

Sorption and Release of Dissolved Pollutants Via Bioretention Media

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Executive Summary

Stormwater runoff has become a primary non-point source of pollution that contains many pollutants that have deleterious effects on the environment. To manage stormwater, different techniques that target specific stormwater pollutants may be implemented in watersheds. One such treatment practice is called bioretention, or rain gardens. This thesis discusses the use of bioretention media as a treatment technique for the removal of toxic metals and investigates the release of phosphorus. A review of previous research and the laboratory experiments will be discussed in two chapters.

Chapter 1 reviews the literature on the concentrations, sources, and effects of 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. Third, Chapter 1 reviews the sorption mechanisms and important variables that aid or hinder sorption of toxic metals to organic materials. Lastly, previous research on sorption of cadmium, copper, lead, and zinc to organic and inorganic sorbent materials is discussed.

Batch and column experiment were performed to investigate the removal of cadmium, copper, and zinc from synthetic stormwater by compost-amended sand. The results of these experiments are discussed in Chapter 2. The batch sorption capacities for Cd and Zn are 2.13 mg/g and 3.82 mg/g, respectively, for Minnesota Compost 1 and 0.02 and 0.07 mg/g, respectively for sand. Copper precipitates as tenorite (CuO) at the pH of the stormwater (7.2) and was only 28% dissolved in the influent, so a sorption capacity was not computed. Column studies using four different ratios of compost (0, 10, 30, and 50%, by volume) were conducted to develop metal breakthrough curves. The breakthrough curves for Cd and Zn were fit to the Thomas Model. The resulting sorption capacities are 0.07, 0.23, 0.37, 0.78 mg Cd/g and 0.10, 0.23, 0.33, 0.61 mg Zn/g for 0, 10, 30, and 50% compost fractions, respectively. These sorption capacities, when adjusted for mass of sand and compost, are consistent with the sorption capacities determined from the batch experiments. Assuming representative values for dissolved metal concentrations, the estimated lifespan of bioretention cells for removal of Cd and Zn ranged from 163 to 205 years for bed depths of 30 cm for a bioretention practice constructed with 30% compost.

Copper was removed in the columns due to filtration and removal increased with increasing compost content.

In the batch and column studies, concentrations of phosphorus exceeded the initial concentrations indicating that phosphorus is exported from the bioretention media to the infiltrating stormwater. The phosphorus concentrations exiting the columns were initially high (0.5 mg P/L), but then decreased to a steady state value of 0.20 - 29 mg P/L (that exceeded the influent value of 0.13 ± 0.03 mg P/L) for the remainder of the experiment. The total yearly load exported from a bioretention practice containing 30% compost is 1.44 g dissolved phosphorus per year per square meter of bioretention area.

Overall, the results suggest that bioretention cells are not likely to fail because of loss of dissolved toxic metal removal capacity as the breakthrough times on the order of hundreds of years far exceed the typical design life of engineering systems of 30 years. Although only one compost was tested in the column experiments, the similarity in batch sorption capacities for several compost samples obtained from Minnesota and around the country suggest that the source of compost is not a strong factor in determining dissolved metal removal performance. For metals that are in particulate form or particle-associated, removals will be dictated by the filtration performance of the bioretention cell which is a function of particle size, bioretention media grain size and porosity, and other factors. Copper, 72% of which was in the particulate form in the column influent, was effectively removed by the bioretention columns and removal improved with increasing fraction of compost. Finally, one significant concern regarding bioretention media is that not only are nutrients not removed effectively, but the compost that is key to metals removal may actually release nutrients (i.e., phosphorus). Thus, it is important to consider the installation of alternative media beneath the compost-amended sand to remove phosphorus, such as iron-amended sand. Such hybrid approaches require more investigation.

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CHAPTER 1. Dissolved Toxic Metal Retention by Bioretention Media

1.0 Introduction

Effective management of urban stormwater runoff is an important goal of engineers, planners, and watershed managers. From hydrodynamic separators to infiltration basins, 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 (

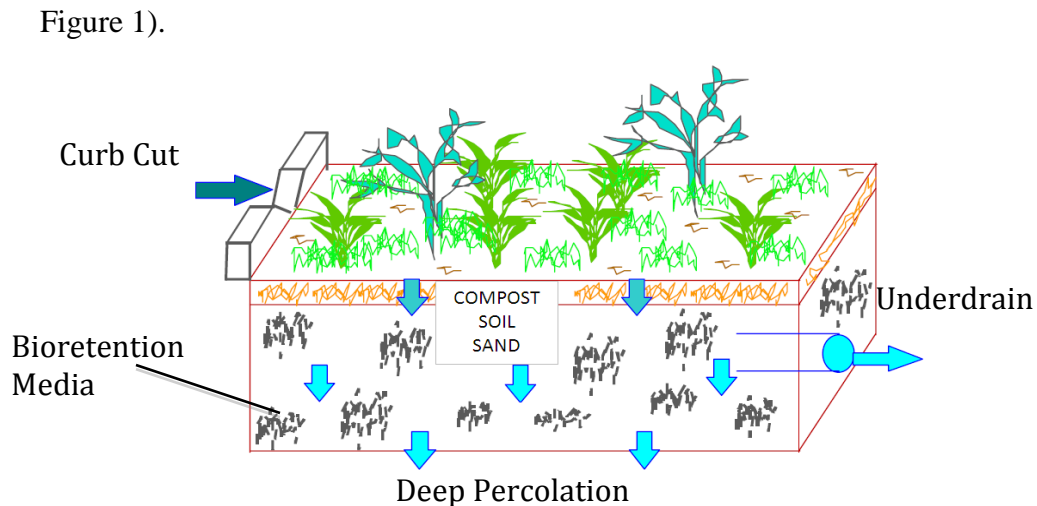


Figure 1. Diagram of a generic rain garden with an underdrain. Polluted stormwater runoff enters from a curb cut or gutter system and infiltrates through the media. Adapted from Davis et al. (2009)

Bioretention practices are shallow depressions that have had native soil removed and replaced with a highly permeable mixture of compost, sand, and soil (Minnesota Stormwater Manual). In Minnesota, compost used in bioretention practices 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 bioretention filter media. Stormwater runoff is routed to bioretention practices via curb

cuts or gutter systems and infiltrates down through the bioretention filter media. Some bioretention practices may have underdrains that outlet into the storm sewer system or to lakes or rivers directly. Commonly used as an aesthetic means to infiltrate stormwater runoff, bioretention practices can also remove pollutants from the stormwater runoff by a variety of mechanisms including filtration, sorption, biodegradation/ biotransformation, and plant uptake (Muthanna et al., 2007; Sun and Davis, 2007).

The objectives of this literature review are to obtain relevant soil parameters including contaminant sorption capacities and contaminant degradation rates. The review will also briefly discuss the sources and problems associated with various stormwater pollutants including suspended solids, total and dissolved phosphorus, petroleum hydrocarbons, pathogens, and toxic metals. Lastly, research on the fate and transport of toxic metals through low impact development practices to the groundwater table will be studied. This literature review is a companion to a previous literature review submitted to the MPCA entitled “Contamination of Soil and Groundwater Due to Stormwater Infiltration Practices” (Weiss et al., 2008).

2.0 Background

Conventional stormwater pollutants include suspended solids, nutrients such as phosphorus and nitrogen, petroleum hydrocarbons, pathogens, and toxic metals. The balance of this review will cover previous research on the removal of toxic metals using materials commonly found in bioretention facilities. The pollutant of choice was narrowed down to toxic metals because similar research has been performed recently by University of Minnesota scientists on phosphorus removal (Erickson et al., 2007) and petroleum hydrocarbons (LeFevre, 2011a, b) and because the background, sources, environmental concerns, and potential fate of each of the other pollutants are discussed in depth in Weiss et al. (2008).

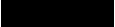

2.1 Toxic Metals

Stormwater runoff contains cadmium, copper, lead, zinc, and other toxic 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 pads and tires (Table 1). Other sources include industrial runoff and zinc coated roofs (Duncan, 1999).

Table 1. Sources of pollutants found in stormwater runoff (Sansalone and Buchberger, 1997)

	Brakes	Tires	Frame Body	Fuels Oil	Concrete Pavement	Asphalt Pavement	De-Icing Salts	Litter
Cadmium	Secondary	Primary						
Chromium	Secondary	Primary						
Copper	Secondary	Primary						
Iron		Primary	Primary					Primary
Lead	Secondary	Secondary		Secondary			Secondary	
Nickel								
Vanadium				Primary				
Zinc	Primary	Primary	Primary					
Chloride							Primary	
Organic Solids						Primary		Primary
Inorganic Solids			Secondary		Secondary			
PAHs				Secondary				
Phenols								

Legend:  Primary Source  Secondary Source

Excessive concentrations of cadmium and copper can cause kidney or liver damage and excessive zinc can cause aesthetic concerns in water. 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). Thus, removal of these pollutants from stormwater runoff is vital to maintaining a healthy ecosystem.

Several studies quantify the concentrations of different stormwater pollutants in road runoff. Pitt et al. (2003) reviewed NPDES MS4 permit results for stormwater characteristics such as pH, hardness, and total and dissolved pollutants including metals and nutrients. Data of a few selected metals are provided in Table 2. The median concentrations in Table 2 only include results from samples that were above detection limits. For cadmium, copper, lead, and zinc, the proportion of each metal that is not dissolved and is associated with particles is 50, 50, 81.1, and 54.5%, respectively. Kayhanian et al. (2007) collected 635 samples from 34 highway sites over a three-year period in California and analyzed them for stormwater pollutants. The results of analysis for toxic metals are shown in Table 3. For cadmium, copper, lead, and zinc the portion

of each metal that is bound to particles is 70.5, 51.7, 90.6, and 63.7%, respectively. The two studies used different methods yet still report similar pollutant concentrations.

Table 2. Concentrations of Selected Metals in Stormwater Runoff (Maestre and Pitt, 2005)

Metal	Fraction	N	Median (µg/L)	Range (µg/L)
As	Total	1425	3.3	0.011 - 310
	Dissolved	209	1.5	0.5 - 13.2
Cd	Total	2481	1	0.04 - 334
	Dissolved	389	0.5	0.1 - 5.7
Cr	Total	1561	7	0.5 - 220
	Dissolved	260	2.08	0.9 - 15
Cu	Total	2770	16	0.17 - 1360
	Dissolved	413	8	0.09 - 195
Ni	Total	1602	9	1 - 120
	Dissolved	246	4	0.8 - 82
Pb	Total	2902	15.9	0.049 - 1200
	Dissolved	446	3	0.5 - 130
Zn	Total	3053	112	0.37 - 22,500
	Dissolved	383	51	3.1 - 13,900

Table 3. Concentrations of select toxic metals in highway stormwater runoff (Kayhanian et al., 2007)

Metal	Fraction	N	Median (µg/L)	Range (µg/L)
As	Total	635	1.1	0.5 - 70
	Dissolved	635	0.7	0.5 - 20
Cd	Total	635	0.44	0.2 - 30
	Dissolved	635	0.13	0.2 - 8.4
Cr	Total	635	5.8	1 - 94
	Dissolved	635	2.2	1 - 23
Cu	Total	635	21.1	1.2 - 270
	Dissolved	635	10.2	1.1 - 130
Ni	Total	635	7.7	1.1 - 130
	Dissolved	635	3.4	1.1 - 40
Pb	Total	635	12.7	1 - 2600
	Dissolved	635	1.2	1 - 480
Zn	Total	635	111.2	5.5 - 1680
	Dissolved	635	40.4	3 - 1017

The concentrations of these metals in wastewater effluent and in surface waters are regulated by the states. For example, in Minnesota the water quality standard for Cd, Cu,

Pb, and Zn are 3.9, 18, 82, and 117 $\mu\text{g/L}$, respectively for Class 2 (fishing and recreational use) surface waters with a total hardness of 100 mg/L (MPCA, 2009). The maximum standard is the highest concentration of a toxicant in water to which aquatic organisms can be exposed for a brief time with zero to slight mortality.

2.2 Pollutant Removal Mechanisms in Stormwater Treatment Practices

Stormwater treatment practices use physical, biological, or chemical processes to clean stormwater. Physical processes such as filtration and sedimentation are useful for removing suspended solids and pollutants associated with those solids. Biological activity, including plant growth and microbial growth, can result in uptake and sequestration of nutrients, toxic metals, or other pollutants as well as degradation of organic contaminants. Chemical processes such as sorption are used to remove metals and phosphate using organic matter and minerals (Erickson et al., 2007). Bioretention practices combine physical, biological, and chemical treatment processes to remove stormwater pollutants.

3.0 Removal of Toxic Metals

Dissolved cadmium, copper, and zinc are removed from stormwater runoff by adsorbing to the bioretention filter media. Adsorption, or movement of a solute from the bulk fluid onto a solid surface, is a chemical process typically used in drinking water treatment for removal of taste and odor compounds and removal of synthetic organic chemicals (Crittenden et al. 2005). Absorption is the movement of a solute from the bulk fluid into the structure of the sorbent material. The term sorption is used when both adsorption and absorption are occurring or the actual mechanism is not known. Sorption in bioretention practices occurs in a similar manner by using organic or inorganic materials to remove dissolved metals. The sorption mechanisms to organic materials will be discussed herein because they are the primary focus of this research.

3.1 Sorption to Organic Material

Sorption to organic material, such as compost, in bioretention filter media is highly dependent on the functional groups. The relevant functional groups in soil organic matter

include carboxyl, phenolic-OH, carbonyl, sulfonic, amine, and imide functional groups (Essington, 2004). The sorption ability of these groups depends on functional group pK_a value, the molecules to which they are attached, and the solution pH. Metals ions, like Cd^{2+} or metal hydroxides, like $CdOH^+$, for example, bind to negatively charged sorbent surfaces. The preference that a particular metal has for a 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). Carboxyl groups are deprotonated at runoff pH values (6.5 to 8.4) and therefore can attract cations under neutral pH soil conditions. Phenolic-OH has a pK_a value of 9.98 and is not deprotonated in typical soil and infiltration situations (Essington, 2004). When bonded to certain molecules, however, the pK_a of phenolic-OH can decrease and the surface charge may change to be more negative or positive. At pH values similar to what we find in nature, organic matter, which contains a combination of these different functional groups, typically has an overall net negative charge and may sorb dissolved toxic metals.

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 ($NaOC_2H_5$), NaOH, or $NaHCO_3$. The amount of each functional group was calculated assuming that the $NaHCO_3$ neutralizes only the carboxyl 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 concentration of carboxyl and phenol groups. Other researchers have also reported that carboxyl and phenolic groups of a soil organic matter are the primary sites for metal sorption (Schiewer & Volesky, 1999; Toles et al., 1999). Thus, it is not surprising that removal of organic material from soils decreases the metal sorption capacity of the soils (Elliott et al. 1986; Grimes et al. 1999).

3.2 Effects of pH on sorption

Solution pH affects the sorption of dissolved metals onto soil, sand, compost, or mulch (Elliott et al., 1986; Grimes et al., 1999; Davis et al., 2001; Harmita et al., 2009). Davis et al. (2001) studied mulch, top soil, and sand for removal of copper, lead, zinc,

phosphorus, and nitrate. A batch study was performed on sandy loam soil from pH 3 to 9 to determine how removal efficiency is affected by pH (Figure 2).

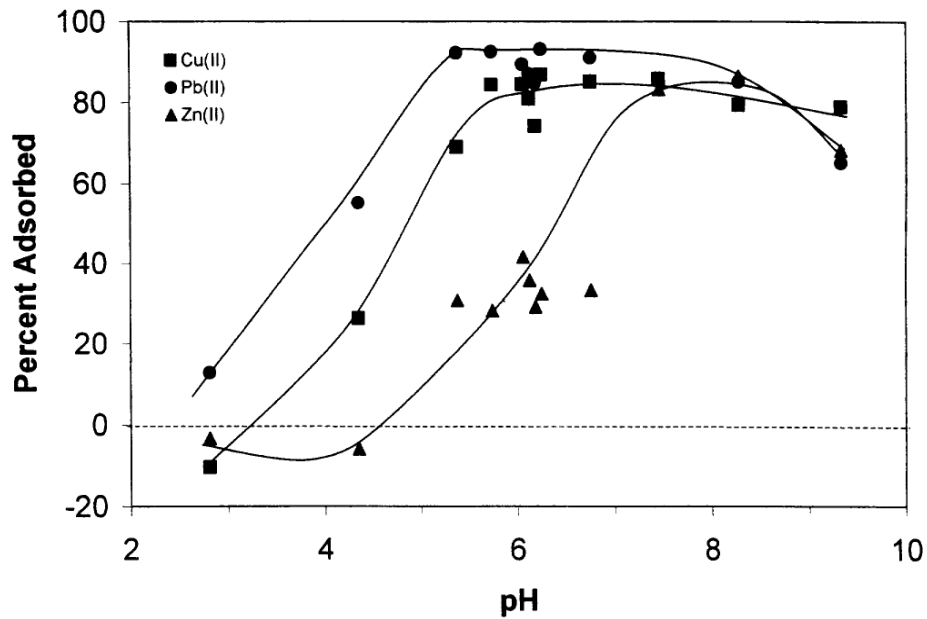


Figure 2. Metal Sorption to Sandy Loam soil (2 g/L) with an organic carbon content of 0.6%. Initial metal concentrations: Cu-106 µg/L, Pb-72 µg/L, Zn-600 µg/L (Davis et al., 2001)

Removal efficiency peaked at 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 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. Sorption sites are protonated at this pH and provide little sorption of cations.

