established (USEPA, 1972). The TMDL determines a specific pollutant load coming from contributing watersheds that a water body can receive and still meet the water quality standards and allocates a specific allowable pollutant load to each contributing source. Stormwater runoff is difficult to treat and regulate because the amount and composition varies spatially, temporally, and in constitution (Pitt et al., 1995; Marselek et al., 1999; Kayhanian et al., 2008). Pollutants carried by runoff such as suspended solids, oil and grease, nutrients, pathogens, petroleum hydrocarbons, and toxic metals come from a variety of sources, including vehicle deposition on roads or parking lots, industrial or construction sources, and other anthropogenic activities. These pollutants are transported during rain events through the stormwater system to surface waters, often with little or no treatment. If the TMDL load allocation from a drainage area is known, then strategic implementation of treatment practices designed to target specific stormwater pollutants is possible.

Toxic metals are a specific stormwater pollutant of concern that contributes to the impairment of ecosystems. These metals, which include cadmium, copper, lead, and zinc, increase lesion rates, limit reproduction by delaying or inhibiting hatching, and cause negative developmental effects on freshwater organisms (Gagne et al., 2009; Heier et al., 2009; Chung et al., 2009; Gross et al., 2009). The primary source of cadmium, copper, and zinc in stormwater runoff is vehicle deterioration, such as brake pads and tires (Sansalone and Buchberger, 1997; McKenzie et al., 2009). Other sources include industrial runoff and zinc coated roofs (Duncan, 1999). Maestre and Pitt (2005) reviewed NPDES MS4 permit reports for the concentration of pollutants in stormwater and found median total concentrations of cadmium, copper, lead, and zinc of 1, 16, 3, and 112 µg/L, respectively. Dissolved concentrations were approximately half of the total concentration except for lead, which was primarily associated with the particulate phase. Kayhanian et al. (2007) sampled 34 highway sites over a three-year period in California and found median total concentrations of cadmium, copper, lead, and zinc of 0.4, 21, 7.6 and 111 µg/L, respectively. The maximum allowable concentration to avoid acute toxicity effects on aquatic life is 2, ~10, 65, and 120 µg/L for cadmium, copper, lead, and zinc, respectively (USEPA, 2003; USEPA, 2007). Based on the data used in Maestre and Pitt (2005), 31, 66, 15 and 40% of the total cadmium, copper, lead, and zinc samples exceed the EPA ambient water quality criteria. Because lead is primarily associated with the particulate stage, this investigation on the fate of dissolved metals will focus on cadmium, copper, and zinc.

One stormwater management practice that may aid in the removal of toxic metals from stormwater runoff is bioretention. Bioretention practices, or rain gardens, are shallow depressions where native soil is removed and replaced with a mixture of compost, sand, soil, and/or other engineered media designed to facilitate infiltration of stormwater runoff. The engineering sciences of unit operations such as filtration and sorption, used in drinking and wastewater treatment, can be applied to bioretention facilities to understand the physical and chemical processes used to remove pollutants found in stormwater runoff.

While it is known that solution pH greatly affects sorption, many studies are done at a pH less than what is found in stormwater runoff to enhance the solubility of the metals in solution. Kayhanian et al. (2007) report a mean runoff pH of 7.1 (SD = 0.7, Median = 7, N = 633) for highway runoff sites in California. Maestre and Pitt (2005) surveyed stormwater runoff results of NPDES studies and report a median pH value of 7.4 with 10th and 90th percentiles of 6.47 and 8.4, respectively. At a pH < 6, batch studies using common organic sorbents, such as wood mulch, tree leaves, compost, and sawdust to remove cadmium, copper, lead, and zinc yield a range of sorption capacities from 10 to 80 mg/g (Ulmanu et al., 2003; Jang et al., 2005; Seelsaen et al., 2006; Sangi et al., 2008; Xiao et al., 2009). There is much research on sorption of metals to various sorbents, but it may not be applicable for removal of stormwater pollutants via sorption because of the low pH used in the experiments. Thus, research is needed to determine the effectiveness of sorbent materials at a pH comparable to stormwater runoff.

Development of a full breakthrough curve using a fixed bed column enables prediction of the lifespan for a similarly constructed bioretention facility. Breakthrough results for column studies in the literature are given in Table 1. Despite the abundance of column study research, commonly used filter materials such as compost have not been analyzed and there exists a need to describe the removal efficiency of the compost and sand used often in the construction of bioretention facilities at a pH representative of runoff.

Bioretention may prove to be effective at removing dissolved metals, but literature indicates inconsistent results on the removal of nutrients. Laboratory studies and field studies using mulch and sandy loam soil show reductions in total phosphorus of 71-81% (Davis et al., 2001) and 77-87% for laboratory bioretention boxes and 65 and 87% reduction with effluent concentrations of 0.1 mg/L for two bioretention practices (Davis et al., 2006). Column studies made of sand, sandy loam soil, and various amendments including compost and mulch indicate phosphorus removal in the sand columns alone but phosphorus release from the columns of sandy loam soil amended with compost and mulch (Hatt et al. 2007, 2008). Lastly, field studies indicate variable performance of bioretention practices for phosphorus removal (Hunt et al., 2006; Hatt et al., 2009; Brown and Hunt, 2011). Hunt et al. (2006) relates the release of phosphorus directly to the P-index of the filter media used. Soil that had a low P-index (low amount of adsorbed phosphorus) was able to effectively remove phosphorus from runoff whereas soil with a high P-index released significantly more phosphorus than what entered the bioretention facility. This study seeks to quantify the degree of phosphorus retention or release from filter media commonly used in bioretention practices.

Table 1. Breakthrough (BT) and exhaustion (EX) for column studies with specific metals sorbing to bioretention amendments and media.

Metal	Sorbent	Definition of		q at BT (mg/g)	q at EX (mg/g)	pH	Paper
		Breakthrough	Exhaustion				
Cu	Sandy Loam Soil	$C/C_o = 0.2$	-	> 0.05	-	7	Davis et al. (2001)
	Mulch	$C/C_o = 0.1$	-	> 0.10	-	7	
Pb	Sandy Loam Soil	$C/C_o = 0.29$	-	> 0.016	-	7	
	Mulch	$C/C_o = 0.19$	-	> 0.039	-	7	
Zn	Sandy Loam Soil	$C/C_o = 0.50$	-	> 0.300	-	7	
	Mulch	$C/C_o = 0.16$	-	> 0.89	-	7	
Cd	Black gram husk	$C/C_o = 0.01$	$C/C_o = 1.0$	49.74		5	Saeed & Iqbal (2003)
Zn	Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	<0.001	<0.001	6.5	Liu et al. (2005)
	GAC	$C/C_o = 0.1$	$C/C_o = 0.9$	0.4	1.63	6.5	
	Iron Oxide Coated Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	0.013	0.019	6.5	
	Mn Oxide Coated Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	<0.001	<0.001	7	
Cu	Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	<0.001	0.0016	6.5	
	GAC	$C/C_o = 0.1$	$C/C_o = 0.9$	3.51	4.1	6.5	
	Iron Oxide Coated Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	0.006	0.122	6.5	
	Mn Oxide Coated Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	0.028	0.15	7	
Cd	Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	<0.001	<0.001	6.5	
	GAC	$C/C_o = 0.1$	$C/C_o = 0.9$	0.02	1.11	6.5	
	Iron Oxide Coated Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	0.013	0.017	6.5	
	Mn Oxide Coated Sand	$C/C_o = 0.1$	$C/C_o = 0.9$	<0.001	<0.001	7	
Cd	Organoclay/anthracite	-	$C/C_o = 0.95$	-	0.78	6.41	Tillman et al. (2005)
	Organoclay	-	$C/C_o = 0.95$	-	1.84	6.41	
	Zeolite	-	$C/C_o = 0.95$	-	25.98	6.41	
	Bone Char	-	$C/C_o = 0.95$	-	63.91	6.41	
Cu	Organoclay/anthracite	-	$C/C_o = 0.95$	-	0.59	5.58	
	Organoclay	-	$C/C_o = 0.95$	-	1.23	5.58	
	Zeolite	-	$C/C_o = 0.95$	-	16.37	5.58	
	Bone Char	-	$C/C_o = 0.95$	-	42.45	5.58	
Zn	Organoclay/anthracite	-	$C/C_o = 0.95$	-	0.68	3.1	
	Organoclay	-	$C/C_o = 0.95$	-	0.95	3.1	
	Zeolite	-	$C/C_o = 0.95$	-	8.96	3.1	
	Bone Char	-	$C/C_o = 0.95$	-	28.72	3.1	
Cu	Tea Waste	$C/C_o = 0.2$	$C/C_o = 1.0$	6	13	-	Amarasinghe and Williams (2007)
	GAC	$C/C_o = 0.2$	$C/C_o = 1.0$	3	8	-	
Pb	Tea Waste	$C/C_o = 0.2$	$C/C_o = 1.0$	33	46	-	
	GAC	$C/C_o = 0.2$	$C/C_o = 1.0$	8	19	-	
Cd	Ferrosorp (iron sorbent)	$C/C_o = 0.016$	$C/C_o = 1.0$	0.34	1.59	6.80	Genc-Fuhrman et al. (2008)
Cu	Ferrosorp (iron sorbent)	$C/C_o = 0.07$	$C/C_o = 1.0$	0.17	0.82	6.80	
Zn	Ferrosorp (iron sorbent)	$C/C_o = 0.60$	$C/C_o = 1.0$	0.17	0.72	6.80	
Cu	Sand	$C/C_o = 0.01$	-	0.07	-	6.9	Zhang et al. (2008)
	Sand + 2.5% Fly Ash	$C/C_o = 0.01$	-	0.07	-	11.1	
	Sand + 5% Fly Ash	$C/C_o = 0.01$	-	0.06	-	11.3	
Pb	Sand	$C/C_o = 0.01$	-	0.06	-	7.4	
	Sand + 2.5% Fly Ash	$C/C_o = 0.01$	-	0.06	-	11.1	
	Sand + 5% Fly Ash	$C/C_o = 0.01$	-	0.06	-	11.2	
Zn	Sand	$C/C_o = 0.01$	-	0.05	-	7.2	
	Sand + 2.5% Fly Ash	$C/C_o = 0.01$	-	0.06	-	11	
	Sand + 5% Fly Ash	$C/C_o = 0.01$	-	0.05	-	11.3	
Cu	Peat	$C/C_o = 0.05$	$C/C_o = 1.0$	18.08	36.61	6	Izquierdo et al. (2009)

This study will report on batch sorption experiments and column experiments performed to investigate the ability of bioretention practice media to remove and retain dissolved toxic metals under controlled conditions designed to mimic representative stormwater qualities and loading rates. This study will also investigate dissolved phosphorus release from the media under similar, controlled conditions. The implications for bioretention practice design will be illuminated.

2.0 Materials and Methods

The sorption of cadmium, copper, and zinc to compost and sand and the release of phosphorus by both media were investigated using batch sorption experiments and column studies.

2.1 Sorbent Materials

Compost and sand are commonly used as the filter media for bioretention facilities. The sorbent materials tested in this study include two compost samples from Minnesota (Minnesota Mulch and Soil, Maplewood, MN and The Mulch Store, Burnsville, MN), one compost sample from Texas (City of McAllen Composting Facility, McAllen, TX), and sand (Minnesota Mulch and Soil). All compost samples, which conform to the MNDOT grade 2 specification, are derived from leaves, grass, and woody debris without any food or animal waste added and the sand used in this study conforms to the ASTM C-33 standard (ASTM, 2003). All materials were air dried and sieved to remove particles greater than 2 mm prior to testing. After sieving, samples of compost and sand were analyzed for organic matter content, cation exchange capacity (CEC), and background concentration of cadmium, copper, zinc and phosphorus.