The solution pH will also effect the speciation of the metals in solution. The hydrolysis of a metal depends on the pK value of the specific metal. The pK value describes the propensity of a compound to change structure. In the case of metal hydrolysis, the pK value indicates the pH value at which a metal will add a hydroxide. 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). When the pH of the solution is less than the indicated pK values, then the metals remain as ions in an ideal solution. When then pH value is greater than the pK value, then the metals hydrolyze (i.e. Cd^{2+} goes to CdOH^+). 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^+ , for example, than for the metal ion alone, Cd^{+2} . The pH of stormwater runoff and subsequent pH changes in the infiltration practice can impact the degree the metal removal.

4.0 Previous Research

In the field of environmental engineering, sorption studies have more commonly been used for drinking 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 performed to look at cadmium, copper, lead, and zinc removal by both organic and inorganic sorption media, 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. The maximum sorption capacity of each material allow for comparison between different metals and materials. Batch study results are presented in Table 4 through Table 7.

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

Sorbent	Langmuir		Freundlich		Conditions	Paper
	q_{max} (mg/g)	K_L (L/mg)	K_f (L/g)	n		
Fly Ash	374.3	1.14E-03	-	-	Raw	Apak et al. (1998)
Fly Ash	223.2	1.17E-03	-	-	Washed	
Fly Ash	217.2	6.07E-03	-	-	Acid Treated	
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	
Black Gram Husk	38.76	0.38	-	-		Saeed & Iqbal (2003)
Activated Carbon	11.27	0.02	0.61	1.89	pH=6.0, Single Ion	Ulmanu et al. (2003)
Kaolin	3.04	0.07	0.78	3.57	pH=6.0, Single Ion	
Compost	9.34	0.68	3.79	3.03	pH=6.0, Single Ion	
Cellulose Pulp Waste	5.82	0.05	0.9	2.70	pH=6.0, Single Ion	Ulmanu et al. (2003)
Compost	5.36	0.76	2.76	5.26	pH=6.0, Co-ion	
Cellulose Pulp Waste	1.82	0.39	1.38	16.67	pH=6.0, Co-ion	
Juniper fibers	29.54	1.00E-05	950	1.72	pH=4.2	Min et al. (2004)
Coffee	6.47	0.49	1.06E-03	2.78	pH=6.7	Minamisawa et al. (2004)
Green Tea	6.37	0.26	3.33E-03	2.13	pH=6.7	
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 et al. (2005)
Organoclay	5.00	3.00E-09	-	-		
Zeolite	25.00	1.50E-08	-	-		
Bone Char	60.00	2.00E-07	-	-		
Bark	-	-	260	1.15	pH=6.5, IS=10mM	Genc & Fuhrman et al. (2007)
Fly Ash	-	-	5010	0.64	pH=6.5, IS=10mM	
Sand	-	-	420	3.57	pH=6.5, IS=10mM	
Fraxinus Tree Leaf	67.2	-	-	-	pH=5.0	Sangi et al. (2008)
Ulmus Tree Leaf	80.0	-	-	-	pH=5.0	

Table 5. Sorption model coefficients for sorption of copper onto various materials

Sorbent	Langmuir		Freundlich		Conditions	Paper
	q _{max} (mg/g)	K _L (L/mg)	K _f (L/g)	n		
FlyAsh	335.2	9.4E-04	-	-	Raw	Apakietal(1998)
FlyAsh	328.2	7.5E-04	-	-	Washed	
FlyAsh	283.9	7.3E-04	-	-	AcidTreated	
RedMud	90.0	9.6E-04	-	-	RawMaterial	
RedMud	65.4	1.0E-03	-	-	AcidTreated	
RedMud	87.8	7.9E-04	-	-	HeatTreated	
SandyLoamSoil	-	-	2.5	1	pH=7.0	Davisetal(2001)
ActivatedCarbon	6.61	0.06	0.81	0.45	pH=6.0,Singleion	Ulmanuetal(2003)
Kaolin	4.47	0.15	1.46	0.24	pH=6.0,Singleion	
Compost	12.77	0.35	3.51	0.48	pH=6.0,Singleion	
CellulosePulpWaste	4.98	0.20	1.92	0.22	pH=6.0,Singleion	
ActivatedCarbon	4.77	0.20	1.99	0.19	pH=6.0,Co-ion	Ulmanuetal(2003)
Kaolin	4.36	0.17	2.74	0.09	pH=6.0,Co-ion	
Compost	8.90	0.64	3.7	0.29	pH=6.0,Co-ion	
CellulosePulpWaste	4.55	0.13	1.55	0.23	pH=6.0,Co-ion	
HardwoodMulch	20.59	0.11	0.325	2.42	pH=5.0,Singlemetal	Jangetal(2005)
HardwoodMulch	22.81	0.12	0.379	2.30	pH=6.0,Singlemetal	
HardwoodMulch	6.588	-	-	-	pH=5.0,Co-ion	
HardwoodMulch	6.388	-	-	-	pH=6.0,Co-ion	
Organoclay/anthracite	2.50	1.30E-08	-	-		Tillmanetal(2005)
Organoclay	3.33	3.30E-07	-	-		
Zeolite	20.00	3.00E-08	-	-		
BoneChar	50.00	2.00E-07	-	-		
TurbinariaOrnataBiomass	57.47	2.00E-03	0.235	1.28	pH=8.0	Vijayaraghavanetal(2005)
	71.43	2.20E-03	0.361	1.33	pH=8.5	
	96.15	2.60E-03	0.596	1.36	pH=9.0	
	104.17	2.80E-03	0.787	1.41	pH=9.5	
	119.05	2.90E-03	0.947	1.43	pH=10.0	
	125.10	3.40E-03	1.266	1.49	pH=10.5	
	147.06	4.30E-03	2.287	1.64	pH=11.0	
Compost	-	-	0.56	1.27	pH=5,part.size=2360-4750um	Seelsaenetal(2006)
Compost	-	-	0.67	1.43	pH=5,part.size=1181-2360um	
Compost	-	-	0.71	1.15	pH=5,part.size=601-1180um	
Compost	-	-	0.96	1.10	pH=5,part.size=151-600um	
Compost	-	-	1.24	1.02	pH=5,part.size=<150um	
Bark	-	-	90	-0.42		Gencihurmanetal(2007)
FlyAsh	-	-	100	0.46		
Sand	-	-	100	1.57		Amarasinghetal(2008)
BlackTeawaste	48.0	0.0076	0.7012	1.35	pH=5.5	
Compost	29.8	0.016	-	-	NoPHSet	Nwachukwuetal(2008)
GreenWasteCompst	30.2	0.022	-	-	NoPHSet	
Peat	11.8	0.034	-	-	NoPHSet	
WoodBark	17.1	0.034	-	-	NoPHSet	
FraxinusTreeLeaf	33.1	-	-	-	pH=5.0	Sangietal(2008)
UlmusTreeLeaf	69.5	-	-	-	pH=5.0	
Na-Montmorillonite	33.3	-	-	-	pH=5.6,IS=1mM	Xiaoretal(2009)
FlyAsh	18.8	-	-	-	pH=5.6,IS=1mM	
FlyAsh	126.7	-	-	-	pH=8.7,IS=1mM	
Goethitepowder	10.3	-	-	-	pH=5.6,IS=1mM	
CamelliaTreeLeaf	47.6	-	-	-	pH=5.6,IS=1mM	
PrimarySludge	41.7	-	-	-	pH=5.6,IS=1mM	
PinewoodSawdust	22.6	-	-	-	pH=5.6,IS=1mM	
FraxinusTreeLeaf	33.1	-	-	-	pH=5.0	

Table 6. Sorption model coefficients for sorption of lead onto various materials

Sorbent	Langmuir		Freundlich		Conditions	Paper
	q _{max} (mg/g)	K _L (L/mg)	K _F (L/g)	n		
FlyAsh	526.0	1.1E-03	-	-	Raw	Apak ^{et al.} (1998)
FlyAsh	490.7	1.1E-03	-	-	Washed	
FlyAsh	483.0	8.4E-04	-	-	AcidTreated	
RedMud	158.9	6.6E-04	-	-	RawMaterial	
RedMud	118.5	1.6E-03	-	-	AcidTreated	
RedMud	137.2	1.2E-03	-	-	HeatTreated	
SandyLoamSoil	-	-	4.5	1	pH=7.0	Davis ^{et al.} (2001)
Coffee	16.5	0.20	7.5E-03	1.89	pH=4.0	Minamisawa ^{et al.} (2004)
GreenTea	24.0	0.29	3.8E-03	2.38	pH=4.0	
ActivatedCarbon	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	
HardwoodMulch	63.40	0.23	0.35	4.51	pH=5.0,Singlemetal	Jang ^{et al.} (2005)
HardwoodMulch	72.52	0.26	0.43	4.03	pH=6.0,Singlemetal	
HardwoodMulch	31.70	-	-	-	pH=5.0,Co-ion	
HardwoodMulch	34.81	-	-	-	pH=6.0,Co-ion	
BlackTeawaste	65.0	0.049	9.65	2.57	pH=5.5	Amarasinghe ^{et al.} (2008)
Compost	58.9	0.030	-	-	NoPHSet	Nwachukwu ^{et al.} (2008)
GreenWasteCmpst	86.5	0.044	-	-	NoPHSet	
Peat	47.8	0.021	-	-	NoPHSet	
WoodBark	75.3	0.011	-	-	NoPHSet	
FraxinusTreeLeaf	172.0	-	-	-	pH=5.0	Sang ^{et al.} (2008)
UlmusTreeLeaf	201.1	-	-	-	pH=5.0	

Table 7. Sorption model coefficients for sorption of zinc onto various materials

Sorbent	Langmuir		Freundlich		Conditions	Paper
	q _{max} (mg/g)	K _L (L/mg)	K _F (L/g)	n		
SandyLoamSoil	-	-	0.15	1	pH=7.0	Davis ^{et al.} (2001)
HardwoodMulch	12.10	0.37	0.196	4.22	pH=5.0,Singlemetal	Jang ^{et al.} (2005)
HardwoodMulch	12.23	0.41	0.200	4.43	pH=6.0,Singlemetal	
HardwoodMulch	1.210	-	-	-	pH=5.0,Co-ion	
HardwoodMulch	0.978	-	-	-	pH=6.0,Co-ion	
Organoclay/anthracite	0.83	2.30E-08	-	-		Tillman ^{et al.} (2005)
Organoclay	5.00	2.00E-09	-	-		
Zeolite	16.67	4.00E-08	-	-		
BoneChar	43.00	1.00E-07	-	-		
Zeolites	4.25	6.92E-03	0.94	0.19	pH=5.0	Seelsaen ^{et al.} (2006)
Compost	11.20	3.16E-02	4.09	7.00	pH=5.0	
Bark	-	-	1	0.63		Genc ^{et al.} (2007)
FlyAsh	-	-	40	0.42		
Sand	-	-	30	1.37		
Compost	13.4	0.093	-	-	NoPHSet	Nwachukwu ^{et al.} (2008)
GreenWaste	13.9	0.098	-	-	NoPHSet	
Peat	4.2	0.041	-	-	NoPHSet	
WoodBark	11.0	0.022	-	-	NoPHSet	

Elliott (1986) showed that competition exists between different metals for sorption sites. The relative order of sorption preference for organic soil is Pb > Cu > Cd > Zn and the competition effect has been observed in other studies (Al-Asheh et al., 1997; Jang et al., 2005; Nwachukwu et al., 2008). Comparing similar materials in Table 4 through Table 6 shows that lead has the highest affinity for sorption, followed by copper, zinc, and cadmium based on the Langmuir maximum sorption capacity.

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. The sorption capacities found during experiments using multiple metals may be a more realistic expectation for the ideal capacity of a material.

4.2 Column Study research

Fixed bed, flow through column experiments are a valuable tool for studying sorption because they are typically cheaper, quicker, and more controlled than field monitoring in an actual rain garden. Examples of the variation of experimental conditions in column studies include alternating wet and dry periods (Hatt et al., 2007), competitive toxic metal transport (Kratovichil & Volesky, 2000; Tsang & Lo, 2006) or testing various unconventional sorbents. The goal behind studying sorption in a column is to develop a breakthrough curve for a particular pollutant. Results from column studies are presented in (Table 8).

Table 8. Column study results for various metals and sorbents

Metal	Sorbent	Definition of		q _{BT} (mg/g)	q _{EX} (mg/g)	pH	Paper
		Breakthrough	Exhaustion				
Cu	Sandy Loam Soil	C/C ₀ = 0.2	-	> 0.05	-	7	Davis et al. (2001)
	Mulch	C/C ₀ = 0.1	-	> 0.10	-	7	
Pb	Sandy Loam Soil	C/C ₀ = 0.29	-	> 0.016	-	7	
	Mulch	C/C ₀ = 0.19	-	> 0.039	-	7	
Zn	Sandy Loam Soil	C/C ₀ = 0.50	-	> 0.300	-	7	
	Mulch	C/C ₀ = 0.16	-	> 0.89	-	7	
Cd	Black Gram Husk	C/C ₀ = 0.01	C/C ₀ = 1.0	49.74	-	5	Saeed et al. (2003)
Zn	Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	< 0.001	6.5	Liu et al. (2005)
	GAC	C/C ₀ = 0.1	C/C ₀ = 0.9	0.4	1.63	6.5	
	Iron Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	0.013	0.019	6.5	
	Mn Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	< 0.001	7	
Cu	Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	0.0016	6.5	
	GAC	C/C ₀ = 0.1	C/C ₀ = 0.9	3.51	4.1	6.5	
	Iron Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	0.006	0.122	6.5	
	Mn Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	0.028	0.15	7	
Cd	Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	< 0.001	6.5	
	GAC	C/C ₀ = 0.1	C/C ₀ = 0.9	0.02	1.11	6.5	
	Iron Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	0.013	0.017	6.5	
	Mn Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	< 0.001	7	
Cd	Organoclay/anthracite	-	C/C ₀ = 0.95	-	0.78	6.41	Tillman et al. (2005)
	Organoclay	-	C/C ₀ = 0.95	-	1.84	6.41	
	Zeolite	-	C/C ₀ = 0.95	-	25.98	6.41	
	Bone Char	-	C/C ₀ = 0.95	-	63.91	6.41	
Cu	Organoclay/anthracite	-	C/C ₀ = 0.95	-	0.59	5.58	
	Organoclay	-	C/C ₀ = 0.95	-	1.23	5.58	
	Zeolite	-	C/C ₀ = 0.95	-	16.37	5.58	
	Bone Char	-	C/C ₀ = 0.95	-	42.45	5.58	
Zn	Organoclay/anthracite	-	C/C ₀ = 0.95	-	0.68	3.1	
	Organoclay	-	C/C ₀ = 0.95	-	0.95	3.1	
	Zeolite	-	C/C ₀ = 0.95	-	8.96	3.1	
	Bone Char	-	C/C ₀ = 0.95	-	28.72	3.1	
Cu	Tea Waste	C/C ₀ = 0.2	C/C ₀ = 1.0	6	13	-	Amarasinghe and Williams (2007)
	GAC	C/C ₀ = 0.2	C/C ₀ = 1.0	3	8	-	
Pb	Tea Waste	C/C ₀ = 0.2	C/C ₀ = 1.0	33	46	-	
	GAC	C/C ₀ = 0.2	C/C ₀ = 1.0	8	19	-	
Cd	Ferrosorp (Iron Sorbent)	C/C ₀ = 0.016	C/C ₀ = 1.0	0.34	1.59	6.80	Genc-Fuhrman et al. (2008)
Cu	Ferrosorp (Iron Sorbent)	C/C ₀ = 0.07	C/C ₀ = 1.0	0.17	0.82	6.80	
Zn	Ferrosorp (Iron Sorbent)	C/C ₀ = 0.60	C/C ₀ = 1.0	0.17	0.72	6.80	
Cu	Sand	C/C ₀ = 0.01	-	0.07	-	6.9	Zhang et al. (2008)
	Sand + 2.5% Fly Ash	C/C ₀ = 0.01	-	0.07	-	11.1	
	Sand + 5% Fly Ash	C/C ₀ = 0.01	-	0.06	-	11.3	
Pb	Sand	C/C ₀ = 0.01	-	0.06	-	7.4	
	Sand + 2.5% Fly Ash	C/C ₀ = 0.01	-	0.06	-	11.1	
	Sand + 5% Fly Ash	C/C ₀ = 0.01	-	0.06	-	11.2	
Zn	Sand	C/C ₀ = 0.01	-	0.05	-	7.2	
	Sand + 2.5% Fly Ash	C/C ₀ = 0.01	-	0.06	-	11	
	Sand + 5% Fly Ash	C/C ₀ = 0.01	-	0.05	-	11.3	
Cu	Peat	C/C ₀ = 0.05	C/C ₀ = 1.0	18.08	36.61	6	Izquierdo et al. (2009)

Several 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 toxic metals (Cu, Pb, Zn), phosphorus, nitrogen, and sediments

using fixed bed columns made with sandy loam soil and amendment 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. In another 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.

Gong and Donahoe (1997) studied removal of various toxic 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 3). Potassium, calcium, and magnesium were released, indicating that cation exchange may play a role in removal of the metals.

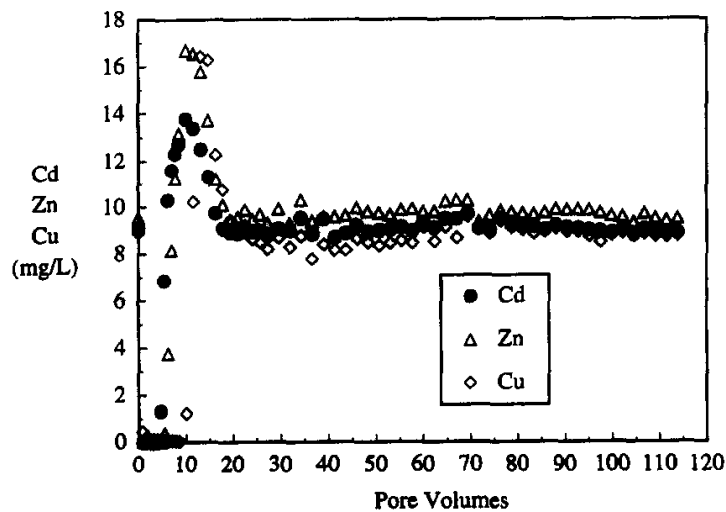


Figure 3. Cd, Cu, and Zn removal by a sandy loam soil. Cd, Cu, Zn $C_0 \sim 9$ mg/L

Furthermore, analysis by scanning electron microscope indicates that specific adsorption to iron, aluminum, or manganese hydroxides is also a dominant removal mechanism. A simulated acid rain test was performed on these sample as well. The pH was approximately 4. Results indicate that all sorbed metals were released, including metals that originated on the soil itself (Gong and Donahoe, 1997).

Simultaneous sorption of copper and cadmium was studied using sandy loam soil in columns (Tsang and Lo, 2006). The authors found that the 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 columns that used a binary solution of cadmium and copper, 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 0.1 mM. 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 bioretention performance for both hydraulics and pollutant removal than batch studies. The column study results may be useful for understanding the longevity of bioretention practices using these materials.

4.3 Field Study research

The effectiveness of bioretention practices under actual conditions is understood using field studies. The available data summarizes both monitoring of actual storm events and simulations of storm events. In general, bioretention practices effectively remove toxic metals (Table 9 and Table 10). Most papers report the percent reduced of each constituent and although this gives an idea of the overall effectiveness of a rain garden using the percent reduced gives incomplete knowledge of the actual water quality. Reporting the effluent concentration, however, enables the reader to better understand if a

particular stormwater management practice will achieve the desired water quality standard.

Some papers do not differentiate between “total” and “dissolved” metals and only report the effluent concentrations or percent reductions for particular metals. For these papers, the data is presented as “total.” When possible, percent reductions are reported as percent reduced in mass load because this method also accounts for water volume attenuation by the rain garden. Simply calculating the percent reduced based on event mean concentrations does not account for the amount of water held inside the rain garden or infiltrated laterally.

Table 9 Field Study Effluent Concentrations (µg/L)

Test Type Site Description	Davis et al. (2003)		Davis (2007)		Muthanna et al. (2007)		Li and Davis (2009)		Chapman and Horner (2010)
	Simulation Greenbelt	Largo	Monitoring Cell A Cell B		Simulation April August		Monitoring CP SS		Monitoring
Total Copper	2	69	4	3	15.2	41.7	16	9	6.3
Total Lead	<2	16	<2	4	0.8	2.5	3	<2	4.5
Total Zinc	<25	390	48	44	22	49	12	3	47
Dissolved Copper	-	-	-	-	-	-	-	-	2.9
Dissolved Lead	-	-	-	-	-	-	-	-	<1
Dissolved Zinc	-	-	-	-	-	-	-	-	26

Table 10 Field Study Percent Reduced (%)

Test Type Site Description	Davis et al. (2003)		Hunt et al. (2006)		Davis (2007)		Muthanna et al. (2007)		Li and Davis (2009)		Hatt et al. (2009)		Chapman and Horner (2010)
	Simulation Greenbelt Largo		Monitoring Greensboro Chapel Hill		Monitoring Cell A Cell B		Simulation April August		Monitoring CP SS		Simulation McDowall	Monitoring Clayton	Monitoring Method A
Total Copper	97	43	99	-	51	57	60.0	74.7	65	96	98	67	80
Total Lead	>95	70	81	-	79	86	83.3	89.2	83	100	98	80	86
Total Zinc	>95	64	98	-	28	63	90.1	89.0	92	99	99	84	80
Dissolved Copper	-	-	-	-	-	-	-50.0	-100.0	-	-	-	-	58
Dissolved Lead	-	-	-	-	-	-	100.0	28.6	-	-	-	-	-
Dissolved Zinc	-	-	-	-	-	-	80.0	74.2	-	-	-	-	72

As indicated in Table 9, the effluent concentrations for copper, lead, and zinc from bioretention facilities are close to the water quality standard for Minnesota Class 2 waters (18, 82, and 117 $\mu\text{g/L}$, respectively). In two simulated storm studies, the copper standard is exceeded. In one simulated storm study the zinc standard is exceeded. The effluent concentrations for copper, lead, and zinc from bioretention facilities are all below the water quality standard for monitoring studies. The effluent concentrations from simulation events compare favorably with the effluent concentrations found from monitoring.

In all studies, the total metals were reduced except in the study by Muthanna et al. (2007), who found that dissolved copper leached from the bioretention facility. The field studies show that monitoring actual rain events yields lower removal than the simulated stormwater runoff tests. The difference between simulated stormwater events and monitoring may be due to the difference in influent concentrations. Davis et al. (2003) used influent copper, lead, and zinc concentrations of 80, 80, and 600 $\mu\text{g/L}$ for a simulated stormwater runoff test and Hatt et al. (2009) used influent concentrations of 50, 140, and 250 $\mu\text{g/L}$ for copper, lead, and zinc in a simulated stormwater test. As Table 2 indicates, the concentrations of each metals used in the simulated events is higher than what is commonly found in stormwater runoff. Chapman and Horner (2010) measured influent concentrations of 16, 17, and 120 $\mu\text{g/L}$ for total copper, lead, and zinc and 3.6, <1, and 49 $\mu\text{g/L}$ for dissolved copper, lead, and zinc. Despite reporting lower removal percentages, the monitoring data indicates that bioretention facilities effectively remove toxic metals from stormwater runoff. More information and research is needed to determine the lifespan of bioretention practices in real world situations, yet the available information on the effectiveness of bioretention facilities is promising.

5.0 Discussion and Conclusions

A wide variety of materials have been examined in batch, column, and field experiments to determine the sorption capacity for dissolved toxic metals and the

effectiveness of bioretention practices at removing dissolved metals from stormwater runoff.

Batch experiments tested common bioretention materials such as sandy loam soil, mulch, and sand and uncommon soil amendments such as fly ash, red mud, and zeolites to remove cadmium, copper, lead, and zinc. In general, the uncommon soil amendments had a higher sorption capacity than the common organic materials. Second, the order of sorption preference is lead > copper > cadmium > zinc, showing that more lead will be removed than copper, cadmium, and zinc. Lastly, the individual sorption capacities for cadmium, copper, lead, and zinc are suppressed when mixed in solutions containing more than one metal at a time.

Column studies show the time necessary for breakthrough of pollutants in the effluent. The results from the column studies validate the conclusions from the batch studies. Full breakthrough curves are useful for predicting total lifespan of a bioretention practice using similar materials and solution conditions. However, many column studies are performed at a pH less than that in stormwater runoff to enhance solubility of the metals in solution. This inhibits direct comparison between real world bioretention practices and column studies.

Lastly, field studies using simulated runoff tests and long term monitoring both indicate excellent removal of total and dissolved toxic metals from stormwater runoff, though more research is needed.

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CHAPTER 2: Evaluation of Removal and Release of Dissolved Pollutants from Bioretention Media

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 $\mu\text{g/L}$, 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 $\mu\text{g/L}$, respectively. The maximum allowable concentration to avoid acute toxicity effects on aquatic life is 2, ~10, 65, and 120 $\mu\text{g/L}$ 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 11. 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 bioretention 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 bioretention media commonly used in bioretention practices.

Table 11. Breakthrough (BT) and exhaustion (EX) for column studies with specific metals sorbing to bioretention amendments and media.

Metal	Sorbent	Definition of		q _{BT} (mg/g)	q _{EX} (mg/g)	pH	Paper
		Breakthrough	Exhaustion				
Cu	Sandy Loam Soil	C/C ₀ = 0.2	-	> 0.05	-	7	Davis et al. (2001)
	Mulch	C/C ₀ = 0.1	-	> 0.10	-	7	
Pb	Sandy Loam Soil	C/C ₀ = 0.29	-	> 0.016	-	7	
	Mulch	C/C ₀ = 0.19	-	> 0.039	-	7	
Zn	Sandy Loam Soil	C/C ₀ = 0.50	-	> 0.300	-	7	
	Mulch	C/C ₀ = 0.16	-	> 0.89	-	7	
Cd	Black Gram Husk	C/C ₀ = 0.01	C/C ₀ = 1.0	49.74	-	5	Saeed & Iqbal (2003)
Zn	Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	< 0.001	6.5	Liu et al. (2005)
	GAC	C/C ₀ = 0.1	C/C ₀ = 0.9	0.4	1.63	6.5	
	Iron Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	0.013	0.019	6.5	
	Mn Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	< 0.001	7	
Cu	Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	0.0016	6.5	
	GAC	C/C ₀ = 0.1	C/C ₀ = 0.9	3.51	4.1	6.5	
	Iron Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	0.006	0.122	6.5	
	Mn Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	0.028	0.15	7	
Cd	Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	< 0.001	6.5	
	GAC	C/C ₀ = 0.1	C/C ₀ = 0.9	0.02	1.11	6.5	
	Iron Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	0.013	0.017	6.5	
	Mn Oxide Coated Sand	C/C ₀ = 0.1	C/C ₀ = 0.9	< 0.001	< 0.001	7	
Cd	Organoclay/anthracite	-	C/C ₀ = 0.95	-	0.78	6.41	Tillman et al. (2005)
	Organoclay	-	C/C ₀ = 0.95	-	1.84	6.41	
	Zeolite	-	C/C ₀ = 0.95	-	25.98	6.41	
	Bone Char	-	C/C ₀ = 0.95	-	63.91	6.41	
Cu	Organoclay/anthracite	-	C/C ₀ = 0.95	-	0.59	5.58	
	Organoclay	-	C/C ₀ = 0.95	-	1.23	5.58	
	Zeolite	-	C/C ₀ = 0.95	-	16.37	5.58	
	Bone Char	-	C/C ₀ = 0.95	-	42.45	5.58	
Zn	Organoclay/anthracite	-	C/C ₀ = 0.95	-	0.68	3.1	
	Organoclay	-	C/C ₀ = 0.95	-	0.95	3.1	
	Zeolite	-	C/C ₀ = 0.95	-	8.96	3.1	
	Bone Char	-	C/C ₀ = 0.95	-	28.72	3.1	
Cu	Tea Waste	C/C ₀ = 0.2	C/C ₀ = 1.0	6	13	-	Amarasinghe & Williams (2007)
	GAC	C/C ₀ = 0.2	C/C ₀ = 1.0	3	8	-	
Pb	Tea Waste	C/C ₀ = 0.2	C/C ₀ = 1.0	33	46	-	
	GAC	C/C ₀ = 0.2	C/C ₀ = 1.0	8	19	-	
Cd	Ferrosorb (iron sorbent)	C/C ₀ = 0.016	C/C ₀ = 1.0	0.34	1.59	6.80	Genc-Fuhrman et al. (2008)
Cu	Ferrosorb (iron sorbent)	C/C ₀ = 0.07	C/C ₀ = 1.0	0.17	0.82	6.80	
Zn	Ferrosorb (iron sorbent)	C/C ₀ = 0.60	C/C ₀ = 1.0	0.17	0.72	6.80	
Cu	Sand	C/C ₀ = 0.01	-	0.07	-	6.9	Zhang et al. (2008)
	Sand + 2.5% Fly Ash	C/C ₀ = 0.01	-	0.07	-	11.1	
	Sand + 5% Fly Ash	C/C ₀ = 0.01	-	0.06	-	11.3	
Pb	Sand	C/C ₀ = 0.01	-	0.06	-	7.4	
	Sand + 2.5% Fly Ash	C/C ₀ = 0.01	-	0.06	-	11.1	
	Sand + 5% Fly Ash	C/C ₀ = 0.01	-	0.06	-	11.2	
Zn	Sand	C/C ₀ = 0.01	-	0.05	-	7.2	
	Sand + 2.5% Fly Ash	C/C ₀ = 0.01	-	0.06	-	11	
	Sand + 5% Fly Ash	C/C ₀ = 0.01	-	0.05	-	11.3	
Cu	Peat	C/C ₀ = 0.05	C/C ₀ = 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 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 NaHCO₃ 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 CdCl₂·2.5H₂O, CuSO₄·5H₂O, and ZnSO₄·7H₂O 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 $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 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 Experimental Setup

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 4). 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 bioretention media in three 5 cm segments, with a 2.5 cm layer of sand separating each segment of bioretention media. A 5 cm gravel bed was in the bottom of each column to support the bioretention 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 bioretention media (intermediate sampling port). The 2.5 cm sand layers serve to protect the intermediate sampling port from clogging by fine materials from the compost bioretention 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 bioretention 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.

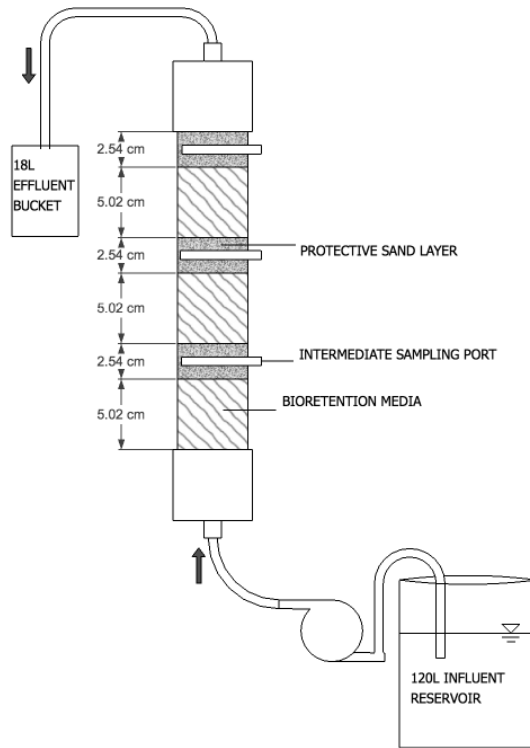


Figure 4. Schematic diagram of the laboratory-scale bioretention column system used to investigate metals removal and retention (Not to scale).

All effluent was collected in 18 L buckets with a known depth-volume relationship. The bioretention media was made from MN compost 1 (The Mulch Store, Minneapolis, MN) and C-33 sand, mixed in four 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 bioretention 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 bioretention media ratio was taken apart and two samples from the bioretention 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 5. 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 5. 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 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:

$$q = \frac{q_{max} * k_L * C_{eq}}{1 + k_L * C_{eq}} \quad (1)$$

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:

$$q = k C_{eq}^{1/n} \quad (2)$$

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.

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp \left[\frac{k_{TH}(q_{max}m - C_0V)}{Q} \right]} \quad (3)$$

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_{max} 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 12).

Table 12. Fraction organic matter (OM), cation exchange capacity (CEC), and background concentration of metals and phosphorus for bioretention 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
Phosphorus (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 12 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 phosphorus 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 Pseudo-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 12).

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 13). The experimental parameters, data, and figures for all batch experiments are included in Appendix A.

Table 13. Summary of Batch Test Results.

Cadmium						
Material	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						
Material	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) as shown in Figure 6 through Figure 8. 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.