2.2 Synthetic Stormwater

A synthetic stormwater recipe was developed to mimic actual stormwater runoff. Synthetic stormwater for the batch experiments was prepared using the following reagent grade salts: 58.4 mg NaCl and 252.04 mg $NaHCO_3$ per liter of deionized water to control ionic strength and pH. The solution was then amended by adding one or all three of the following salts $CdCl_2$-2.5H_20, $CuSO_4$-5H_20, and $ZnSO_4$-7H_20 at a concentration of 0.5 mg/L as dissolved metal. Finally, pH was adjusted to 7.2 using 10 mM HCL as needed. For the column experiments, the synthetic stormwater was prepared by adding $CdCl_2$-

$2.5H_20$, $CuSO_4$-$5H_20$, and $ZnSO_4$-$7H_20$ to tap water at a concentration of 1 mg/L each as dissolved metal. Tap water was used because of the large volumes needed (~50 L per day). The pH of the synthetic stormwater used for the column experiments was not adjusted but was similar to that used for the batch experiments (7.46 +/- 0.15). No phosphorus was added to either the batch test or column test stock solutions. The cadmium, copper, and zinc concentrations for this research are 1000, 100, and 10 times larger than reported values for natural stormwater, respectively. This was to accommodate limitations on analytical equipment detection levels, adequately quantify removals, and complete the experiments in a timely manner.

2.3 Analytical Methods

All liquid samples collected during the experiments were filtered through 0.45 µm PTFE Acrodisc membrane filters immediately after sampling and analyzed using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer Optima 3000DV) with reporting limits of 3, 2, 3, 42 ppb for cadmium, copper, zinc, and phosphorus, respectively. The organic matter content, as determined by loss on ignition, and the background concentration of metals on the compost and sand samples were also determined. All analysis was performed by the Research Analytical Laboratory at the University of Minnesota, St. Paul, MN. Blanks and standards that range over the concentrations used the experiments were also analyzed for quality assurance and control. The pH of all aqueous samples was measured during the experiments using a Beckman pH meter calibrated to standards of pH 4, 7, and 10.

2.4 Experiments

2.4.1 Batch Test

Batch test experiments were performed to measure sorption equilibrium under controlled experimental conditions. For each batch test experiment, 250 mL Teflon bottles were filled with varying masses of compost or sand, 230 mL of the synthetic stormwater solution was added, and the bottles were placed on a Labline Orbital Shaker table at 100 RPM for 72 hrs.

Sorption kinetics was measured to determine the rate of sorption and an appropriate run time for the sorption equilibrium experiments. Approximately one gram of compost was added to each bottle and then placed on the shaker table. Bottles were sacrificially removed at 2, 6, 12, 24, 48, 72, and 96 hours to determine solution concentration. For equilibrium studies, varying masses of compost or sand (0, 0.01, 0.05, 0.1, 0.25, and 0.5 grams) were mixed with the synthetic stormwater and the results were used to develop a sorption isotherm. The effects of competition were studied by comparing the sorption in solutions with one metal to the solutions containing three metals. All batch experiments were performed using triplicate bottles, including a no mass bottle for control. Samples of the stock solution were analyzed as standards.

2.4.2 Column Study

Vertical continuous-flow columns were designed and built with materials selected to represent bioretention media (Figure 1). Ten columns were built and tested at the St. Anthony Falls Laboratory (Minneapolis, MN) at an air and water temperature of 19.4°C (SD = 1.8°C).

Each column was constructed from a 31 cm long, 5 cm diameter clear PVC pipe designed to hold 15 cm of filter media in three 5 cm segments, with a 2.54 cm layer of sand separating each segment of filter media. A 5 cm gravel bed was in the bottom of each column to support the filter media and to distribute flow evenly. Ports were drilled in the side of each column in the middle of each sand layer and a 0.64 cm tube, perforated on both sides at 1 cm intervals, was inserted across the diameter of the column as it was being packed with filter media (intermediate sampling port). The 2.54 cm sand layers serve to protect the intermediate sampling port from clogging by fine materials from the compost filter media. Each intermediate sampling port was fitted with a Luer Lock to barb connection and a Luer Lock valve. For sampling, a Kendall Monoject 20 mL syringe with Luer Lock was attached to the port, the valve was opened, and a sample was collected slowly. Four Easy-Lock II peristaltic pump heads (Cole Parmer, Vernon Hills, IL) and Tygon 3603 PVC tubing (0.6 cm ID) were used to pump synthetic stormwater from an adjacent 120-L influent reservoir up through the columns from bottom to top to ensure saturation of the filter media. The flow rate through the columns was adjusted daily to a target value of 4 mL/min using clamps attached to the influent and effluent tube lines because head loss increased as the experiment progressed. A separate pump circulated the water in the influent reservoir to prevent settling of any insoluble particles.

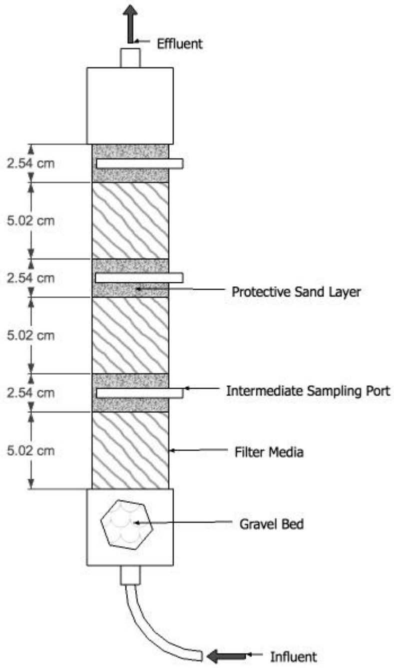


Figure 1. Column Diagram

All effluent was collected in 18 L buckets with a known depth-volume relationship. The filter media was made from MN compost 1 (The Mulch Store, Minneapolis, MN) and C-33 sand, mixed in three ratios by bulk volume: 50% compost and 50% sand; 30% compost and 70% sand; 10% compost and 90% sand; and 100% sand. The compost fractions for 50, 30, and 10% by volume correspond to 27.21, 13.81, and 3.99% by mass, respectively. The experiment was run with three replicate columns for each media fraction. The porosity of the filter media was 0.42 and one pore volume in the media is equal to 0.195 L. The hydraulic residence time of the columns was 116 minutes.

Upon completion of the column study, a representative column for each filter media ratio was taken apart and two samples from the filter media from each layer were analyzed to determine the concentration of metals retained on the media. In the other two column replicates, the influent water was changed from the solution that contained metals to a solution containing 1 g/L of NaCl and no metals. The salt solution was used a conservative tracer to determine porosity, dispersion, and to show consistency in the construction of each column. Conductivity was measured in the effluent of two of the three compost fraction replicates. This experiment also measures the effect of salt on the retention of metals by mimicking infiltration of road salt through a bioretention practice during winter or spring snowmelt.

2.4.3 Field Study

Infiltration tests and soil core sampling were conducted at six existing bioretention practices with various service times and sources of urban runoff in the Twin Cities area. One bioretention practice is shown in Figure 2. The bioretention practices tested in this study were previously studied by Asleson et al, (2009). Sorbed toxic metals data from a bioretention practice on the University of Minnesota's St. Paul campus located at the corner of Gortner Avenue and Commonwealth Avenue will be presented here. The data was as an overview of where metals are accumulated.

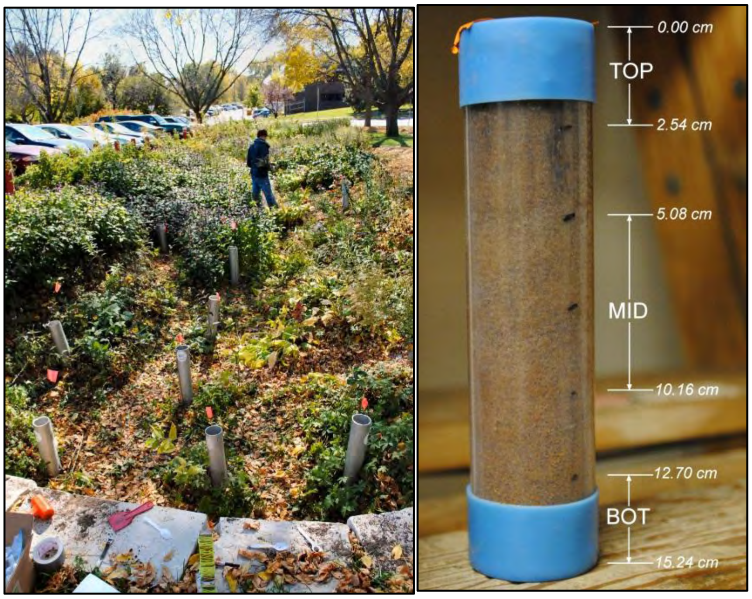


Figure 2. Running infiltration tests on a bioretention practice to map its spatial capability to infiltrate water (Left Picture) and soil core collected to determine the depth of higher metals concentration (Right Picture)

Undisturbed core samples were also collected from the bioretention practice. The cores were divided into subsections of 1 inch in the laboratory and analyzed for cadmium, copper, zinc, and organic matter. Adsorption isotherm experiments were conducted on different sections from two cores that were considered uncontaminated in order to investigate the capacity of cadmium and zinc sorption onto the bioretention filter media. The sorption isotherms were described by the Langmuir and the Freundlich models.

2.5 Data Analysis

Batch study data were fitted to the Langmuir and Freundlich isotherm models to determine the sorption capacity and the relative affinity for sorption. Sorption capacity refers to the mass of pollutant removed per mass of media. The Langmuir equation is:

$$q = \frac{q_{max} * K_L * C_{eq}}{1+K_L*C_{eq}} \tag{1}$$

where q_{max} is the maximum sorption capacity of the media (mg/g) and K_L is the sorption isotherm constant (L/mg pollutant). As q_{max} increases, the amount of pollutant that a sorbent may remove also increases. Similarly, as K_L increases, the sorbent has a greater affinity for sorption of a particular pollutant (Langmuir, 1916).

The Freundlich isotherm, on the other hand, is an empirical power law curve that relates sorption capacity to equilibrium concentration. The Freundlich equation is:

$$q = K_f C_{eq}^{1/n} \tag{2}$$

where K_f is the Freundlich isotherm constant related to sorption capacity, and n refers to the intensity of sorption (unitless). The batch study data in this experiment were fit to both equations and used for comparison to existing literature data and subsequent research described herein.

Results from the column studies were modeled using the Thomas Model (Thomas, 1948). The Thomas Model considers a relationship between the influent and effluent concentrations based upon volume of water treated, sorption capacity, sorbent mass, and a kinetic rate constant.

$$\frac{C_e}{C_0} = \frac{1}{1+exp\left[\frac{K_{TH}(q_0 m - C_0 V)}{Q}\right]} \tag{3}$$

where C_e is the effluent concentration, C_0 is the influent concentration, K_{TH} is the Thomas Coefficient (L/min-mg), m (g) is the mass of sorbent in the column, q_0 is the sorption capacity (mg/g), V is the volume of water treated by the column (L), and Q is the flow rate through the column (L/min). At equilibrium, the reaction law equation used as the basis for deriving the Thomas Model approaches a Langmuir isotherm. Thus, the sorption capacities between the Langmuir isotherm and the Thomas Model may be directly compared. The experimental data were fit to the Thomas Model using a non-linear least squares regression in Stata, a statistical software program (StataCorp, 2007).