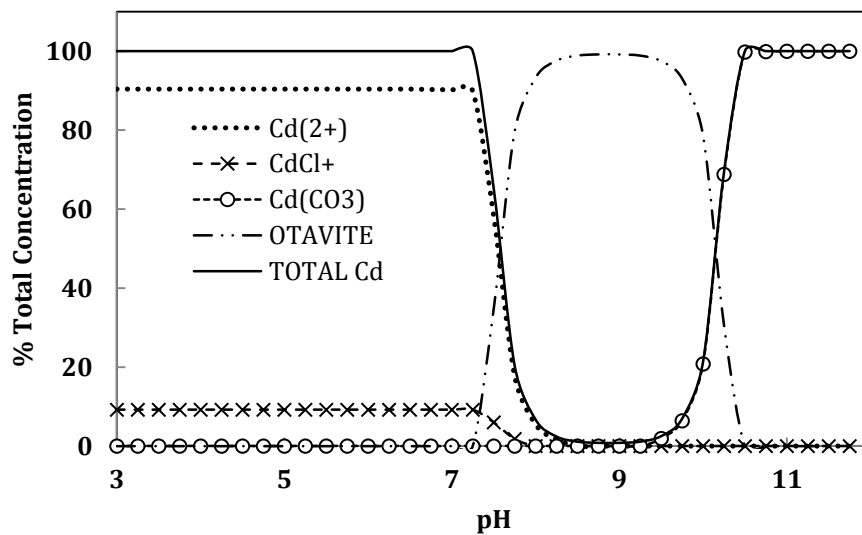


Figure 6. Cadmium speciation in synthetic stormwater recipe determined from MIN-EQL analysis.

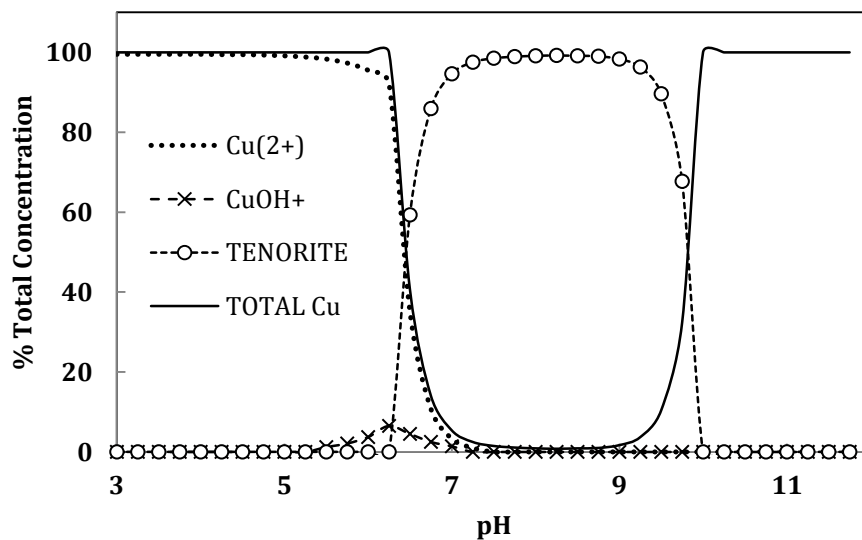


Figure 7. Copper speciation in synthetic stormwater recipe determined using MIN-EQL speciation software.

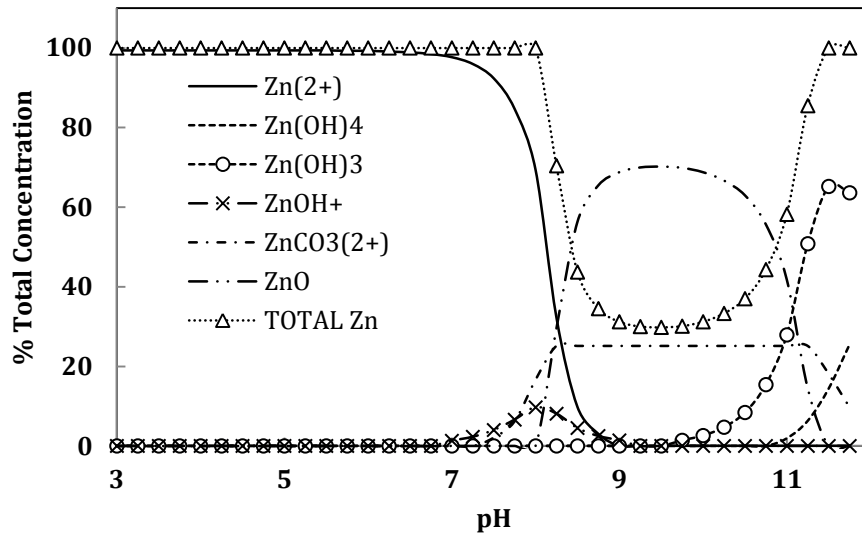


Figure 8. Zinc speciation in synthetic stormwater recipe determined using MIN-EQL speciation software.

The results show that approximately 153 mg phosphorus per kg of compost leaches off the compost (Figure 9). 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.

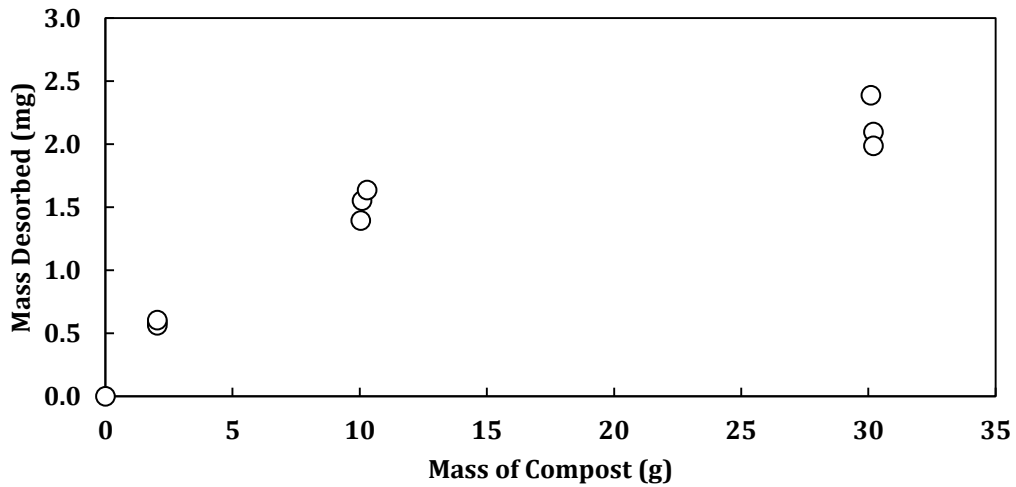


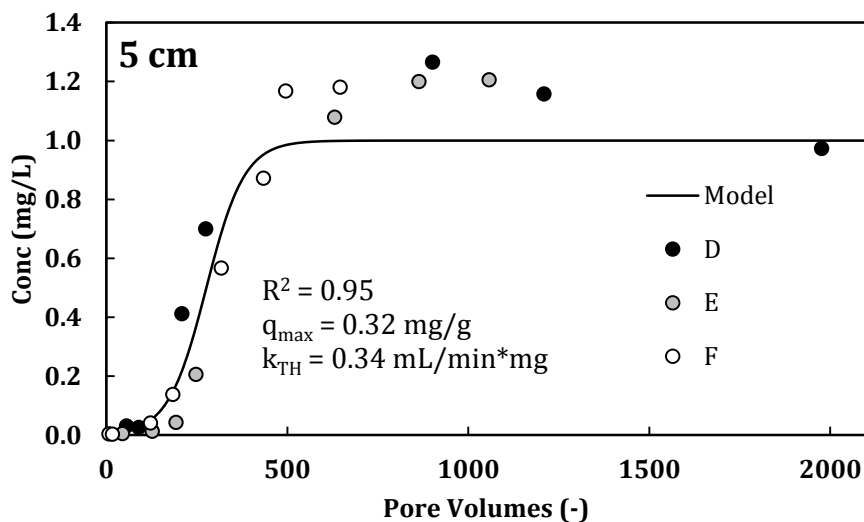
Figure 9. Release of phosphorus by MN compost 1 into 230 mL of batch study stock solution.

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 bioretention media depth. Sample results for cadmium are shown in Figure 10 with results for all experimental runs provided in Appendix B. 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 bioretention 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 copper, calcium, potassium, magnesium, or sodium. Tsang and Lo (2006) found that cadmium was released from a column study using sandy loam soil in favor of copper.



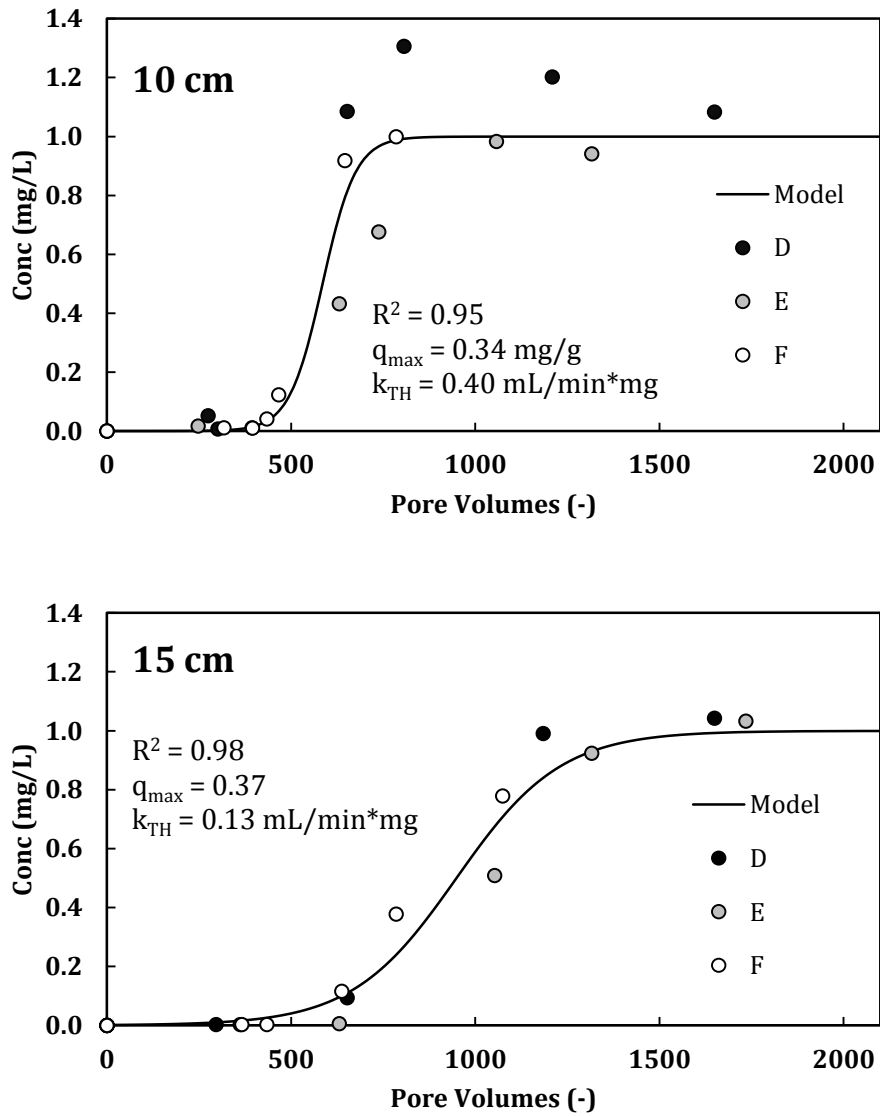


Figure 10. Effect of bed depth on removal of cadmium by 30% compost columns. Data from the three 30% compost replicates (D, E, F) are presented along with the Thomas Model.

3.3.2 Effect of Compost Fraction

The compost fraction within the bioretention media affects the retention of metals in the columns. Figure 11 shows the Thomas Model fit to the breakthrough data collected at 15 cm of bioretention media.

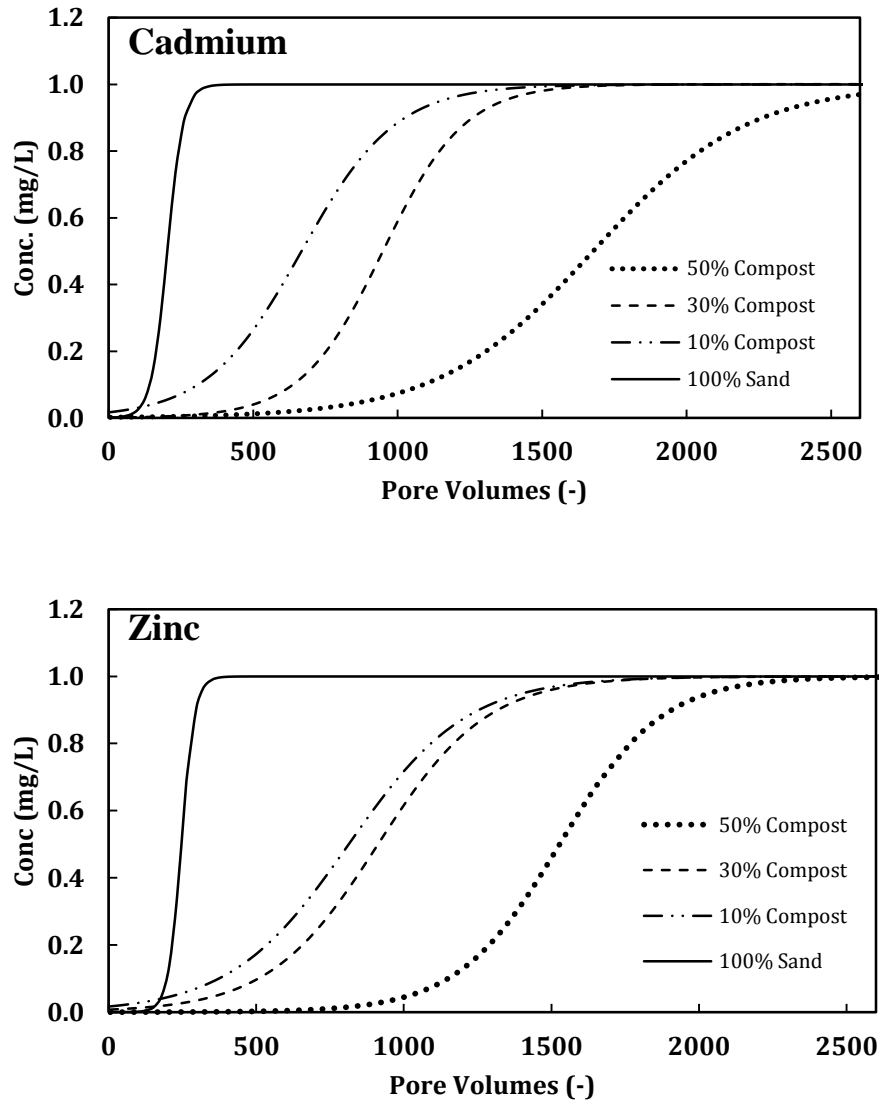


Figure 11. Thomas Model fits for cadmium (top) and zinc (bottom) at 15.24 cm bioretention media depth indicating the effect of compost fraction on removal.

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 0, 10, 30 and 50% compost fraction columns are $0.08 (\pm 0.011)$, $0.19 (\pm 0.011)$, $0.34 (\pm 0.012)$, and $0.73 (\pm 0.016)$ 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 bioretention 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 12). The data indicates excellent removal of copper, compared to cadmium and zinc. After 15 cm of bioretention media, the average removal efficiencies were 64%, 95, 99, and 99 for the 0, 10, 30, and 50% compost fraction columns after 1700 bed volumes.

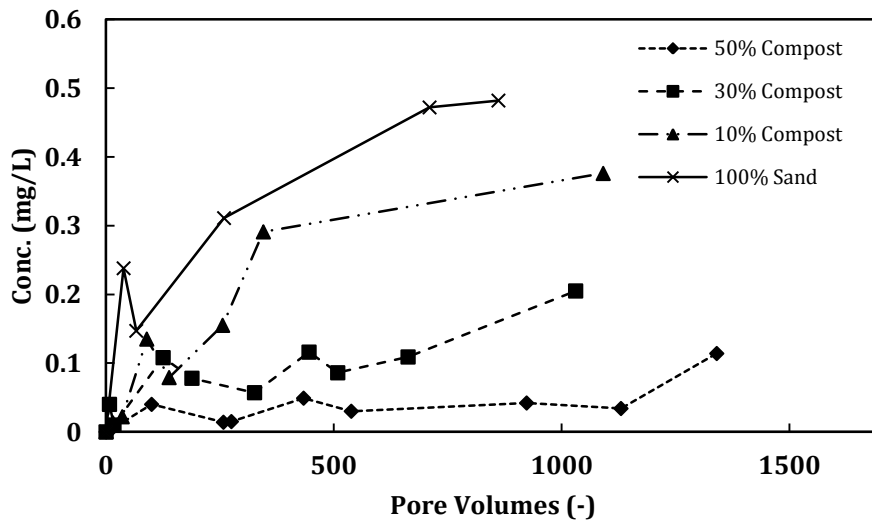


Figure 12. Effect of compost fraction dissolved copper removal at 5 cm of bioretention media depth.

3.3.3 Summary of Column Study Modeling

The rate constants (k_{TH}) and sorption capacities (q_{max}) calculated for cadmium and zinc using the Thomas Model are shown in Table 14. There were three columns at each compost fraction and the Thomas Model was simultaneously fit to the data from all three columns

Table 14. Fit of Thomas Model Coefficients for Cadmium and Zinc with MN Compost 1

Compost %	Depth cm	Cadmium				Zinc			
		k_{TH} [mL/mg/min]		Capacity q_{max} (mg/g)		k_{TH} [mL/mg/min]		Capacity q_{max} (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 14 except the sand column, indicating a delay in breakthrough time with increasing bioretention 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 14 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 100% sand 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.

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

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 (cm²), n is the column porosity, D_x is the vertical dispersion coefficient (cm²/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 cm²/min for 0, 10, 30, and 50% compost columns, respectively. Dispersion did not interfere with the curve-fit parameters of the Thomas Model and was low relative to adsorption/sorption in the columns. 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. For example, 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 13). 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.

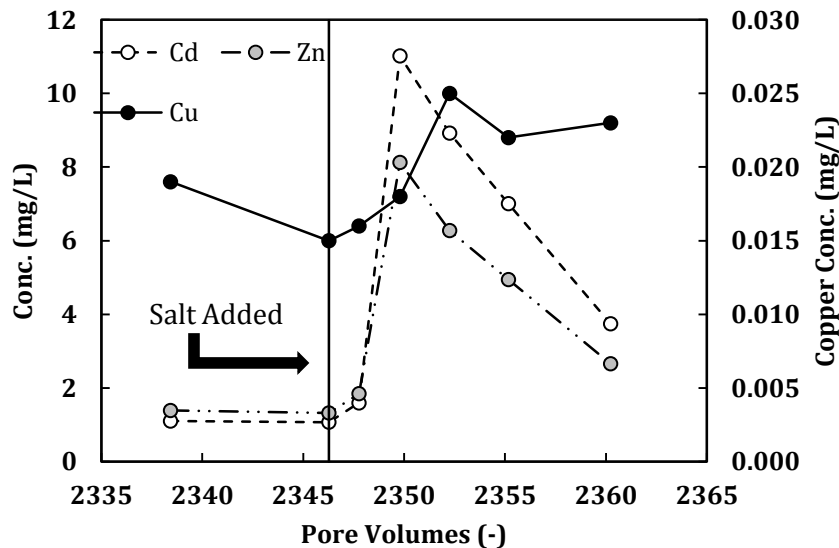


Figure 13. Release of cadmium, copper, and zinc from one 30% compost fraction column after introducing NaCl. Copper is plotted on the right axis.

3.3.5 Mass Balance Results

The sorption capacities for the MN Compost 1 and sand materials in the batch studies, shown in Table 13, 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 14 and Figure 15. 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.

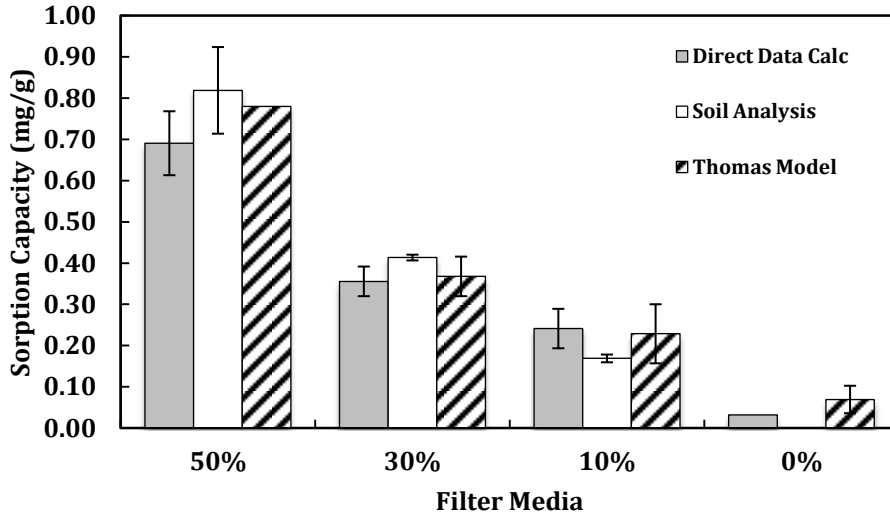


Figure 14. Cadmium removal measured by concentration difference and by sorption onto the media. Error bars indicate 1 standard deviation. A soil analysis was not performed on the 0% column.

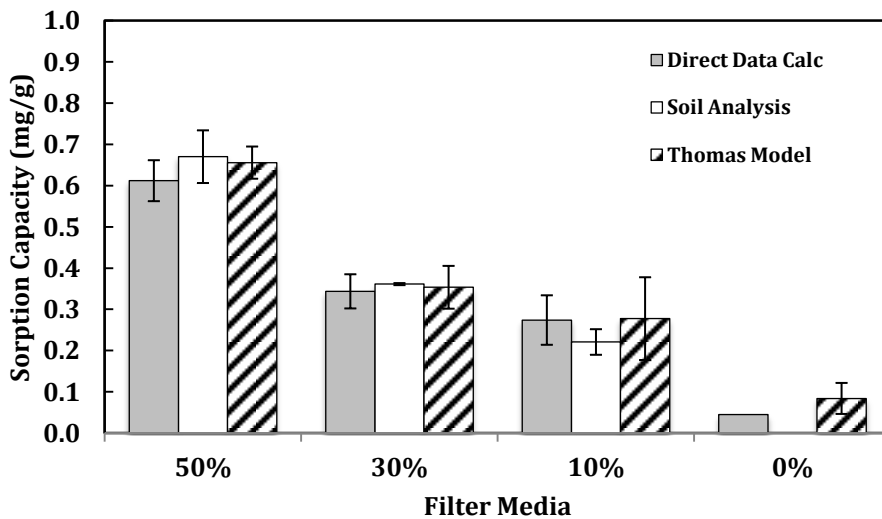


Figure 15. Zinc removal computed by differences in concentration and by sorption to the media. Error bars indicate 1 standard deviation. A soil analysis was not performed on the 0% column.

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 16 shows the cumulative mass of phosphorus released normalized by the mass of bioretention media when water passed through the column.

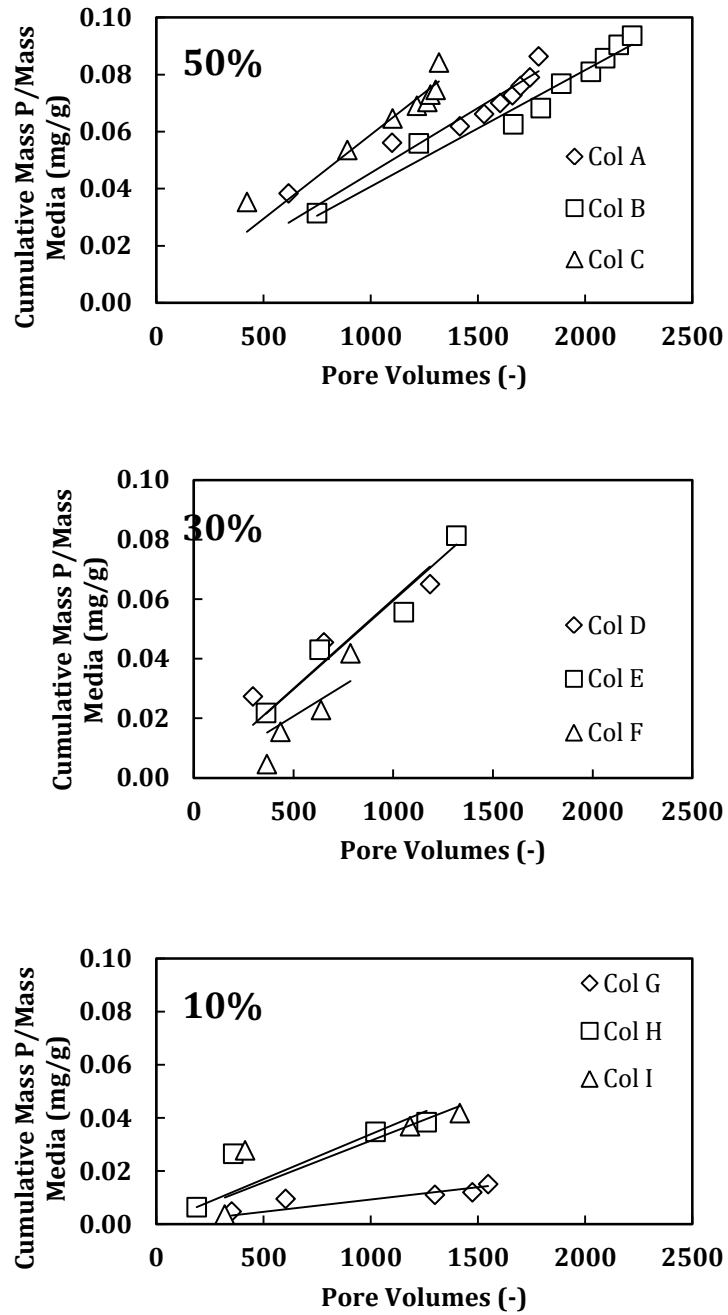


Figure 16. Phosphorus Export from 50, 30, and 10% compost columns

The linear fit to the data indicates that phosphorus release was approximately constant throughout the tests for between 1,500 and 2,500 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 17 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 $5.5 \pm 3.3\%$ 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.

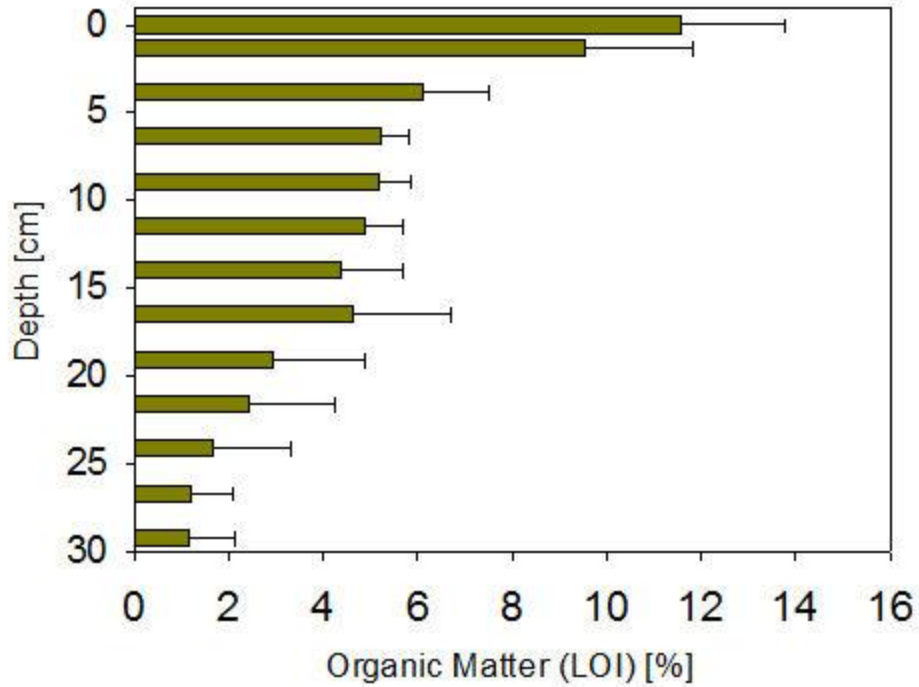


Figure 17. (Left) Organic matter profile in St. Paul campus bioretention practice

Bioretention 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 18 shows a comparison between organic matter in the bioretention practices and the concentration of zinc attached to the bioretention media.

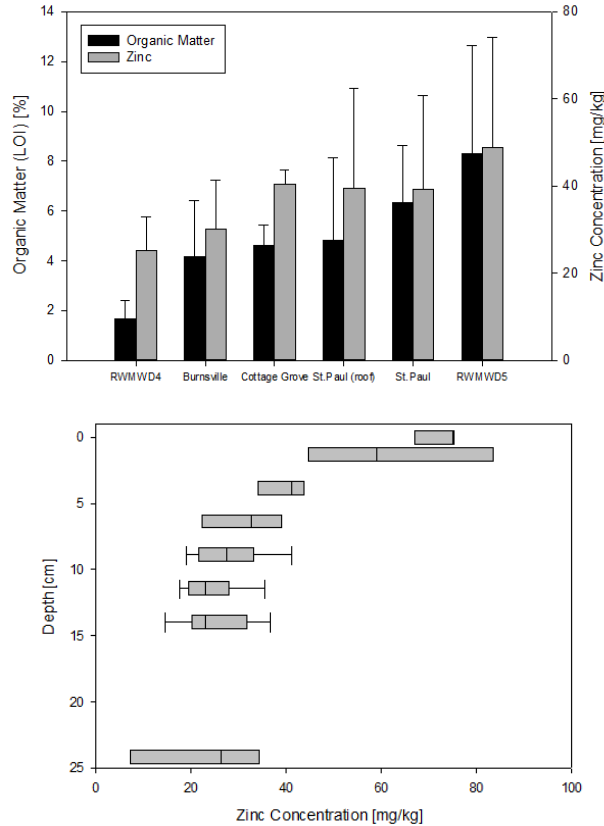


Figure 18. (Top) Zinc and organic matter concentration in the first 14 cm of depth and (Bottom) Average zinc concentration profile in the six bioretention practices investigated in this study.

Figure 18 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 18 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 19, 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.

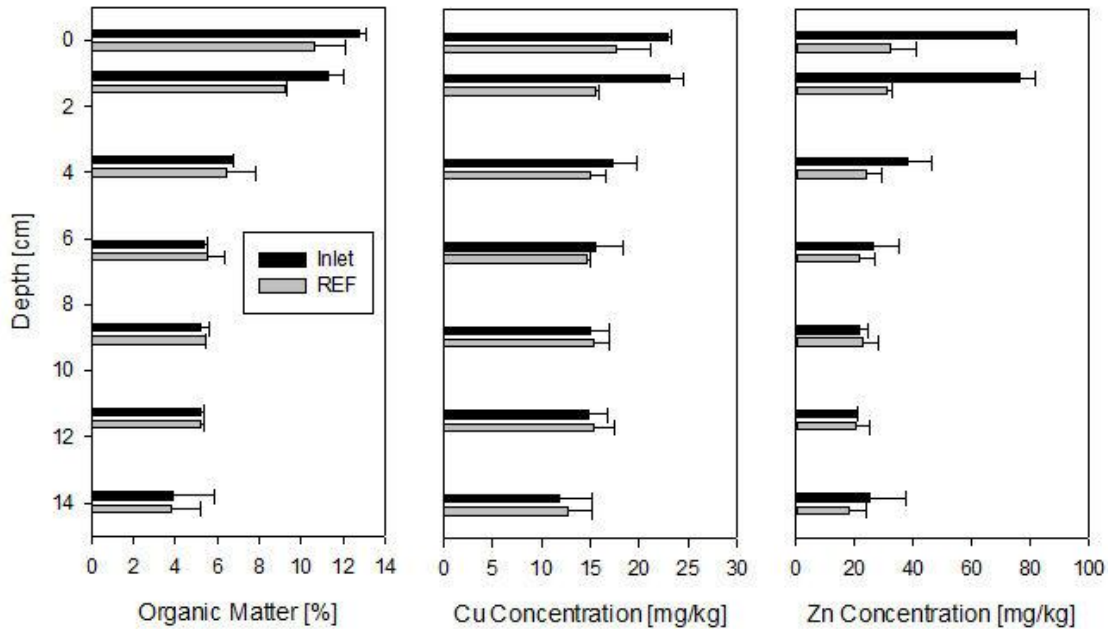


Figure 19. Profiles of organic matter, copper, and zinc concentrations at two different cores in the St. Paul campus bioretention practice. Samples were collected near the inlet pipes (INLET) and from a reference location outside the bioretention practice (REF).

Adsorption isotherm experiments were conducted on uncontaminated bioretention media cores from the existing St. Paul bioretention practice. The results from these experiments (Figure 20) suggest that the bioretention media has a significant ability to retain cadmium and zinc, and that this ability relates very much to the organic matter content in the bioretention media.