3.0 Results and Discussion

3.1 Material Characteristics

An analysis of the cation exchange capacity and the presence of organic matter indicate that compost and sand both have an ability to adsorb toxic metals (Table 2).

Table 2. Fraction organic matter (OM), cation exchange capacity (CEC), and background concentration of metals and phosphorus for filter media materials

	MN Comp 1	MN Comp 2	Sand
OM (%)	27.6	26.7	0.2
CEC (mg/100 g)	73.8	75.9	13.9
Cadmium (mg/kg)	<1.76	<1.76	<1.76
Copper (mg/kg)	30.5	35.8	5.3
Zinc (mg/kg)	82.8	75.4	14.0
Phosporus (mg/kg)	2323.7	2126.3	154.4

Sand has a smaller cation exchange capacity and organic matter fraction than compost. However, the results of Table 2 indicate that sand will have some, albeit limited, removal capacity for dissolved metals. The two different composts have similar organic matter content, cation exchange capacity, and background metals and phosphors levels indicating consistent composition despite coming from two different suppliers.

3.2 Batch Studies

The sorption kinetic results were used to determine the length of time needed for the equilibrium experiments. The Lagergren Psuedo-Second order equation (Ho and McKay, 1999) was fit to the data and used to predict temporal proximity to an equilibrium sorption capacity. The sorption capacity for cadmium, copper, and zinc at 72 hours was determined to be 97.4%, 91.1%, and 96.1% of the predicted equilibrium sorption capacity, respectively. Thus, the duration of all equilibrium batch experiments was 72 hours.

Compost was mixed with the stock solution for 72 hours without any metals added to determine the extent to which cadmium, copper, and zinc desorbed. Negligible desorption of cadmium was observed. While 0.32 mg zinc per kg of compost and 0.10 mg copper per kg compost desorbed, these values are much smaller than the background metal concentrations in the soils (Table 2).

The sorption capacity of the compost and sand were determined from the equilibrium experiments. The Freundlich and Langmuir isotherms were fit to the Cd and Zn data to determine the model coefficients (Table 3).

Table 3. Summary of Batch Test Results

	Cadmium					
	Langmuir			Freundlich		
	K_L	q_{max} (mg/g)	R^2	K_F (L/g)	1/n	R^2
MN Comp 1	7.20	2.13	0.70	10.11	0.93	0.77
MN Comp 2	2.45	4.57	0.27	17.43	1.06	0.51
TX Comp				8.41	0.99	0.44
Sand	4.17	0.02	0.35	0.18	1.49	0.62

	Zinc					
	Langmuir			Freundlich		
	K_L	q_{max} (mg/g)	R^2	K_F (L/g)	1/n	R^2
MN Comp 1	2.55	3.82	0.73	8.82	1.00	0.79
MN Comp 2	7.46	1.06	0.12	14.32	1.64	0.39
TX Comp				6.58	0.97	0.42
Sand	1.23	0.07	0.58	0.29	1.53	0.74

The Langmuir isotherm predicts a larger sorption capacity for Zn than Cd for MN Compost 1; yet predicts the opposite for MN Compost 2. The difference in sorption capacities and small R^2 for the two Minnesota composts may be due to the small masses of compost used, competition for sorption sites, and the heterogeneity of compost. No Langmuir coefficients are reported for the Texas compost because the scatter in the data yielded negative coefficients for the model fit to the data. As indicated by the value of q_{max}, the compost has a larger capacity for zinc and cadmium sorption than the sand.

The speciation of each metal varies based upon the solution pH and will affect the removal by sorption. The behavior of the synthetic stormwater solution was modeled using MINEQL (Schecher, 1998). The results of the model indicate that 95% of the copper exists as tenorite (CuO) at a pH of 7.2, precipitating out of solution, whereas cadmium and zinc are still predominantly soluble. The copper data does not fit to either the Freundlich or Langmuir isotherms and hence, sorption may not be the primary removal mechanism for copper at a pH of 7.2 and a concentration of 1 mg/L as dissolved metal.

The results show that approximately 153 mg phosphorus per kg of compost leaches off the compost (Figure 3). The ICP-OES measures total P in the sample and because the samples are filtered through a 0.45 µm filter, by definition the leached phosphorus is in the dissolved, and probably bioavailable, form.

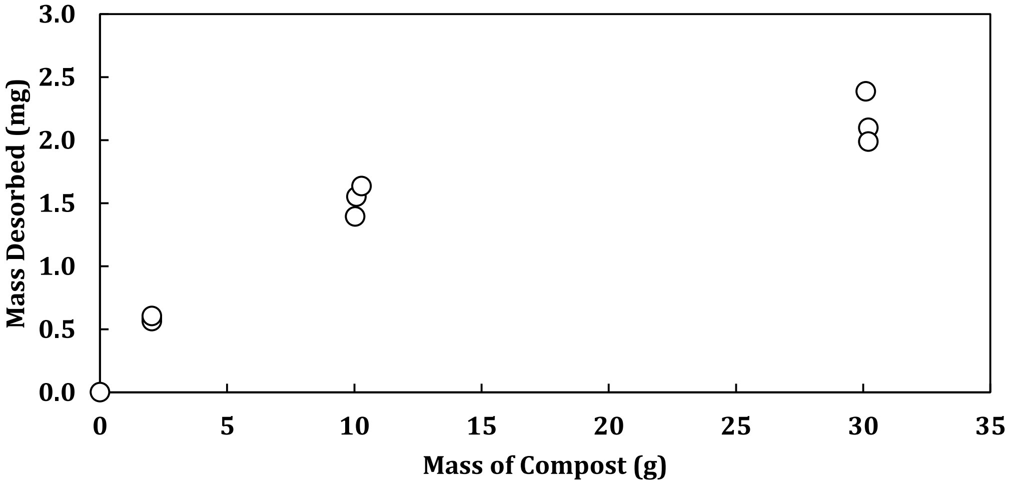


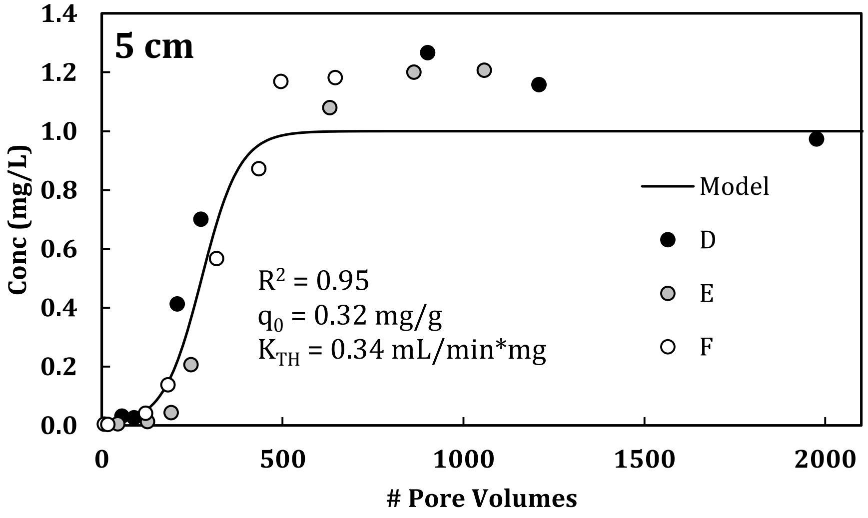
Figure 3. Release of phosphorus by MN compost 1 into 230 mL of batch study stock solution.

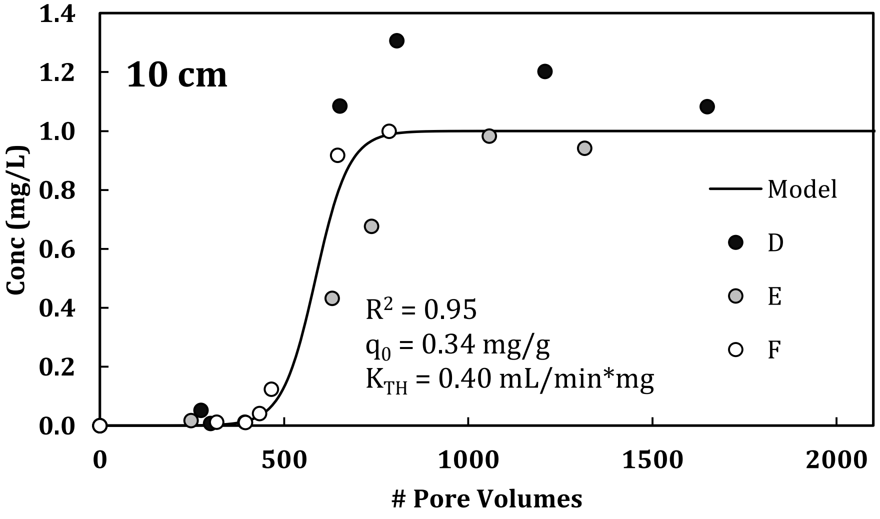
3.3 Column Studies

Results from the column studies were used to determine the effect of bed depth and the effect of compost fraction on removal of cadmium, copper, and zinc and the release of phosphorus. The results of metal retention will be discussed first followed by results from phosphorus release.

3.3.1 Effect of Bed Depth

The intermediate sampling ports allow samples to be collected at 5, 10, and 15 cm of filter media depth. Sample results for cadmium are shown in Figure 4 with results for all experimental runs provided in Appendix A. At each equal numbers of treated pore volumes each replicate had similar concentration values, and so the Thomas Model was fit to the three replicates simultaneously. The Thomas Model fits to the cadmium and zinc data with an $R^2 > 0.94$ for all experimental runs. The sorption capacity is approximately constant at each depth and the Thomas Coefficient (K_{TH}) decreases as filter media depth increases. Some data is greater than the influent concentration of 1 mg/L possibly due to preferential sorption for increasingly limited sorption sites. Cd or Zn that attached to weakly bonding sorption sites may have been released off the compost in favor of other cations such as calcium, potassium, magnesium, or sodium.





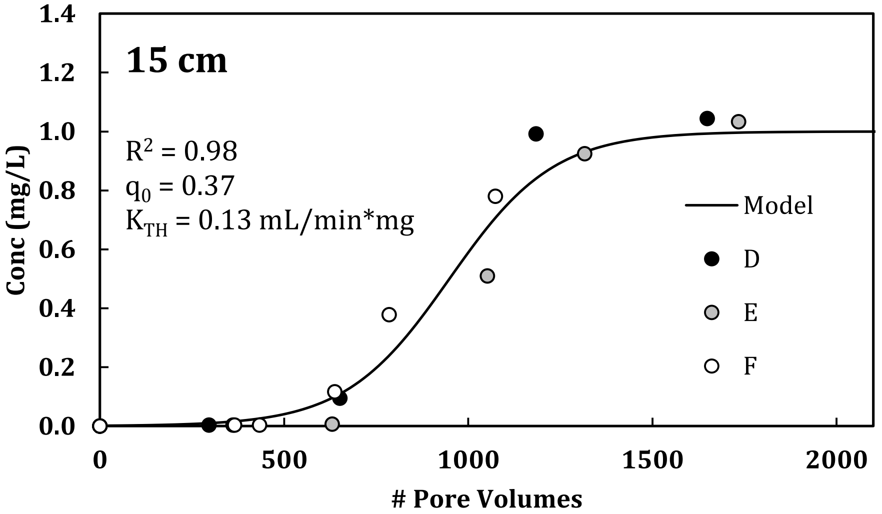
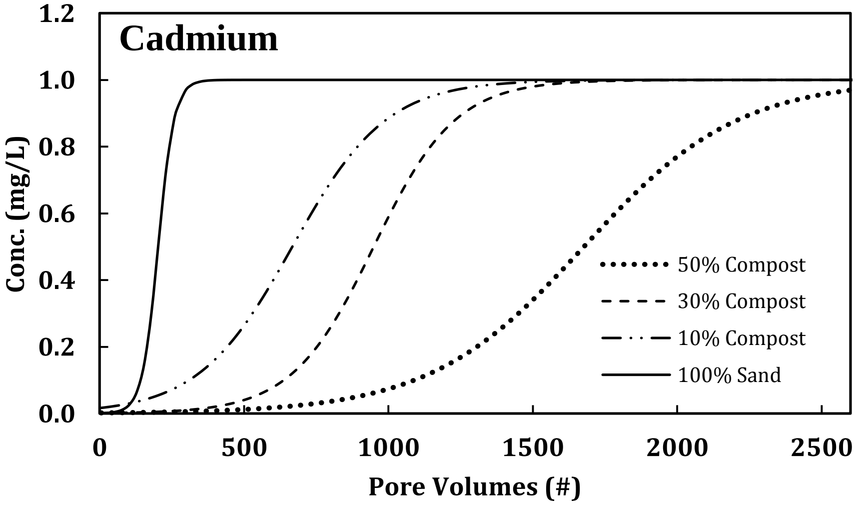


Figure 4. Effect of bed depth on removal of cadmium by 30% compost columns. Data from the three 30% compost replicates (D, E, F) are presented along with the Thomas Model.