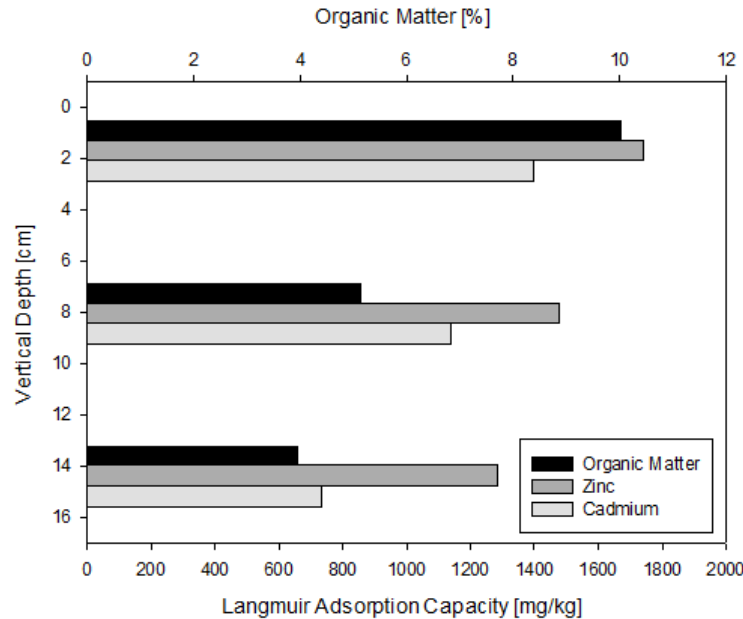


Figure 20. Zinc and cadmium adsorption capacities (Langmuir) as a function of depth and organic matter content.

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 bioretention 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:

$$D_W = \frac{V}{A} \quad (5)$$

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):

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

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%). “ $\text{Min}(C * R, 0.0127)$ ” 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:

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

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_{max}) 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 15.24 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 21 and Figure 22), though this will not be significant compared to the total time needed for breakthrough.

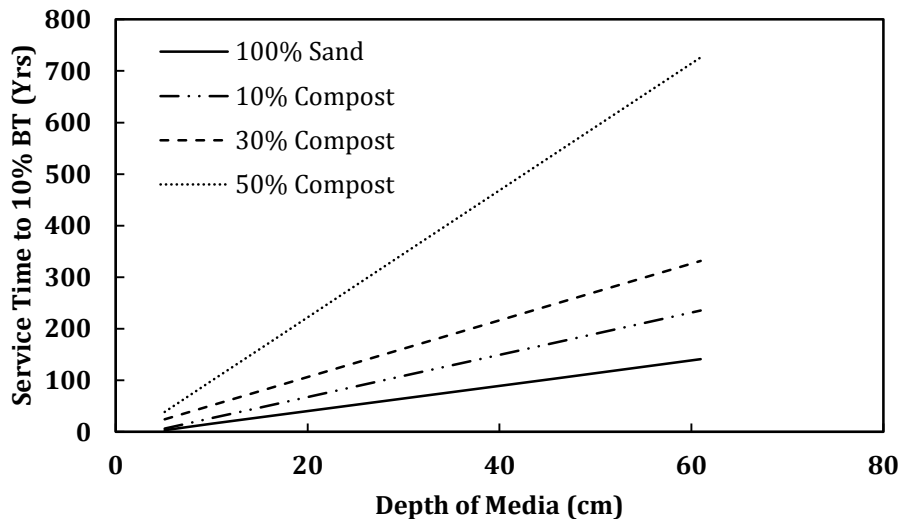


Figure 21. Lifespan predictions for zinc removal with $C_0 = 0.1$ mg/L

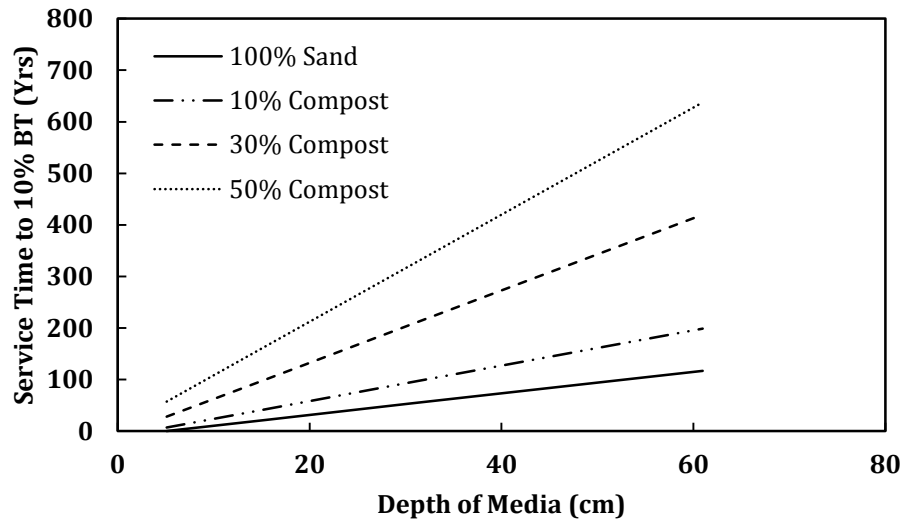


Figure 22. Lifespan predictions for cadmium removal with $C_0 = 1$ mg/L.

Assuming that the modeling parameters remain constant at lower influent concentrations, a bioretention 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 bioretention 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 bioretention 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 m² 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 bioretention media. If we assume that the rain garden is 30 cm deep, has a surface area of 100 m², and the bioretention media has a bulk density of 1,200 kg/m³, then the total mass of dissolved phosphorus released from the bioretention media over 15 years is 2.16 kg. The yearly load is 144 g phosphorus released from the bioretention 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 bioretention 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 bioretention 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 23). 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.

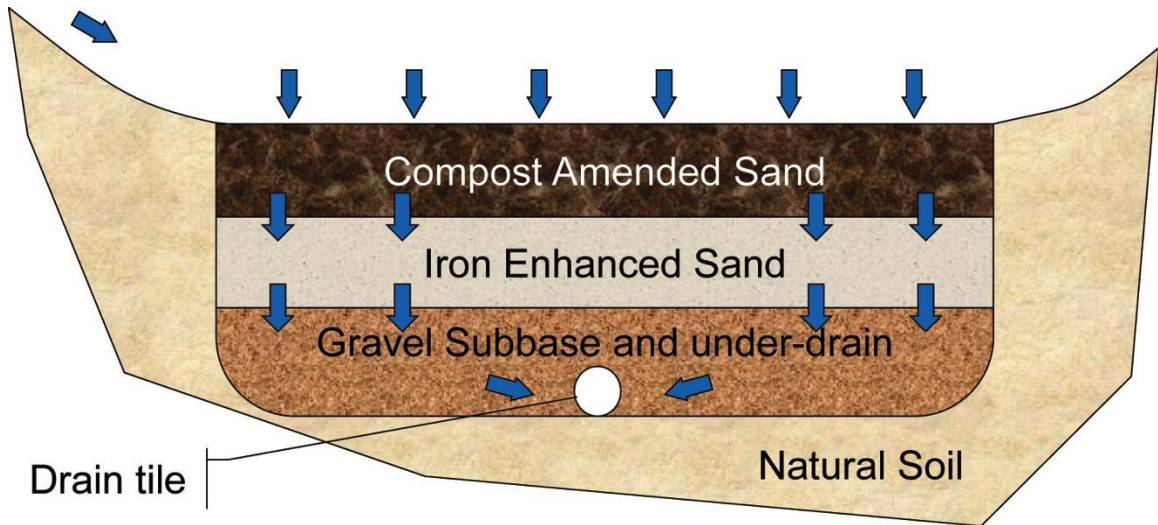


Figure 23. Proposed construction of bioretention facilities.

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:

- 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 bioretention media. Increasing the compost fraction from 0% to 10% more than doubles the expected lifespan for 10% breakthrough in 15 cm of bioretention 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.

- 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 occurs first in the upper few centimeters of the bioretention media. This is also supported by results from the adsorption isotherm experiments. Thus, by maintaining and replacing only the first few centimeters of the bioretention media, most of the metals can be retained in the bioretention facility and removed upon replacement
- Cadmium and zinc were sorbed to the bioretention media at a pH representing stormwater runoff whereas copper precipitated at the concentrations supplied to the media.
- The bioretention media consistently leached phosphorus over the duration of the column studies. The concentration of dissolved phosphorus leached is approximately 0.29 mg/L and the median dissolved phosphorus concentration in runoff is 0.12 mg/L. This must be accounted for in TMDL load reduction calculations.

5.1 Future Work

The results from this work may be useful for modeling the fate of dissolved toxic metals in additional stormwater management practices such as infiltration basins. The results may also assist engineers and watershed planners in choosing appropriate stormwater management practices for TMDL implementation.

Much research has been performed on various materials that may be used to adsorb toxic metals from stormwater runoff, yet there are still some questions that should be investigated. As one can see from the batch and column study tables, the variability in sorption capacity for materials lends importance to choosing bioretention materials wisely. Sand based materials have a low expected life span, but will not adversely affect the initial hydraulics or chemical characteristics of the effluent. Native soil, while it may have a greater sorption capacity, may 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.

Second, batch and column studies are often performed at a solution pH less than the pH of stormwater runoff. This limits the application of the results from these experiments. Research is required on commonly used filtration media at conditions similar to stormwater.

Third, more research is needed on the long term effectiveness of bioretention practices. Field study data is limited to either simulated stormwater events or short term monitoring (Hunt et al., 2006; Davis, 2007; Hatt et al, 2009; Li and Davis, 2009). Only one monitoring report spent more than one year studying a bioretention practice (Chapman and Horner, 2010). No monitoring data exists that covers the lifespan of a bioretention practice. Long term monitoring or periodic grab samples should be taken from bioretention practices for a longer period of time to judge the removal capacity and efficiency.

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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Appendix A. Batch Test

A.1 Batch Test Photos



Figure 24. Shaker table and bottles used in batch study (left) and close-up of bottles on table (right).

A.2 Kinetic Test Data and Results

All data was fit to the Lagergren Pseudo Second order equation, which is,

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

where 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:

$$\frac{t}{q} = \frac{1}{k * q_e^2} + \frac{t}{q_e}$$

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 to plot a model fit.

Table 15. Sorption kinetic data.

Sample	Mass(g)	Time(hr)	CADMIUM				COPPER				Zinc				Phosphorus			
			Cs	q(ug/g)	ln(qe/q)	t/q	Cs	q(ug/g)	log(qe/q)	t/q	Cs	q(ug/g)	ln(qe/q)	t/q	Cds	q(ug/g)	ln(Ce/C)	t/C
A11	1.00	0	0	0.00	3.65		0.00	0.00	5.73		0.00	0.00	2.17		0.00	0.00	6.91	
A11	1.00	2	106	21.20	2.84	0.09	-2.00	-0.40	5.73	-5.00	17.00	3.40	1.68	0.59	0.00	0.00	6.91	
A21	1.00	2	115	23.00	2.73	0.09	-2.00	-0.40	5.73	-5.00	23.00	4.60	1.43	0.43	0.00	0.00	6.91	
A31	1.02	2	92	18.04	3.01	0.11	-17.00	-3.33	5.74	-0.60	18.00	3.53	1.66	0.57	0.00	0.00	6.91	
A31d	1.02	2	93	18.24	3.00	0.11	-17.00	-3.33	5.74	-0.60	11.00	2.16	1.89	0.93	0.00	0.00	6.91	
A12	1.00	6	175	35.00	1.20	0.16	13.00	2.60	5.72	2.18	47.00	9.40	-		460.00	92.00	6.30	0.01
A22	1.01	6	192	38.02	-1.19	0.15	27.00	5.35	5.71	1.06	39.00	7.72	0.05	0.73	518.00	102.57	6.18	0.01
A32	1.00	6	184	36.80	0.42	0.15	28.00	5.60	5.71	1.01	37.00	7.40	0.32	0.77	445.00	89.00	6.32	0.01
A32d	1.00	6	181	36.20	0.75	0.16	28.00	5.60	5.71	1.01	39.00	7.80	-0.02	0.73	450.00	90.00	6.31	0.01
A13	1.04	12	176	33.85	1.50	0.35	26.00	5.00	5.71	2.40	41.00	7.88	-0.12	1.52	706.00	135.77	5.69	0.02
A23	1.01	12	193	38.22	-2.26	0.31	31.00	6.14	5.71	1.95	47.00	9.31	-		699.00	138.42	5.72	0.02
A33	1.01	12	176	34.85	1.24	0.34	14.00	2.77	5.72	4.33	33.00	6.53	0.81	1.84	572.00	113.27	6.07	0.02
A14	1.00	24	187	37.40	-0.08	0.64	22.00	4.40	5.72	-5.45	38.00	7.60	0.16	3.16	855.00	171.00	5.00	0.03
A24	1.01	24	171	33.86	1.50	0.71	10.00	1.98	5.72	12.12	44.00	8.71	-2.77	2.75	778.00	154.06	5.42	0.03
A34	1.00	24	191	38.20	-2.10	0.63	29.00	5.80	5.71	4.14	44.00	8.80	-	2.73	819.00	163.80	5.21	0.03
A34d	1.00	24	194	38.80	-	0.62	26.00	5.20	5.71	4.62	45.00	9.00	-	2.67	781.00	156.20	5.40	0.03
A15	1.00	48	198	39.60	-	1.21	34.00	6.80	5.71	7.02	43.00	8.60	-1.74	5.55	923.00	184.60	4.38	0.05
A25	1.00	48	206	41.20	-	1.16	42.00	8.40	5.70	5.68	46.00	9.20	-	5.19	976.00	195.20	3.29	0.05
A35	1.00	48	207	41.40	-	1.15	48.00	9.60	5.70	4.97	49.00	9.80	-	4.87	1150.00	230.00	-	0.04
A11	1.00	2	501	100.20	-	0.01996008	114	22.80	5.65	0.0877193	160	32.00	-	0.0625				
A12	1.00	29	923	184.60	-	0.16	263	52.60	5.54	0.56	313	62.60	-	0.47				
A14	1.00	24	826	165.20	-	0.14	209	41.80	5.58	0.56	269	53.80	-	0.44				
A61	1.00	72	894	178.80	-	0.40	272	54.40	5.53	1.32	289	57.80	-	1.24				
A62	1.00	72	921	184.20	-	0.39	294	58.80	5.52	1.22	303	60.60	-	1.19				
A63	1.00	72	937	187.40	-	0.38	313	62.60	5.50	1.15	282	56.40	-	1.28				
A71	1.00	96	949	189.80	-	0.51	334	66.80	5.48	1.44	279	55.80	-	1.72				
A72	1.00	96	943	188.60	-	0.51	335	67.00	5.48	1.43	311	62.20	-	1.54				
A73	1.00	96	863	172.60	-	0.56	243	48.60	5.56	1.98	281	56.20	-	1.71				

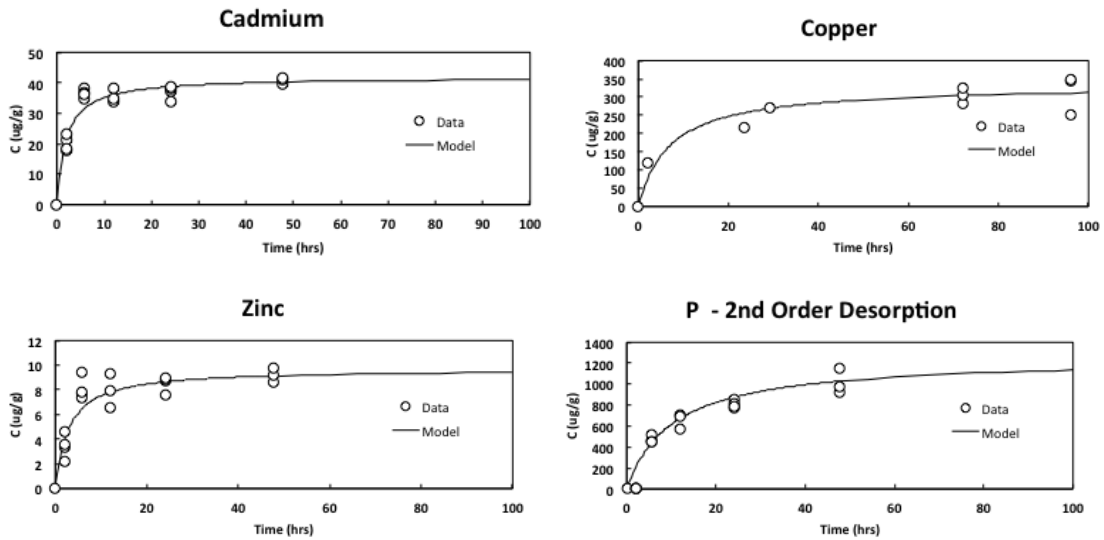


Figure 25. Sorption kinetic plots. The data was fit to second-order Lagergren equation (Ho and McKay, 1999).

A.3 Equilibrium Test Data and Results

The composition of each batch test, including media mass, volume of water, and solution pH, is shown below for the sorption isotherms to MN Compost 1, MN Compost 2, and the sand. The sorption results for each test are included as well.