3.3.2 Effect of Compost Fraction

The compost fraction within the filter media affects the retention of metals in the columns. Figure 5 shows the Thomas Model fit to the breakthrough data collected at 15 cm of filter media.



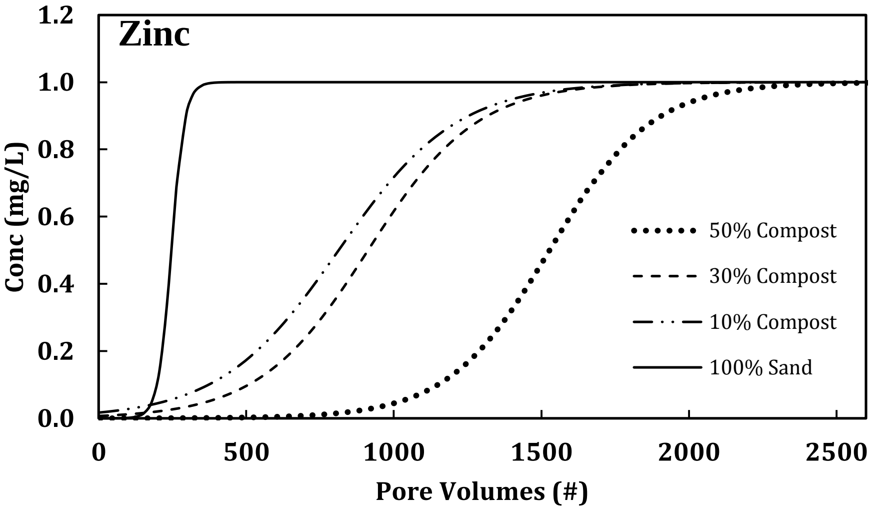


Figure 5. Thomas Model fits for cadmium (top) and zinc (bottom) at 15.24 cm filter media depth indicating the effect of compost fraction on removal.

As expected, the 100% sand column approaches saturation soonest, followed by the 10, 30, and lastly, the 50% compost columns. Time to breakthrough increases as compost fraction increases indicating that sorption capacity is related to compost fraction. This is consistent with the findings from the batch tests that show a larger sorption capacity for compost than sand. The cadmium sorption capacities for the 50, 30, 10, and 0% compost fraction columns are 0.73 (+/- 0.016), 0.34 (+/- 0.012), 0.19 (+/- 0.011), and 0.08 (+/- 0.011) mg/g with p = 0.67, respectively. The significant difference in sorption capacities between columns of different compost fractions shows that the fraction of organic matter impacts the removal of cadmium and zinc.

Copper removal also increased with increasing compost fraction. Copper was not entirely in the soluble form at the experimental concentrations and solution pH, so sorption may not be the primary removal mechanism. The precipitation of copper indicates that it may be removed via filtration, so the effluent concentration never reached the influent concentration of 1 mg/L. The compost and sand used as the filter media were each sieved and the effective diameter (D_{10}) for each component was calculated. The D_{10} for compost is 151.4 µm and the D_{10} for sand is 220.3 µm. This indicates the potential for increased filtration of suspended solids as compost fraction increases (Figure 6). The data indicates excellent removal of copper, compared to cadmium and zinc. After 15.24

cm of filter media, the average removal efficiencies were 99, 99, 95, and 64 % for the 50, 30, 10 and 0% compost fraction columns after 1700 bed volumes.

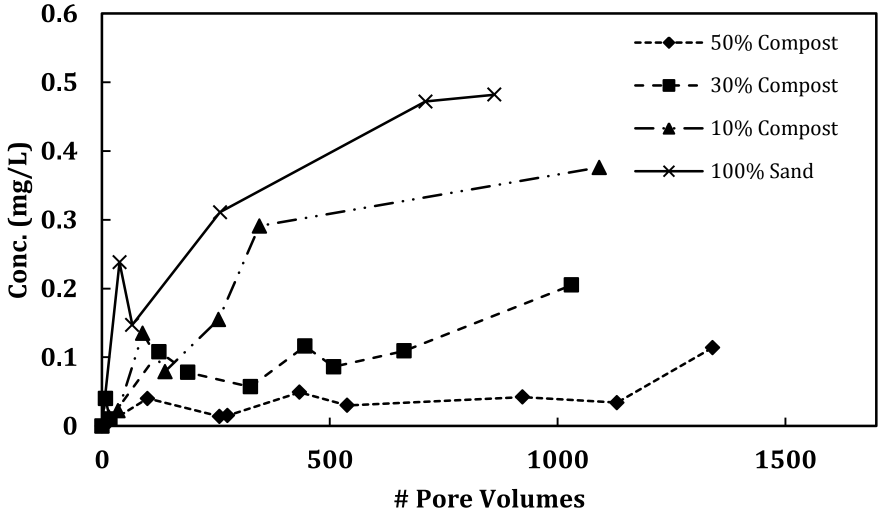


Figure 6. Effect of compost fraction on effluent concentrations at 5 cm of filter media depth

3.3.3 Summary of Column Study Modeling

The rate constants (K_{TH}) and sorption capacities (q_o) calculated for cadmium and zinc using the Thomas Model are shown in Table 4. There were three columns at each compost fraction and the Thomas Model was simultaneously fit to the data from all three columns

Table 4. Fit of Thomas Model Coefficients for Cadmium and Zinc with MN Compost 2

Compost %	Depth cm	Cadmium		Zinc	
		k_{TH} [mL/mg/min]	Capacity q_0 (mg/g)	k_{TH} [mL/mg/min]	Capacity q_0 (mg/g)
50	5.08	0.25 ± 0.09	0.68 ± 0.02	0.31 ± 0.10	0.55 ± 0.03
	10.16	0.14 ± 0.05	0.72 ± 0.03	0.14 ± 0.06	0.61 ± 0.05
	15.24	0.10 ± -	0.78 ± -	0.11 ± 0.01	0.66 ± 0.01
30	5.08	0.34 ± 0.14	0.32 ± 0.03	0.41 ± 0.13	0.27 ± 0.02
	10.16	0.40 ± 0.20	0.34 ± 0.02	0.32 ± 0.07	0.31 ± 0.01
	15.24	0.13 ± 0.02	0.37 ± 0.01	0.10 ± 0.02	0.35 ± 0.01
10	5.08	0.31 ± 0.05	0.21 ± 0.01	0.37 ± 0.05	0.19 ± 0.01
	10.16	0.25 ± 0.07	0.14 ± 0.01	0.26 ± 0.05	0.14 ± 0.01
	15.24	0.11 ± 0.02	0.23 ± 0.02	0.07 ± 0.01	0.28 ± 0.03
0	5.08	0.38 ± 0.24	0.08 ± 0.03	0.51 ± 1.00	0.10 ± 0.08
	10.16	0.76 ± 2.17	0.09 ± 0.01	0.29 ± 0.14	0.13 ± 0.02
	15.24	0.58 ± 0.65	0.07 ± 0.01	0.71 ± 0.58	0.08 ± 0.01

The rate constant, K_{TH}, decreases from 5.08 cm to 15.24 cm depth for all cases in Table 4 except the sand column, indicating a delay in breakthrough time with increasing filter media depth. The same material is used in each layer for a specific column, so the sorption capacities should remain consistent from 5 to 15 cm of depth. The sorption capacity data for each metal in Table 4 generally tends to increase slightly from 5 cm to 15 cm depth, which may be due to a cumulative sorption effect from the three 2.5 cm interlayers of sand. The results from the 0% compost column indicate that the sand has cadmium and zinc sorption capacities so there is a cumulative sorption effect from the interlayers. The modeling also predicts larger sorption capacities for cadmium than zinc, which is consistent with the batch studies for the same compost material.

3.3.4 Salt Tracer Study and Metals Leaching

The conductivity results were modeled using the Ogata-Banks Solution (Ogata and Banks, 1961) to determine porosity and dispersion coefficients in the column. The original equation was modified as follows (Equation 4):

$$\frac{C_e}{C_0} = \frac{1}{2}\left[erfc\left(\frac{L-\frac{V_{eff}}{An}}{\sqrt{4D_x\frac{V_{eff}}{Q}}}\right) + \exp\left(\frac{V_{eff}}{LAn}\right) erfc\left(\frac{L+\frac{V_{eff}}{An}}{\sqrt{4D_x\frac{V_{eff}}{Q}}}\right)\right] \tag{4}$$

where C_e and C_0 are the effluent and influent concentrations of the tracer (mg/L), L is the linear distance where the concentration (cm), V_{eff} is the accumulated water volume from the effluent (L), A is the cross-sectional area in the column (cm^2), n is the column porosity, Dx is the vertical dispersion coefficient (cm^2/min) and Q is the flow rate in the column (mL/min). The dispersion coefficients are 0.24, 0.48, 0.70, and 0.89 cm^2/min for 0, 10, 30, and 50% compost columns, respectively. The porosity values ranged from 0.416 to 0.420 for the 10% to 50% columns. The consistency in porosity reflects the lack of short-circuiting or dead zones in the columns.

In the presence of salt, the columns released metals. The effluent concentration in one 30% compost column increased from a steady-state concentration of 1 mg/L for each metal in the breakthrough experiments to 11 mg/L and 8 mg/L for cadmium and zinc, respectively, during the salt tracer study (Figure 7). In total, the columns released 48, 10, and 10% of the cadmium and 27, 7, 8% of the removed zinc for the 0, 10, and 30% compost columns.

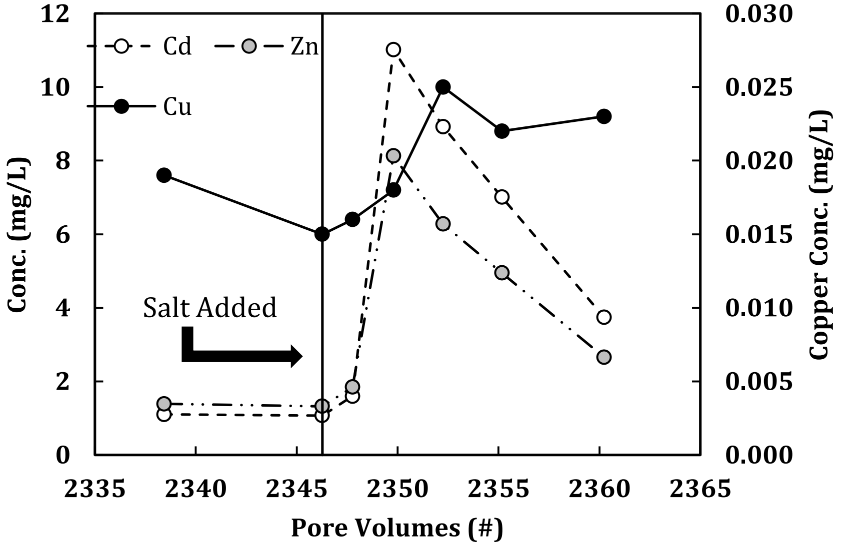


Figure 7. Release of cadmium, copper, and zinc from one 30% compost fraction column after introducing NaCl. Copper is plotted on the right axis.

3.3.5 Mass Balance Results

The sorption capacities for the MN Compost 1 and sand materials in the batch studies, shown in Table 3, were compared to the column study results by calculating sorption capacities for 50, 30, 10% compost volume fractions from the batch study sorption capacities. The capacities for the batch study results predict sorption capacities of 0.59, 0.31, and 0.10 mg Cd/g and 1.1, 0.60, and 0.23 mg Zn/g for the 50, 30, and 10% compost fractions, respectively. The predicted cadmium sorption capacities from the batch studies are slightly less than the column study capacities for each compost fraction whereas the predicted capacities for zinc are almost twice as much as the column study sorption capacities. The natural heterogeneity of compost, especially in comparing the 1-gram used in the batch studies to the 450 grams used in the columns, could be responsible for the small differences between batch and column studies predicted sorption capacities.

The cadmium and zinc sorption capacities calculated directly from the data from the column study, the Thomas Model sorption capacities, and the sorption capacities from the post-column study soil analysis are compared in Figure 8 and Figure 9. The sorption capacity calculated directly from the column data is presented along with the Thomas

Model sorption capacity to show consistency between the data and the model, which is a smoothing of the data. Discrepancies between the column study data and the Thomas Model are due to effluent concentrations that exceed the influent concentrations ($C/C_0 > 1$) for a portion of the column study data set. The soil analysis compared to the direct data and Thomas model provides a mass balance for the columns, as any metal removed from the water would be found on the media. The soil analysis was performed on one of the three replicate columns, whereas the direct data analysis and Thomas model were both based upon three replicate columns. Nevertheless, the soil analysis compares well with the Thomas model and the direct data analysis. This indicates that, within the accuracy of the tests, a mass-flux retention balance on the columns was achieved.

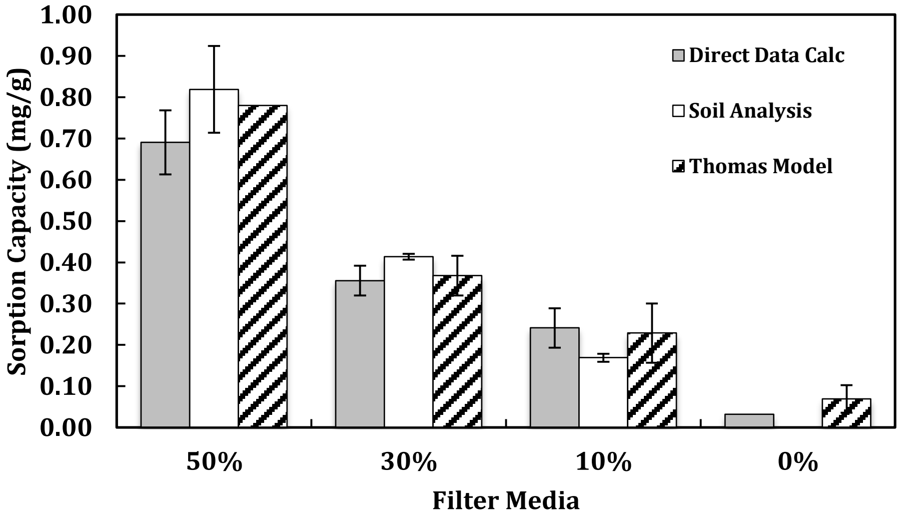


Figure 8. Cadmium removal measured by concentration difference and by sorption onto the media. Error bars indicate 1 standard deviation. A soil analysis was not performed on the 0% column.

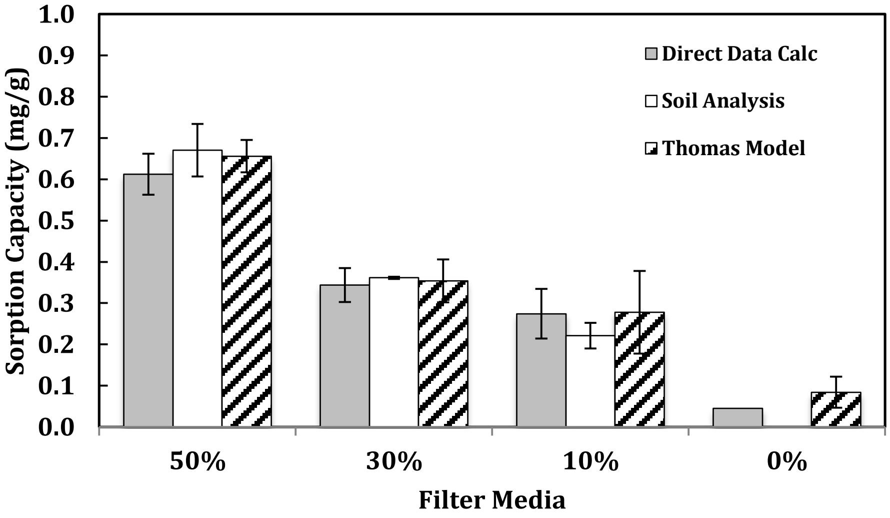


Figure 9. Zinc removal computed by differences in concentration and by sorption to the media. Error bars indicate 1 standard deviation. A soil analysis was not performed on the 0% column.

3.3.5 Phosphorus Release

As with the batch studies, the column study results show that dissolved phosphorus leaches from the columns. The columns released average concentrations of 0.29, 0.29, and 0.21 mg/L from the 50, 30, and 10% compost columns, respectively, at 15 cm of depth. Maestre and Pitt (2005) report median runoff concentrations for total and dissolved phosphorus of 0.27 and 0.12 mg/L, respectively. No phosphorus was added to the simulated stormwater solution, but the tap water used as a source does contain phosphorus at a concentration of 0.13 mg/L (SD = 0.03), which was subtracted from the effluent concentration to compute dissolved phosphorus released. Figure 10 shows the cumulative mass of phosphorus released normalized by the mass of filter media when water passed through the column.

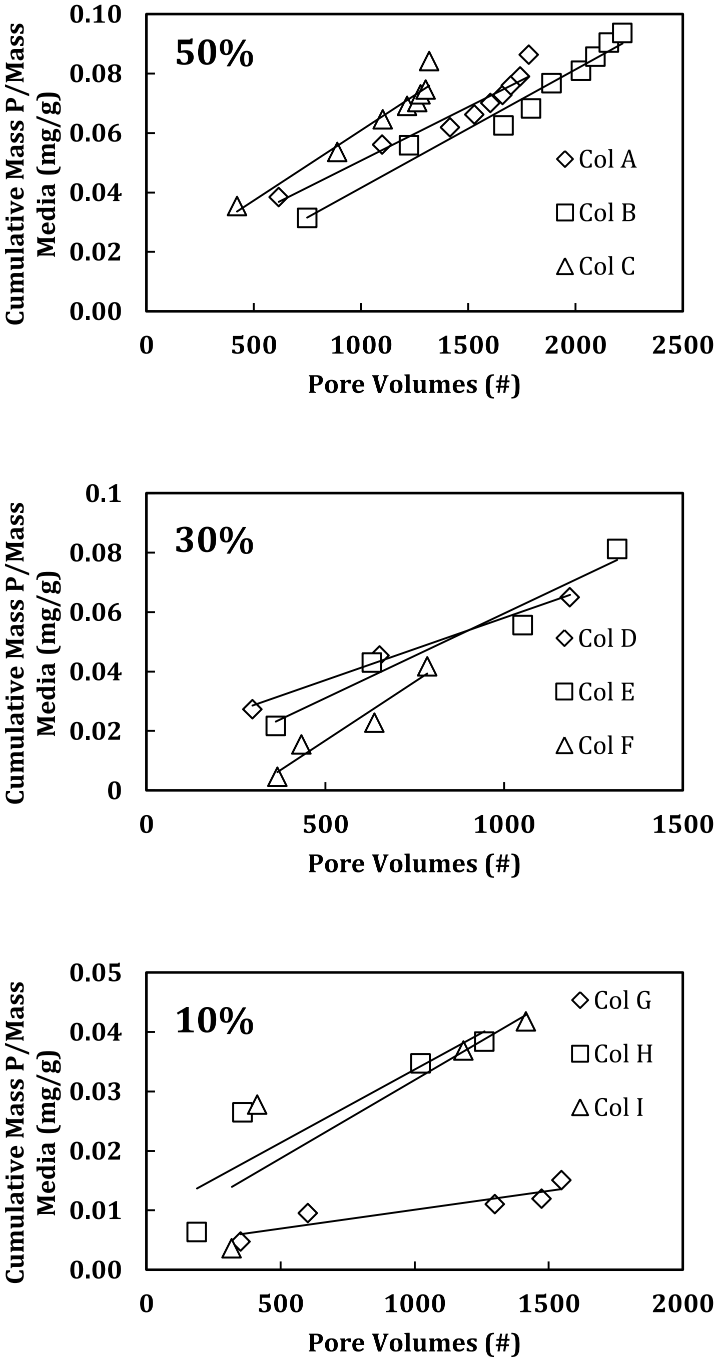


Figure 10. Phosphorus Export from 50, 30, and 10% compost columns

The linear fit to the data indicates that phosphorus release was approximately constant throughout the tests for between 1500 and 2500 pore volumes. It is possible that the leaching rate will remain constant over time because organic compost will continually decompose and release phosphorus. Phosphorus uptake is expected in live plants;

however, upon death, phosphorus will be released back into the media. Lastly, refreshing the top mulch or compost layer will add a phosphorus source to the bioretention practice. The column studies indicate that phosphorus leaches off the compost and leaves the system. If a bioretention practice outlets the infiltrated water to groundwater, then the leaching of phosphorus may not be a concern (Weiss et al., 2008). If, however, the infiltration practice is built with an underdrain or is located near a lake or river where export of phosphorus to surface waters is possible, then degradation of the water bodies due to phosphorus leaching may occur.

3.4 Field Studies

Figure 11 shows that organic matter profiles in bioretention practices have the highest concentrations close the surface. The average organic matter content in the core samples was 5.5 ± 3.3% for the bioretention practices investigated. As seen from the column studies, the presence of organic matter will increase the removal of dissolved toxic metals. The organic matter content decreases with to 30 cm in the bioretention practice.