Table 16. MN Compost 1 batch test parameters

Bottle	MediaMass(g)	WaterMass(g)	Start(hrs)	End(hrs)	Temp(°C)	InitialmV	FinalmV	InitialpH	FinalpH
S00	0.00	229	0.00	72.00	25.00	-15.6	-19.3	7.16	7.22
S11	0.05	232	0.00	72.00	25.00	-14.0	-38.2	7.13	7.56
S12	0.05	229	0.00	72.00	25.00	-14.8	-21.4	7.15	7.26
S13	0.05	230	0.00	72.00	25.00	-15.2	-15.3	7.15	7.15
S21	0.10	232	0.00	72.00	25.00	-11.3	-28.4	7.08	7.38
S22	0.10	231	0.00	72.00	25.00	-10.8	-20.5	7.08	7.25
S23	0.10	231	0.00	72.00	25.00	-9.4	-18.3	7.05	7.21
S31	0.25	231	0.00	72.00	25.00	-12.3	-20.9	7.10	7.25
S32	0.25	230	0.00	72.00	25.00	-21.5	-31.6	7.26	7.44
S33	0.25	231	0.00	72.00	25.00	-20.3	-27.3	7.24	7.36
S41	0.50	231	0.00	72.00	25.00	-20.4	-28.9	7.24	7.39
S42	0.51	231	0.00	72.00	25.00	-21.7	-35.5	7.27	7.51
S43	0.51	231	0.00	72.00	25.00	-10.4	-21.3	7.07	7.26

min 7.05 7.15
 max 7.27 7.56
 avg 7.15 7.34
 stdev 0.081 0.125

Table 17. MN Compost 2 batch test parameters

Bottle	MediaMass(g)	WaterMass(g)	Start(hrs)	End(hrs)	Temp(°C)	InitialmV	FinalmV	InitialpH	FinalpH
T00	0.00	225	0.00	69.00	21.00	-7.9	-32.2	7.08	7.50
T11	0.06	227	0.00	69.00	21.00	-14.3	-32.0	7.19	7.50
T12	0.05	228	0.00	69.00	21.00	-15.7	-50.0	7.22	7.81
T13	0.06	230	0.00	69.00	21.00	-13.1	-38.6	7.17	7.61
T21	0.10	230	0.00	69.00	21.00	-14.6	-50.0	7.20	7.81
T22	0.10	230	0.00	69.00	21.00	-14.1	-59.1	7.19	7.96
T23	0.10	229	0.00	69.00	21.00	-16.1	-38.3	7.22	7.61
T31	0.25	229	0.00	69.00	21.00	-17.4	-64.7	7.25	8.06
T32	0.25	230	0.00	69.00	21.00	-16.1	-76.4	7.22	8.26
T33	0.25	231	0.00	69.00	21.00	-15.0	-60.8	7.21	7.99
T41	0.50	229	0.00	69.00	21.00	-16.9	-59.4	7.24	7.97
T42	0.50	230	0.00	69.00	21.00	-13.4	-40.3	7.18	7.64
T43	0.50	230	0.00	69.00	21.00	-16.3	-60.0	7.23	7.98
T51	1.00	232	0.00	69.00	21.00	-15.4	-55.7	7.21	7.91
T52	1.00	230	0.00	69.00	21.00	-15.4	-53.4	7.21	7.87
T53	1.00	230	0.00	69.00	21.00	-17.8	-61.1	7.25	8.00

min 7.08 7.50
 max 7.25 8.26
 avg 7.20 7.84
 stdev 0.040 0.218

Table 18. Texas Compost batch test parameters.

Bottle	MediaMass(g)	WaterMass(g)	Start(hrs)	End(hrs)	Temp(°C)	InitialmV	FinalmV	InitialpH	FinalpH
V01	0.00	230	0.00	72.00	20.00	-4.1	-57.8	7.02	7.94
V11	0.01	234	0.00	72.00	20.00	-13.4	-27.2	7.18	7.42
V12	0.01	229	0.00	72.00	20.00	-14.3	-26.7	7.19	7.41
V13	0.01	230	0.00	72.00	20.00	-13.4	-23.7	7.18	7.36
V21	0.05	228	0.00	72.00	20.00	-8.5	-61.2	7.09	8.00
V22	0.05	231	0.00	72.00	20.00	-8.9	-37.7	7.10	7.60
V23	0.05	230	0.00	72.00	20.00	-9.1	-25.0	7.10	7.38
V31	0.10	230	0.00	72.00	20.00	-10.1	-60.9	7.12	7.99
V32	0.10	231	0.00	72.00	20.00	-19.2	-38.5	7.28	7.61
V33	0.10	229	0.00	72.00	20.00	-19.4	-39.6	7.28	7.63
V41	0.25	230	0.00	72.00	20.00	-19.2	-46.6	7.28	7.75
V42	0.25	228	0.00	72.00	20.00	-20.5	-55.3	7.30	7.90
V43	0.25	229	0.00	72.00	20.00	-23.0	-75.2	7.34	8.24
V51	0.50	229	0.00	72.00	20.00	-2.0	-35.3	6.98	7.55
V52	0.50	228	0.00	72.00	20.00	2.3	-29.4	6.91	7.45
V53	0.50	228	0.00	72.00	20.00	-7.3	-43.3	7.07	7.69

min 6.91 7.36
 max 7.34 8.24
 avg 7.15 7.68
 stdev 0.124 0.266

Table 19. Sand batch test parameters.

Bottle	MediaMass(g)	WaterMass(g)	Start(hrs)	End(hrs)	Temp(°C)	InitialmV	FinalmV	InitialpH	FinalpH
X00	0.00	233	0.00	72.00	25.00	-12.1	-23.8	7.10	7.30
X11	1.00	229	0.00	72.00	25.00	-9.9	-23.4	7.06	7.30
X12	1.00	230	0.00	72.00	25.00	-10.7	-29.9	7.07	7.41
X13	1.00	229	0.00	72.00	25.00	-11.2	-26.5	7.08	7.35
X21	10.00	232	0.00	72.00	25.00	-10.0	-73.4	7.06	8.17
X22	10.00	230	0.00	72.00	25.00	-11.2	-53.8	7.08	7.83
X23	10.00	230	0.00	72.00	25.00	-11.9	-50.3	7.09	7.77
X31	2.00	229	0.00	72.00	25.00	-12.5	-34.2	7.11	7.49
X32	2.00	231	0.00	72.00	25.00	-19.4	-45.0	7.23	7.67
X33	2.00	229	0.00	72.00	25.00	-22.4	-39.0	7.28	7.57
X41	30.00	230	0.00	72.00	25.00	-22.8	-53.6	7.29	7.82
X42	30.00	229	0.00	72.00	25.00	-22.3	-82.9	7.28	8.34
X43	30.00	229	0.00	72.00	25.00	-12.9	-84.6	7.11	8.37

min 7.06 7.30
 max 7.29 8.37
 avg 7.14 7.72
 stdev 0.089 0.376

Table 20. MN Compost 1 sorption data.

Name Bottle	Cadmium				Copper				Zinc				Phosphorus			
	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed (mg)	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass deSorbed	Sorbed/Sorbent
S00	0.486	0.111		-	0.527	0.121			0.494	0.113			0.059	0.014	0.000	
S11	0.155	0.036	0.075	1.477	0.158	0.037	0.084	1.6476	0.190	0.044	0.069	1.3538	0.145	0.034	0.034	0.660
S12	0.119	0.027	0.084	1.648	0.120	0.027	0.093	1.8275	0.161	0.037	0.076	1.4952	0.163	0.037	0.037	0.732
S13	0.099	0.023	0.089	1.770	0.108	0.025	0.096	1.9169	0.137	0.032	0.082	1.6323	0.126	0.029	0.029	0.580
S21	0.099	0.023	0.088	0.875	0.137	0.032	0.089	0.8802	0.133	0.031	0.082	0.8146	0.185	0.043	0.043	0.425
S22	0.049	0.011	0.100	1.000	0.095	0.022	0.099	0.9874	0.075	0.017	0.096	0.9580	0.206	0.048	0.048	0.476
S23	0.048	0.011	0.100	0.992	0.085	0.020	0.101	1.0005	0.074	0.017	0.096	0.9508	0.262	0.061	0.061	0.599
S31	0.045	0.010	0.101	0.404	0.119	0.027	0.093	0.373	0.067	0.015	0.098	0.391	0.376	0.087	0.087	0.347
S32	0.047	0.011	0.100	0.399	0.125	0.029	0.092	0.365	0.066	0.015	0.098	0.389	0.352	0.081	0.081	0.321
S33	0.028	0.006	0.105	0.418	0.105	0.024	0.096	0.384	0.054	0.012	0.101	0.401	0.362	0.084	0.084	0.333
S41	0.035	0.008	0.103	0.206	0.120	0.028	0.093	0.186	0.053	0.012	0.101	0.201	0.513	0.119	0.119	0.237
S42	0.015	0.003	0.108	0.214	0.086	0.020	0.101	0.200	0.025	0.006	0.107	0.213	0.583	0.135	0.135	0.267
S43	0.014	0.003	0.108	0.214	0.078	0.018	0.103	0.203	0.032	0.007	0.106	0.209	0.608	0.140	0.140	0.278

Table 21. MN Compost 2 sorption data.

Name Bottle	Cadmium				Copper				Zinc				Phosphorus			
	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed (mg)	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass deSorbed	Sorbed/Sorbent
T00	0.469	0.106		-	0.487	0.110			0.486	0.109			0.346	0.078	0.000	
T11	0.162	0.037	0.069	1.228	0.212	0.048	0.061	1.0973	0.184	0.042	0.068	1.2068	0.304	0.069	0.069	1.232
T12	0.054	0.012	0.093	1.759	0.109	0.025	0.085	1.5985	0.074	0.017	0.092	1.7449	0.239	0.054	0.054	1.028
T13	0.081	0.019	0.087	1.552	0.148	0.034	0.076	1.3488	0.117	0.027	0.082	1.4721	0.241	0.055	0.055	0.990
T21	0.048	0.011	0.094	0.945	0.137	0.032	0.078	0.7807	0.066	0.015	0.094	0.9417	0.350	0.081	0.081	0.805
T22	0.030	0.007	0.099	0.986	0.107	0.025	0.085	0.8497	0.046	0.011	0.099	0.9877	0.374	0.086	0.086	0.860
T23	0.030	0.007	0.099	0.987	0.108	0.025	0.085	0.8484	0.048	0.011	0.098	0.9836	0.336	0.077	0.077	0.769
T31	0.013	0.003	0.103	0.410	0.074	0.017	0.093	0.371	0.024	0.005	0.104	0.415	0.614	0.141	0.141	0.562
T32	0.032	0.007	0.098	0.391	0.150	0.035	0.075	0.299	0.051	0.012	0.098	0.389	0.595	0.137	0.137	0.545
T33	0.018	0.004	0.101	0.405	0.062	0.014	0.095	0.381	0.035	0.008	0.101	0.405	0.660	0.152	0.152	0.610
T41	0.018	0.004	0.101	0.203	0.092	0.021	0.089	0.177	0.029	0.007	0.103	0.205	0.932	0.213	0.213	0.427
T42	0.016	0.004	0.102	0.204	0.087	0.020	0.090	0.179	0.030	0.007	0.102	0.205	1.040	0.239	0.239	0.478
T43	0.021	0.005	0.101	0.201	0.101	0.023	0.086	0.173	0.034	0.008	0.102	0.203	0.882	0.203	0.203	0.406
T51	0.018	0.004	0.101	0.101	0.080	0.019	0.091	0.091	0.042	0.010	0.100	0.100	1.368	0.317	0.317	0.317
T52	0.026	0.006	0.100	0.099	0.108	0.025	0.085	0.085	0.048	0.011	0.098	0.098	1.408	0.324	0.324	0.324
T53	0.018	0.004	0.101	0.101	0.090	0.021	0.089	0.089	0.038	0.009	0.101	0.100	1.394	0.321	0.321	0.320

Table 22. Texas Compost sorption data.

Name	Media:Mass(g)	Cadmium				Copper				Zinc				Phosphorus			
		Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed (mg)	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass deSorbed	Sorbed/Sorbent
V00	0.00	0.492	0.113		-	0.523	0.120			0.508	0.117				0.000	0.000	
V11	0.01	0.306	0.072	0.042	3.778	0.325	0.076	0.044	4.0218	0.341	0.080	0.037	3.3678	0.166	0.039	0.039	3.531
V12	0.01	0.310	0.071	0.042	4.217	0.318	0.073	0.047	4.7468	0.350	0.080	0.037	3.6690	0.108	0.025	0.025	2.473
V13	0.01	0.332	0.076	0.037	3.680	0.341	0.078	0.042	4.1860	0.362	0.083	0.034	3.3580	0.120	0.028	0.028	2.760
V21	0.05	0.075	0.017	0.096	1.884	0.148	0.034	0.087	1.6970	0.096	0.022	0.095	1.8618	0.210	0.048	0.048	0.939
V22	0.05	0.084	0.019	0.094	1.875	0.160	0.037	0.083	1.6666	0.117	0.027	0.090	1.7963	0.242	0.056	0.056	1.118
V23	0.05	0.153	0.035	0.078	1.559	0.227	0.052	0.068	1.3616	0.185	0.043	0.074	1.4858	0.222	0.051	0.051	1.021
V31	0.10	0.040	0.009	0.104	1.019	0.145	0.033	0.087	0.852	0.050	0.012	0.105	1.033	0.404	0.093	0.093	0.911
V32	0.10	0.140	0.032	0.081	0.792	0.252	0.058	0.062	0.609	0.175	0.040	0.076	0.749	0.351	0.081	0.081	0.795
V33	0.10	0.036	0.008	0.105	1.029	0.130	0.030	0.091	0.887	0.041	0.009	0.107	1.053	0.417	0.095	0.095	0.936
V41	0.25	0.097	0.022	0.091	0.362	0.239	0.055	0.065	0.260	0.117	0.027	0.090	0.358	0.610	0.140	0.140	0.559
V42	0.25	0.100	0.023	0.090	0.360	0.246	0.056	0.064	0.256	0.116	0.026	0.090	0.360	0.573	0.131	0.131	0.520
V43	0.25	0.104	0.024	0.089	0.356	0.244	0.056	0.064	0.257	0.120	0.027	0.089	0.356	0.552	0.126	0.126	0.504
V51	0.50	0.054	0.012	0.101	0.201	0.190	0.044	0.077	0.153	0.069	0.016	0.101	0.201	1.119	0.256	0.256	0.510
V52	0.50	0.063	0.014	0.099	0.198	0.203	0.046	0.074	0.148	0.076	0.017	0.100	0.199	1.009	0.230	0.230	0.460
V53	0.50	0.039	0.009	0.104	0.209	0.177	0.040	0.080	0.160	0.047	0.011	0.106	0.212	1.119	0.255	0.255	0.510

Table 23. Sand sorption data.