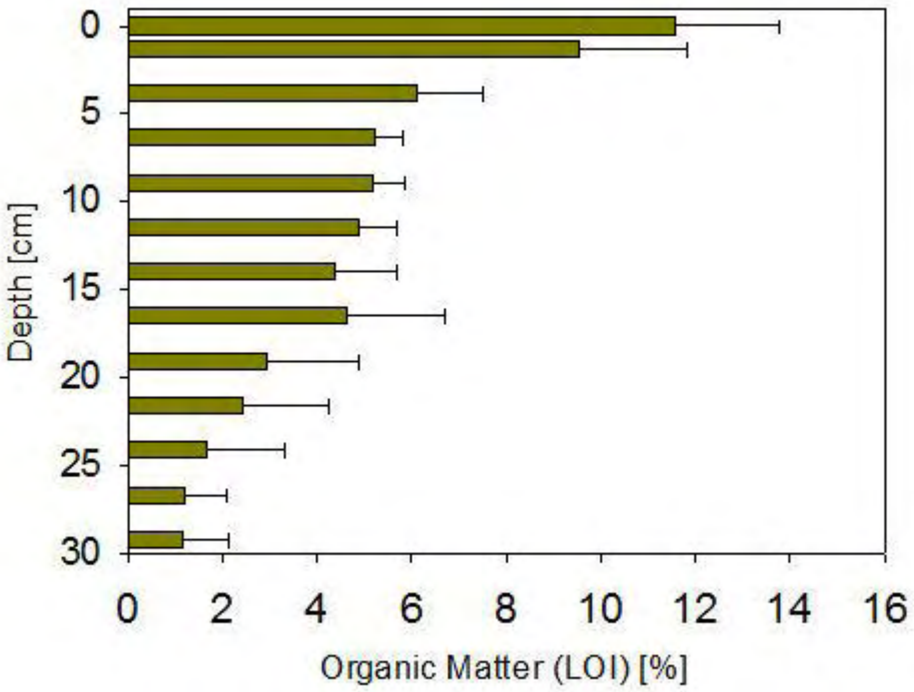


Figure 11. (Left) Organic matter profile in St. Paul campus bioretention practice

Filter media cores were collected from a total of six bioretention practices with various service times and runoff source types in the Twin Cities area. The cores were divided into sections and analyzed for organic matter and metal concentrations at different depths. Figure 12 shows a comparison between organic matter in the bioretention practices and the concentration of zinc attached to the filter media.

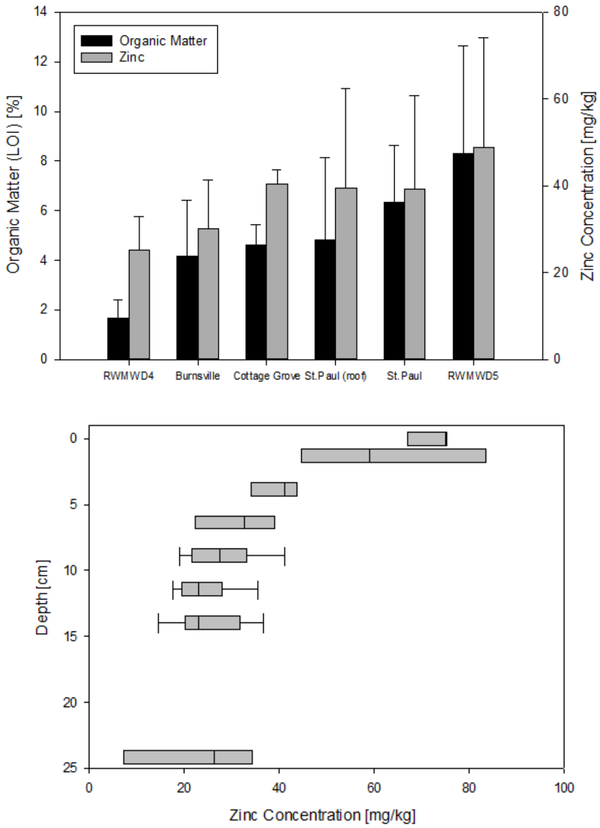


Figure 12. (Top) Zinc and organic matter concentration in the first 14 cm of depth and (Bottom) Average zinc concentration profile in the six bioretention practices investigated in this study.

Figure 12 illustrates that none of these bioretention practices had high concentrations of the metals investigated, compared to the column studies herein. The 30% compost columns, for example, had a capacity of approximately 600 mg/kg of zinc retention. Figure 12 also indicates that enrichment of metals was correlated with organic matter.

A comparison of metal concentration profiles in cores located near the bioretention practice inlet and cores located at the upland side, where no stormwater has infiltrated, was additionally conducted at the St. Paul bioretention practice. All cadmium samples were below analytical detection limits. This is not surprising because cadmium occurs in stormwater at such low concentrations. The organic matter, copper, and zinc results, shown in Figure 13, indicate surface enrichment of zinc and copper in the cores located close to the inlet, but no enrichment at depths of 6 cm or greater. The soil analysis results for depths between 6 and 14 cm show similar organic matter, copper, and zinc concentrations to a reference location outside of the bioretention practice. This means that toxic metals have been predominantly removed in the first 6 cm in this bioretention facility and that it has not approached its maximum capacity for retention of metals in the first 6 cm. The bioretention practice was installed in October 2004 and is sandy loam soil from 0 to 20.3 cm deep.

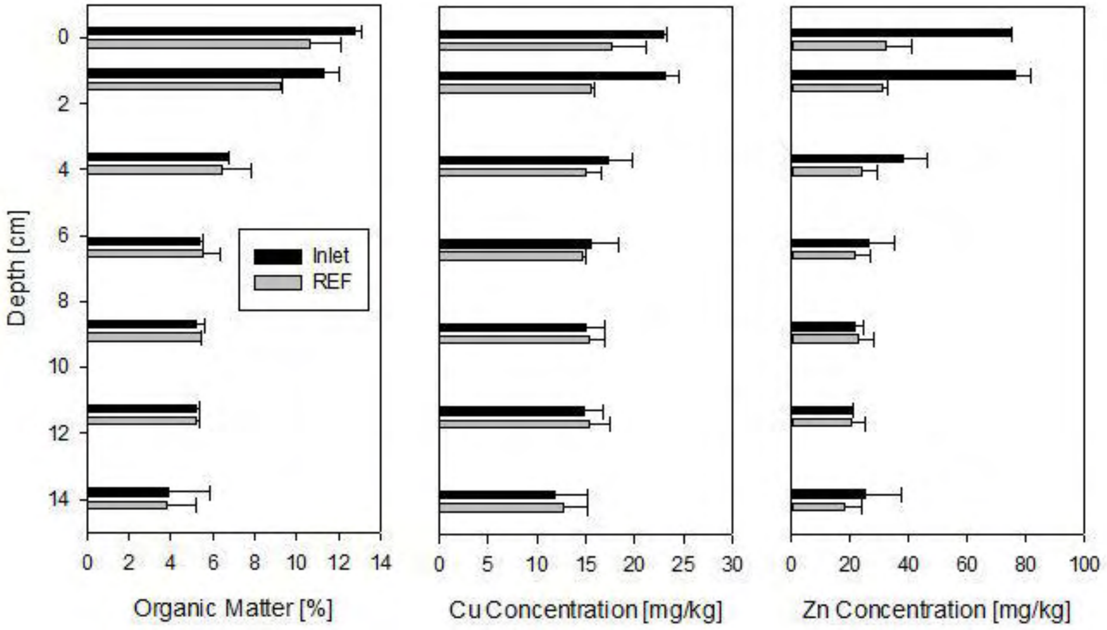


Figure 13. Profiles of organic matter, copper, and zinc concentrations at two different cores in the St. Paul campus bioretention practice. Samples were collected near the inlet pipes (INLET) and from a reference location outside the bioretention practice (REF).

Adsorption isotherm experiments were conducted on uncontaminated filter media cores from the existing St. Paul bioretention practice. The results from these experiments (Figure 14) suggest that the filter media has a significant ability to retain cadmium and zinc, and that this ability relates very much to the organic matter content in the filter media.

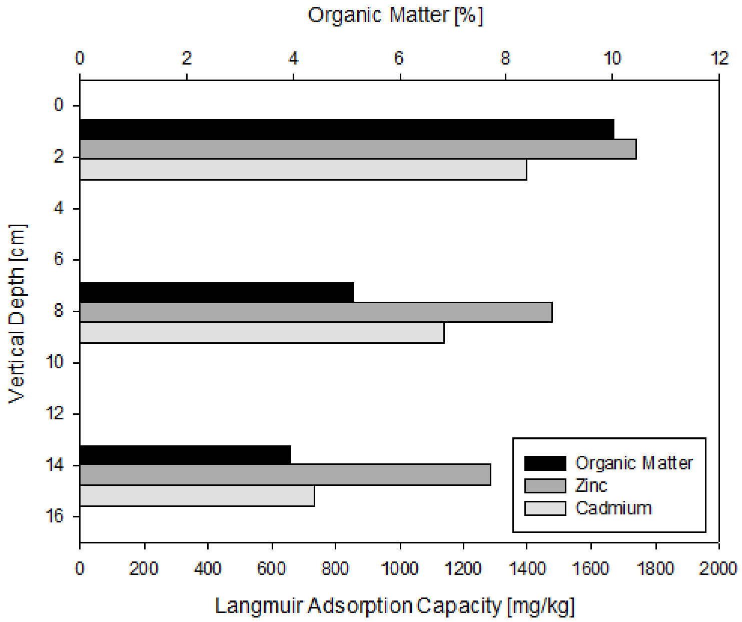


Figure 14. Zinc and cadmium adsorption capacities (Langmuir) as a function of depth and organic matter content.

4.0 Engineering Significance

4.1 Lifespan Prediction

Understanding removal of dissolved toxic metals by compost and sand illuminates the fate of toxic metals in bioretention facilities. Predicting the longevity of a bioretention practice for removal of metals will aid in Total Maximum Daily Load (TMDL) planning and implementation, as well as maintenance. Finally, knowledge of dissolved phosphorus release will be important in the protection of receiving waters when the bioretention practice contains underdrains or is located close to receiving waters. A calculation is shown below for typical hydrologic and rain garden characteristics to compare the results from the column study to a full-size bioretention practice and to show the lifespan of rain gardens that use the same filter media as this experiment.

Bioretention practices are typically constructed with a media depth of 45.7 to 91.4 cm and a surface area that is approximately 5% of the drainage area (MN Stormwater Manual). Bioretention practices are also typically designed to capture the first 1.3 cm of runoff from a particular rain event while all runoff exceeding that depth bypass the bioretention practice. The volume of water treated by the column is scaled up to the water treated by rain garden by comparing the depth of water treated in these experiments to the average annual depth of water received by a typical bioretention practice. The depth of water treated by the column is calculated as the volume of water treated divided by the cross-sectional area of the column:

$$D_W = \frac{V}{A} \tag{5}$$

where D_W is the depth of water treated by the column, V is the volume of water passed through the column, and A is the cross-sectional area of the column.

The average annual depth of runoff is calculated by the following equation (Zhang et al., 2008):

$$D_R = \frac{\sum \min(C*R, 0.0127)}{y*f} \tag{6}$$

where D_R is the average annual depth of runoff treated by a bioretention facility, C is the runoff coefficient (0.5), R is the daily rainfall depth, y is the number of years in the precipitation record, and f is the bioretention to watershed area ratio (5%). "*Min(C*R, 0.0127)*" is the daily runoff depth up to 0.0127 m of runoff depth. For example, if "*C*R"* exceeds 0.0127m, then the maximum treated depth of 0.0127-m is used in the calculation. The daily runoff depth is summed over the entire precipitation record and averaged by the number of years in the precipitation record. The average annual runoff depth is then scaled by the bioretention practice to watershed area ratio to determine the average annual runoff depth treated by the bioretention practice. For the Minneapolis/St. Paul precipitation record from 2000 to 2010, D_R equals 6.51 m/yr. The number of years a bioretention practice can operate is the ratio of depth of water treated to average annual depth of runoff treated:

$$Yrs = \frac{D_W}{D_R} \qquad (7)$$

Concentrations of toxic metals in stormwater runoff are substantially smaller than the influent concentration used in this research. Assuming the kinetic rate constant (K_{th}) and the sorption capacity (q_0) remain the same across concentrations, then the Thomas Model can be used to determine the number of years to breakthrough at influent concentration of 0.1 mg/L for Zn and 0.001 mg/L for Cd. Breakthrough is defined when the effluent concentration is 10% of the influent concentration ($C/C_0 = 0.1$).

The breakthrough times for depths of 5, 10, and 15 cm were calculated directly from the Thomas Model curves. Breakthrough times for 30, 46, and 61 cm of depth were calculated by multiplying the volume of the center of mass for the 15 cm data by 2, 3, and 4, respectively to translate the 15 cm data to a lower depth. The translation of the 15 cm data does not account for increased dispersion with increasing depth; as such, the actual breakthrough time for 30, 46, and 61 cm depth will happen sooner than projected (Figure 15), though this will not be significant compared to the total time needed for breakthrough.

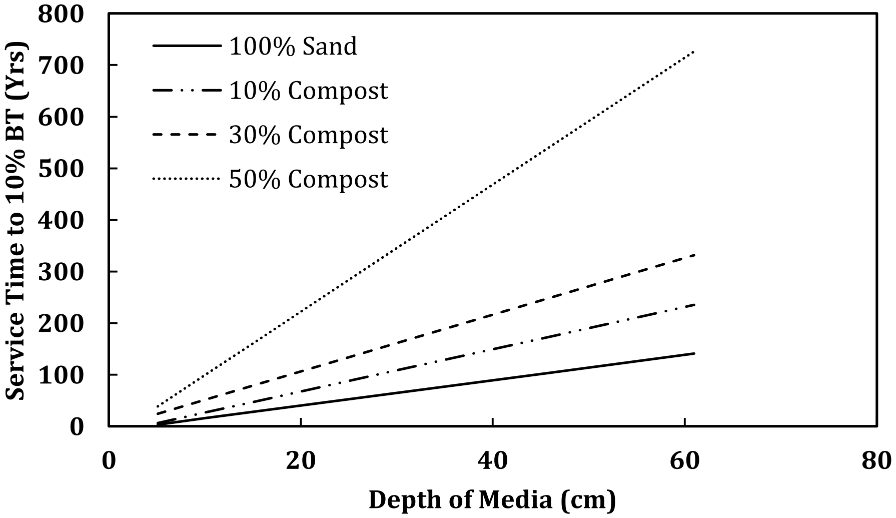


Figure 15. Lifespan predictions for zinc removal with $C_0 = 0.1$ mg/L

Assuming that the modeling parameters remain constant at lower influent concentrations, a filter media composed of 30% compost with an influent concentration of 0.1 mg Zn /L will achieve 10% breakthrough in 76 years at a bioretention depth of 15 cm. At stormwater conditions, the model predicts that over 1,000 years of service are required for cadmium breakthrough at an influent concentration of 0.001 mg/L. Despite a low sorption capacity compared to columns amended with compost, the sand column results predict a lifespan of 28 years for zinc removal at a depth of 15 cm and over 1,000 years for cadmium. Hydraulic failure due to clogging of the pore space by suspended solids is expected to occur before breakthrough or exhaustion of the filter media by toxic metals.

It is possible to look at other research studying removal of dissolved toxic metals and make a conjecture on the removal of other metals such as lead, chromium, or molybdenum when they are studied alongside cadmium, copper, or zinc. Several papers report higher removal for lead than cadmium, copper, or zinc for mulch, wood chips, or sand based filter media (Jang et al., 2005; Zhang et al., 2008; Syring et al., 2009). Batch and column experiments to two different sandy loam soil reveal significantly higher removal for chromium and molybdenum than either cadmium, copper, lead, or zinc (Gong and Donahoe, 1997). Based on the similar research that includes different combinations of metals, one may conclude that bioretention practices will effectively remove lead and other metals found in stormwater runoff.

Phosphorus was released at a steady state rate from the columns, so yearly load exported from bioretention practices can be similarly predicted. For example, 30% compost columns had a constant effluent concentration of 0.29 mg/L. If we assume a surface area of 100 m^2 and an average depth of runoff of 6.51 m/yr, then a bioretention practice after the equivalent of 15 years of runoff, the columns have released a total of 0.06 mg P per g of filter media. If we assume that the rain garden is 30 cm deep, has a surface area of 100 m^2, and the filter media has a bulk density of 1,200 kg/m^3, then the total mass of dissolved phosphorus released from the filter media over 15 years is 2.16 kg. The yearly load is 144 g phosphorus released from the filter media. The column studies show that this is a consistent release rate over time. This calculation does not account for phosphorus bound to suspended solids released from the garden. Net release of phosphorus from bioretention facilities means that they must either be redesigned or not used at all for removal of phosphorus.

4.2 Bioretention Facility Recommendation

Based on the results found from the batch and column studies, it is recommended that the construction of bioretention facilities reflect the ability, or lack thereof, to remove the whole spectrum of pollutants commonly found in stormwater runoff. Compost amended sand is an excellent filter media for the removal of petroleum based products (LeFevre et al. 2011a,b) and toxic metals, yet leaches phosphorus, a major limiting nutrient in most inland waters. Another filter media will be needed to remove the phosphorus or other pollutants that are not removed by the compost/sand filter. Bioretention facilities could be constructed as a two-stage removal filter. The top layer would be constructed of sand amended with compost and should be 15 to 30 cm deep, depending on the necessary root depth for plants. Underneath the compost layer would be an iron-enhanced sand layer (Erickson et al; 2007) to remove phosphorus that passes through and is leached off the compost layer (Figure 16). A bioretention facility constructed in this manner would remove dissolved toxic metals in the compost amended sand layer at the top and would remove phosphorus with the iron enhanced sand layer in the middle.

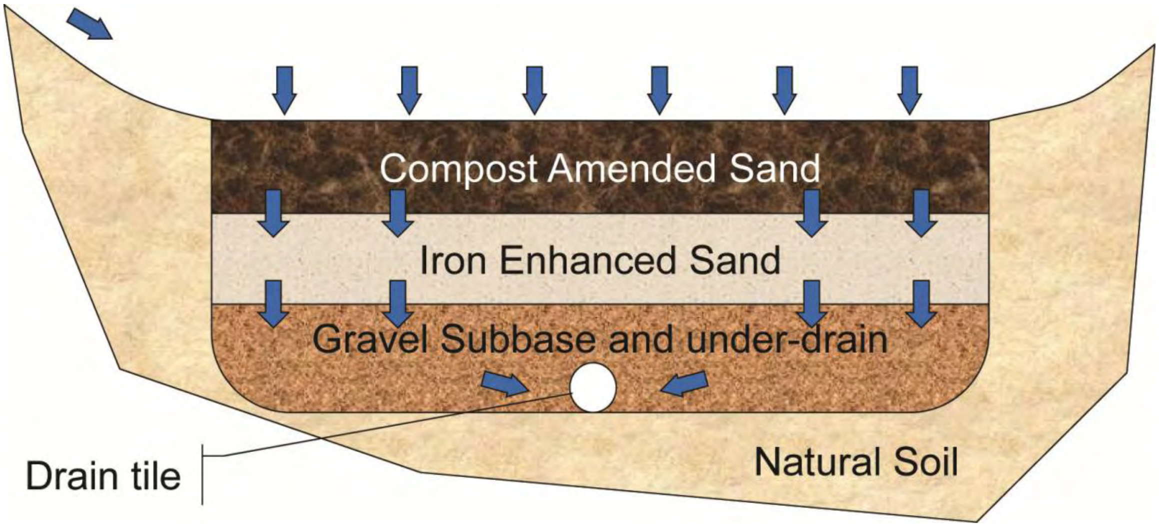


Figure 16. Proposed construction of bioretention facilities.

5.0 Conclusion

Sorption coefficients and breakthrough times for the removal of dissolved cadmium, copper, and zinc on bioretention media, i.e. compost and sand, were determined through batch and column studies. The main conclusions of this work are as follows:

- The batch studies showed sorption capacities of 2 mg Cd/g compost and 3 mg Zn/g compost and approximately 0.08 mg/g sand for both cadmium and zinc. Thus, these materials may be used as sorbents for dissolved toxic metals.
- 153 mg phosphorus/kg compost was released from the compost during the batch study. There was negligible release from the sand.
- The columns studies also show that organic leaf-based compost is an effective material for the removal of dissolved cadmium, zinc, and copper. The fraction of organic matter in a bioretention facility significantly affects the removal capacity of the filter media. Increasing the compost fraction from 0% to 10% more than doubles the expected lifespan for 10% breakthrough in 15 cm of filter media removing cadmium and zinc. Copper was effectively filtered out of the solution with >95% removal for columns with at least 10% compost after 26 years of service.
- Bioretention depth will impact the removal of cadmium, copper, and zinc. The effluent concentration of cadmium from the column matched the influent after 500, 750, and 1,000 pore volumes for 5, 10, and 15 cm of filter media depth, respectively. Removal increases when filter depth increases.
- The filter media consistently leached phosphorus over the duration of the column studies. The concentration of dissolved phosphorus leached was approximately 0.29 mg/L and the median dissolved phosphorus concentration in runoff is 0.12 mg/L. Phosphorus export must be accounted for in TMDL load reduction calculations.
- Both batch and column studies show that cadmium and zinc were sorbed to the filter media at a pH representing stormwater runoff whereas copper precipitated at the concentrations supplied to the media.

- Based on the field study results, organic matter is the most important constituent when considering removal of dissolved toxic metals in a bioretention facility. The vertical profile of organic matter decreased downwards from the surface. This suggests that metal accumulation may at the top of the soil profile. Results from the adsorption isotherm experiments support this conclusion.
- Field study soil analysis showed that metals accumulated in the top 6 cm of the bioretention practice. There was no difference between concentration of metals at depths greater than 6 cm and a soil sample outside of the bioretention practice that had not received and stormwater runoff. Thus, by maintaining and replacing only the first few centimeters of the bioretention filter media, most of the metals can be retained in the bioretention facility and removed upon replacement

The results from this work may be useful for:

- Modeling the fate of dissolved toxic metals in additional stormwater management practices such as bioretention facilities or infiltration basins.
- Assisting engineers and watershed planners in choosing appropriate stormwater management practices for TMDL implementation.

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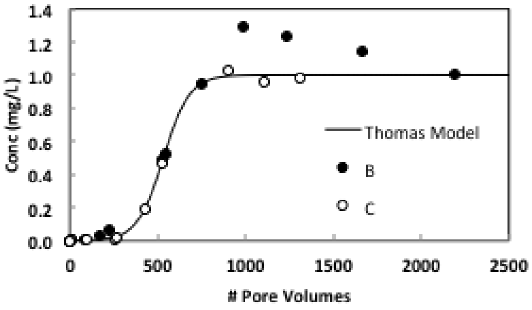
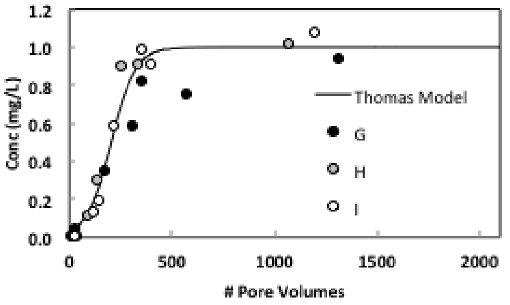
Appendix A: Column Study Results

Cadmium Figures

The figures below represent cadmium data and modeling results that were not presented in the report. The results below show the effect of bed depth (5 cm to 15cm) and compost fraction (0, 10, 30, and 50%).



50% Compost, 5.08 cm depth



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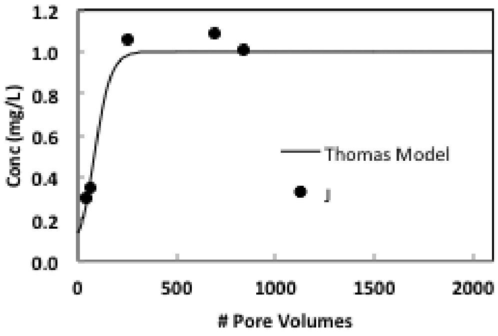

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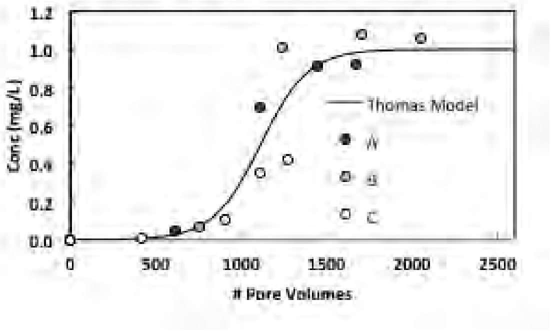

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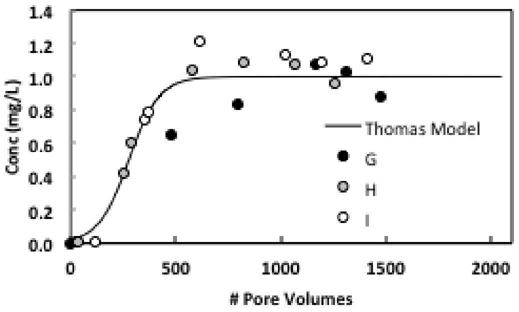

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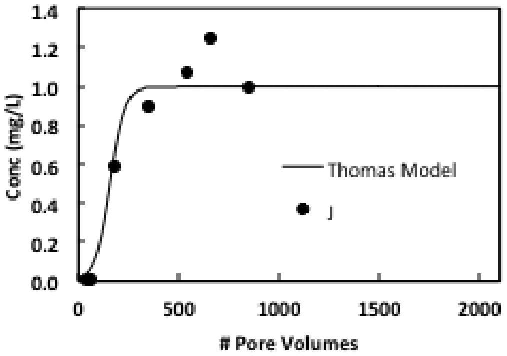
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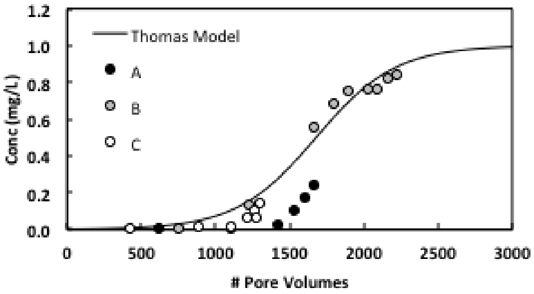
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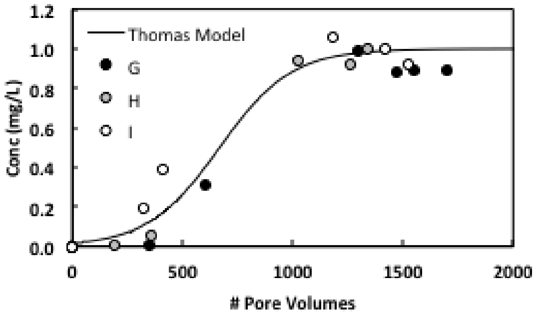
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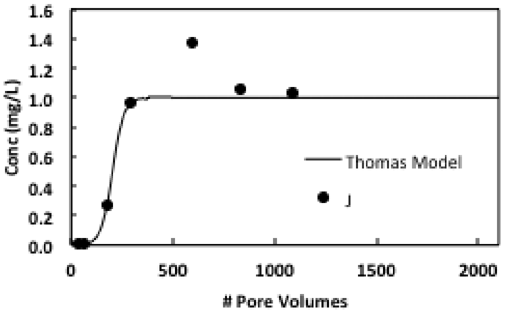
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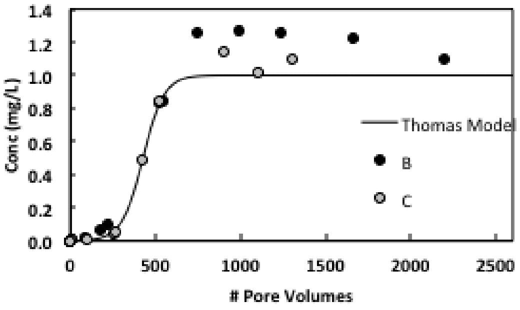
Zinc Figures

The figures below represent all the data and modeling results for zinc removal through the bioretention media.

50% Compost, 5.08 cm Depth



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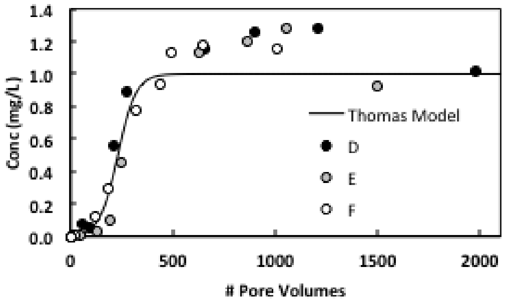

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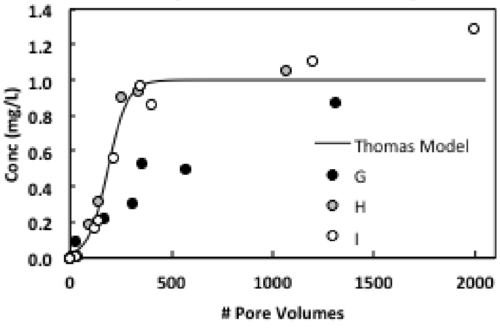

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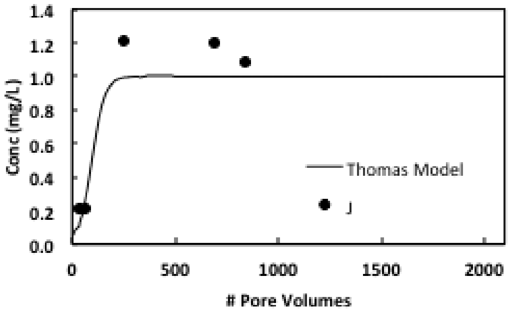

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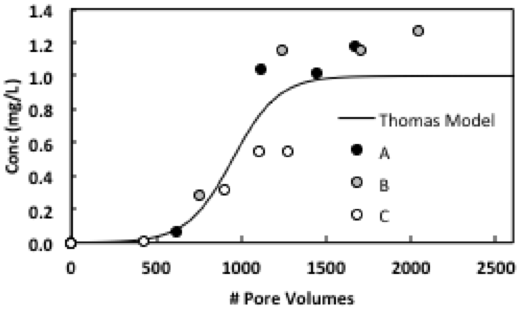

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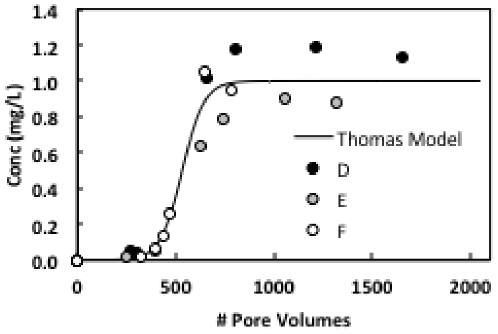

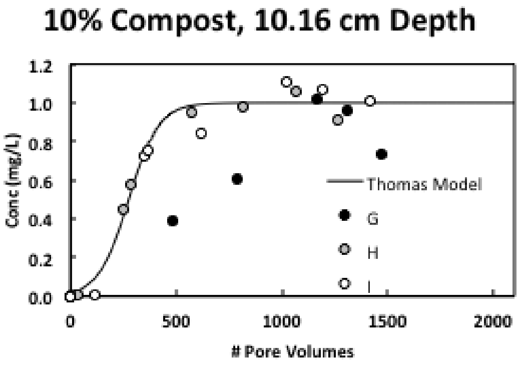
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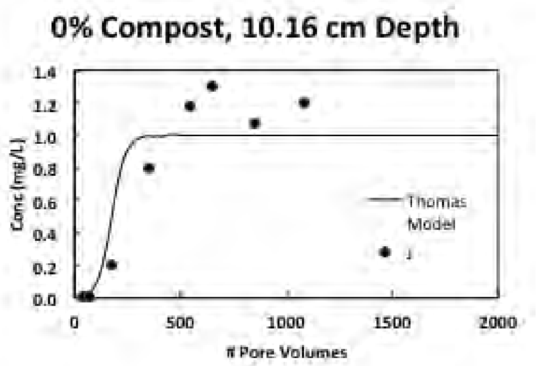
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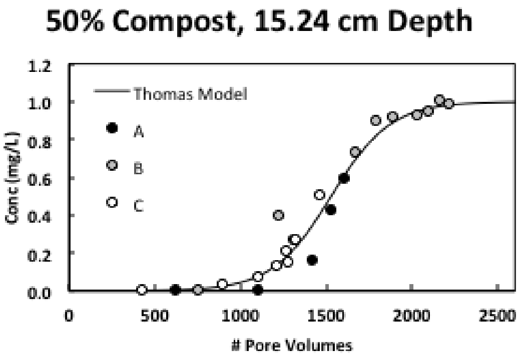
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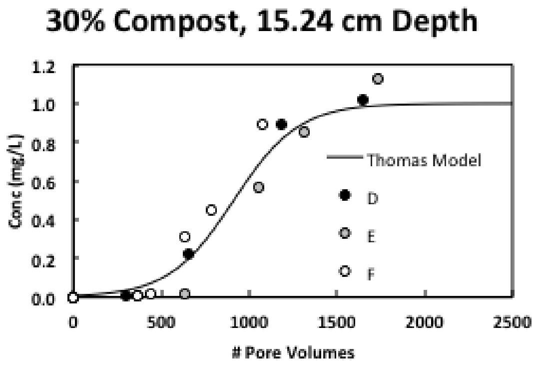
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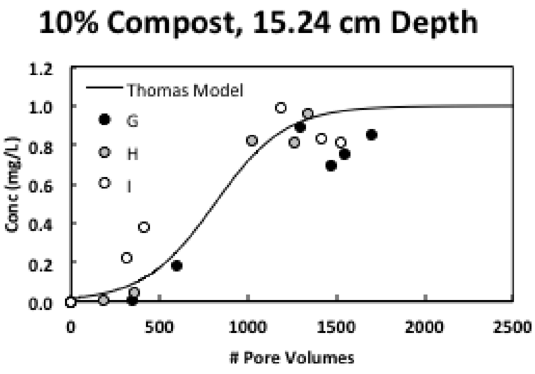
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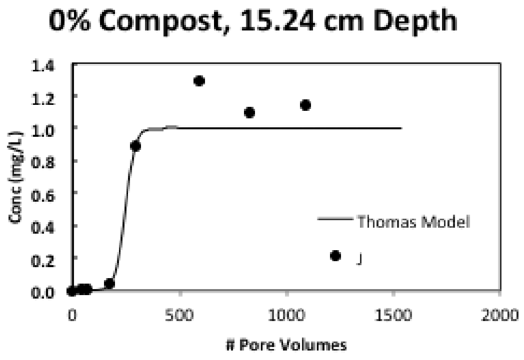
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