Name	Cadmium				Copper				Zinc				Phosphorus				
	Bottle	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed (mg)	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass Sorbed	Sorbed/Sorbent	Ceq (mg/L)	Cont. Mass (mg)	Mass deSorbed	Sorbed/Sorbent
X00		0.468	0.109		-	0.513	0.120			0.528	0.123				0.000	0.000	
X11		0.296	0.068	0.041	0.0413	0.257	0.059	0.061	0.0607	0.325	0.074	0.049	0.0486	< 0.054			
X12		0.288	0.066	0.043	0.0428	0.277	0.064	0.056	0.0558	0.283	0.065	0.058	0.0579	< 0.054			
X13		0.291	0.067	0.042	0.0424	0.235	0.054	0.066	0.0657	0.265	0.061	0.062	0.0623	< 0.054			
X21		0.153	0.035	0.074	0.0074	0.124	0.029	0.091	0.0091	0.130	0.030	0.093	0.0093	< 0.054			
X22		0.197	0.045	0.064	0.0064	0.156	0.036	0.084	0.0084	0.187	0.043	0.080	0.0080	< 0.054			
X23		0.143	0.033	0.076	0.0076	0.116	0.027	0.093	0.0093	0.134	0.031	0.092	0.0092	< 0.054			
X31		0.195	0.045	0.064	0.032	0.142	0.033	0.087	0.044	0.176	0.040	0.083	0.041	< 0.054			
X32		0.229	0.053	0.056	0.028	0.168	0.039	0.081	0.040	0.200	0.046	0.077	0.038	< 0.054			
X33		0.244	0.056	0.053	0.027	0.178	0.041	0.079	0.039	0.224	0.051	0.072	0.036	< 0.054			
X41		0.036	0.008	0.101	0.003	0.037	0.009	0.111	0.004	0.034	0.008	0.115	0.004	< 0.054			
X42		0.134	0.031	0.078	0.003	0.096	0.022	0.098	0.003	0.089	0.020	0.103	0.003	< 0.054			
X43		0.105	0.024	0.085	0.003	0.079	0.018	0.101	0.003	0.072	0.016	0.107	0.004	< 0.054			

A.4 Batch Test Plots

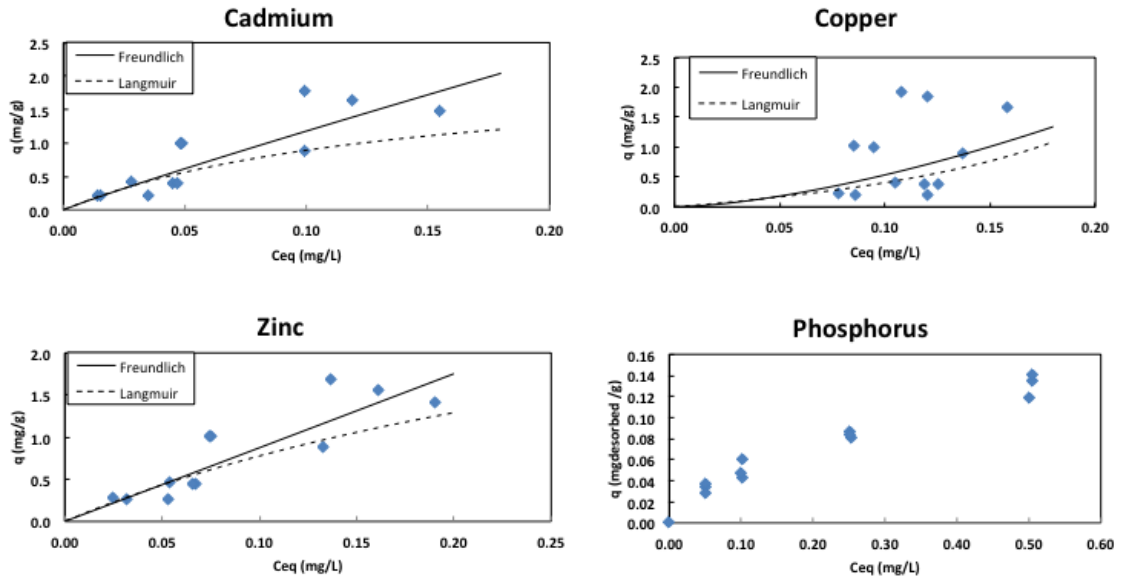


Figure 26. MN Compost 1 metal sorption isotherm plots and phosphorus desorption plot.

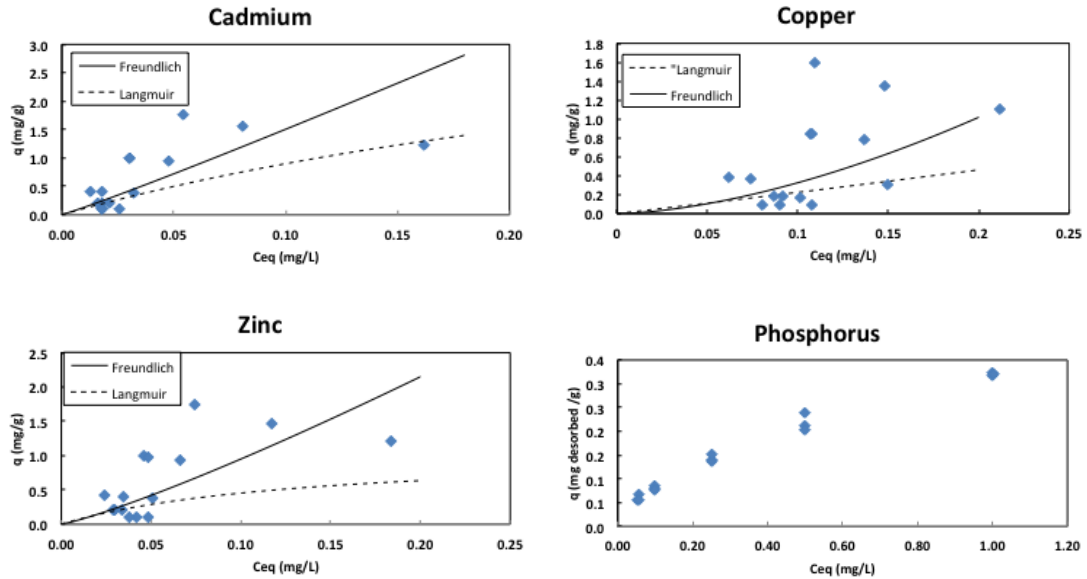


Figure 27. MN Compost 2 metal sorption isotherm plots and phosphorus desorption plot.

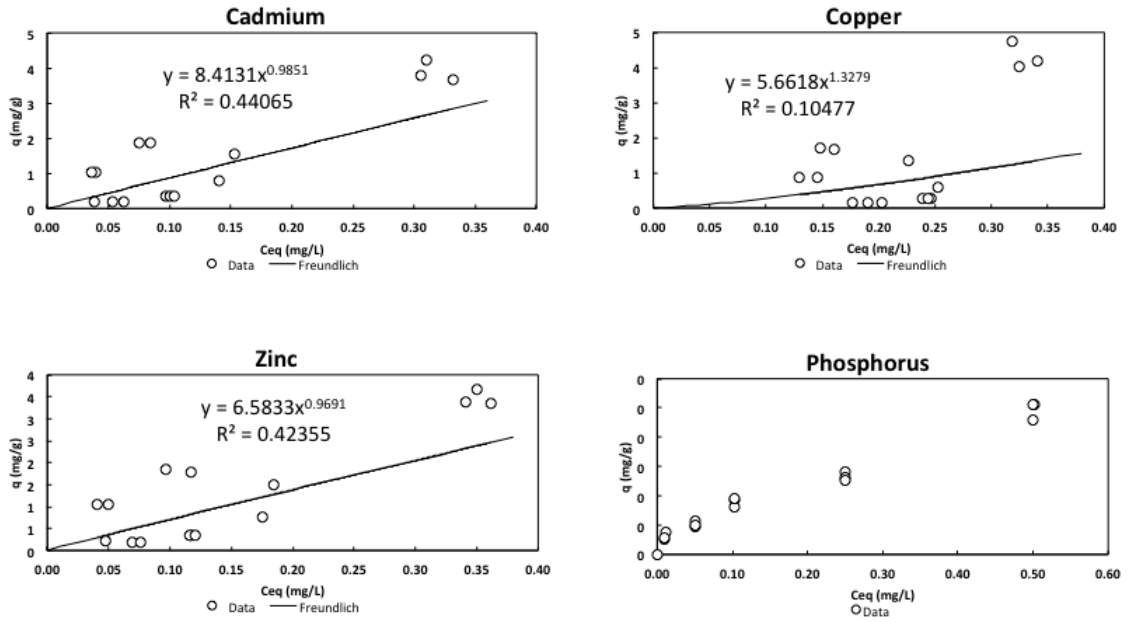


Figure 28. Texas metal sorption isotherm plots and phosphorus desorption plot.

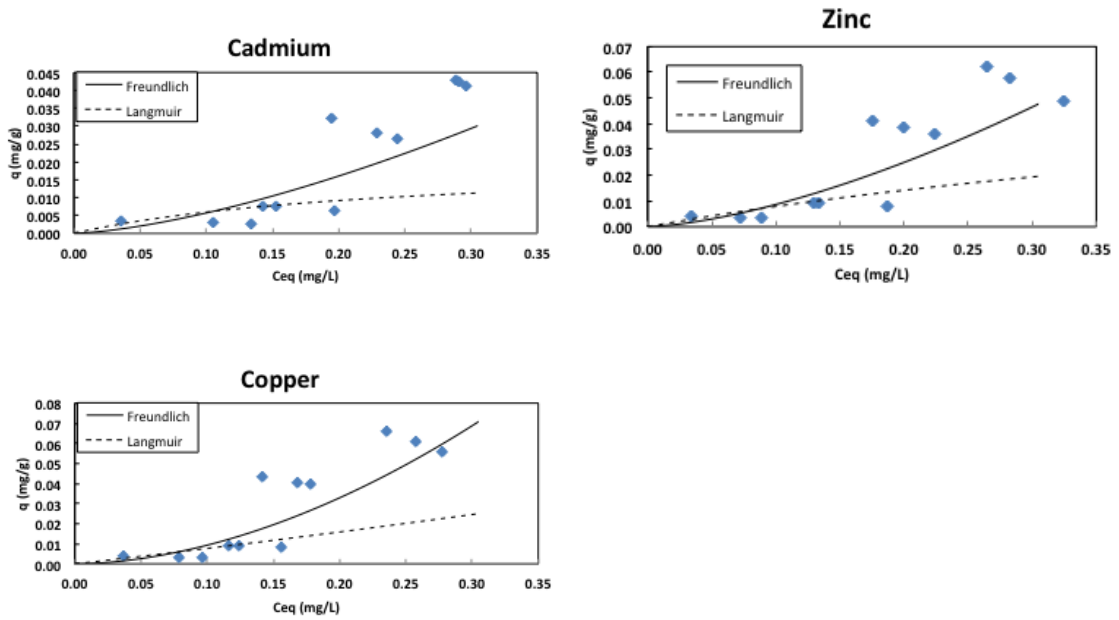


Figure 29. C-33 construction sand metal sorption isotherm plots.

Appendix B: Column Study Results

The results from the column studies are shown below for cadmium, copper, and zinc. The cadmium and zinc data also include the Thomas Model fit to the data. The results from the salt tracer and desorption study are shown after the breakthrough data. Lastly, the complete set of raw data collected from the columns studies will be appended at the end of the document.

B.1 Column Study Photos



Figure 30. Clockwise from top left: 10 columns attached to support structure, Column experiment setup including influent reservoirs and pumps, Close-up of water flowing up through individual columns, Close-up of sampling procedure.

B.2 Column Study Figures

B.2.1 Cadmium Figures

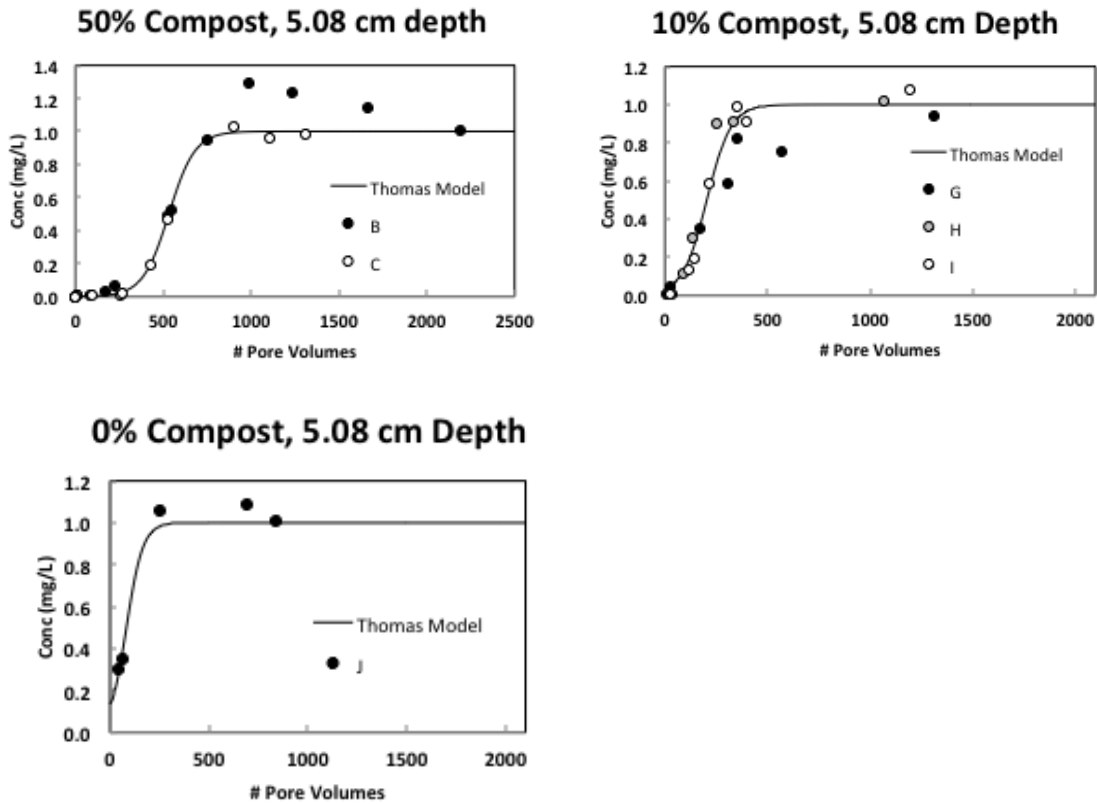
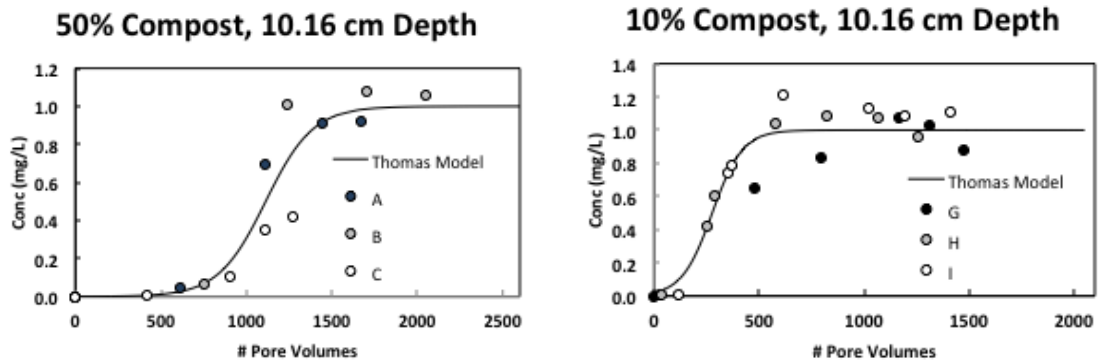


Figure 31. Cadmium data and Thomas Model fit for 5.08 cm of bioretention media.



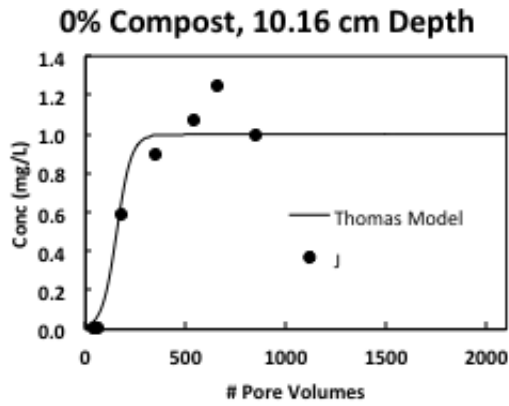


Figure 32. Cadmium data and Thomas Model fit for 10.16 cm of bioretention media.

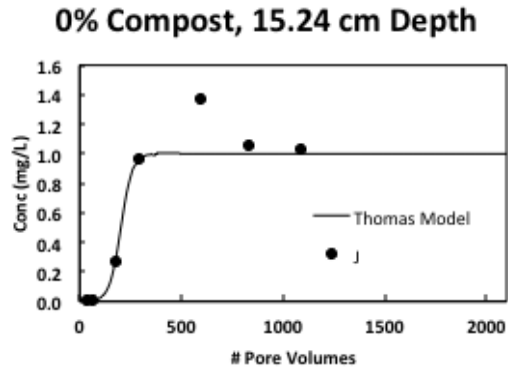
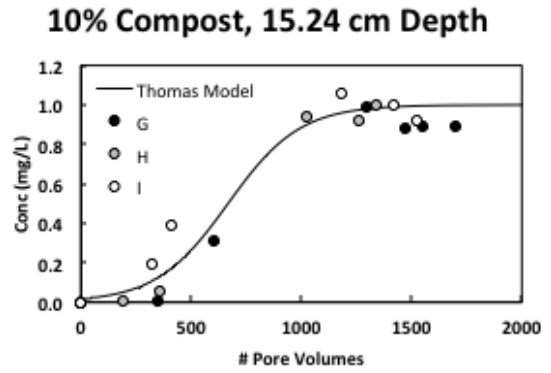
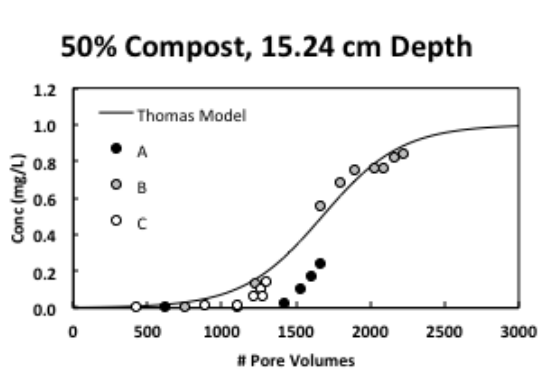
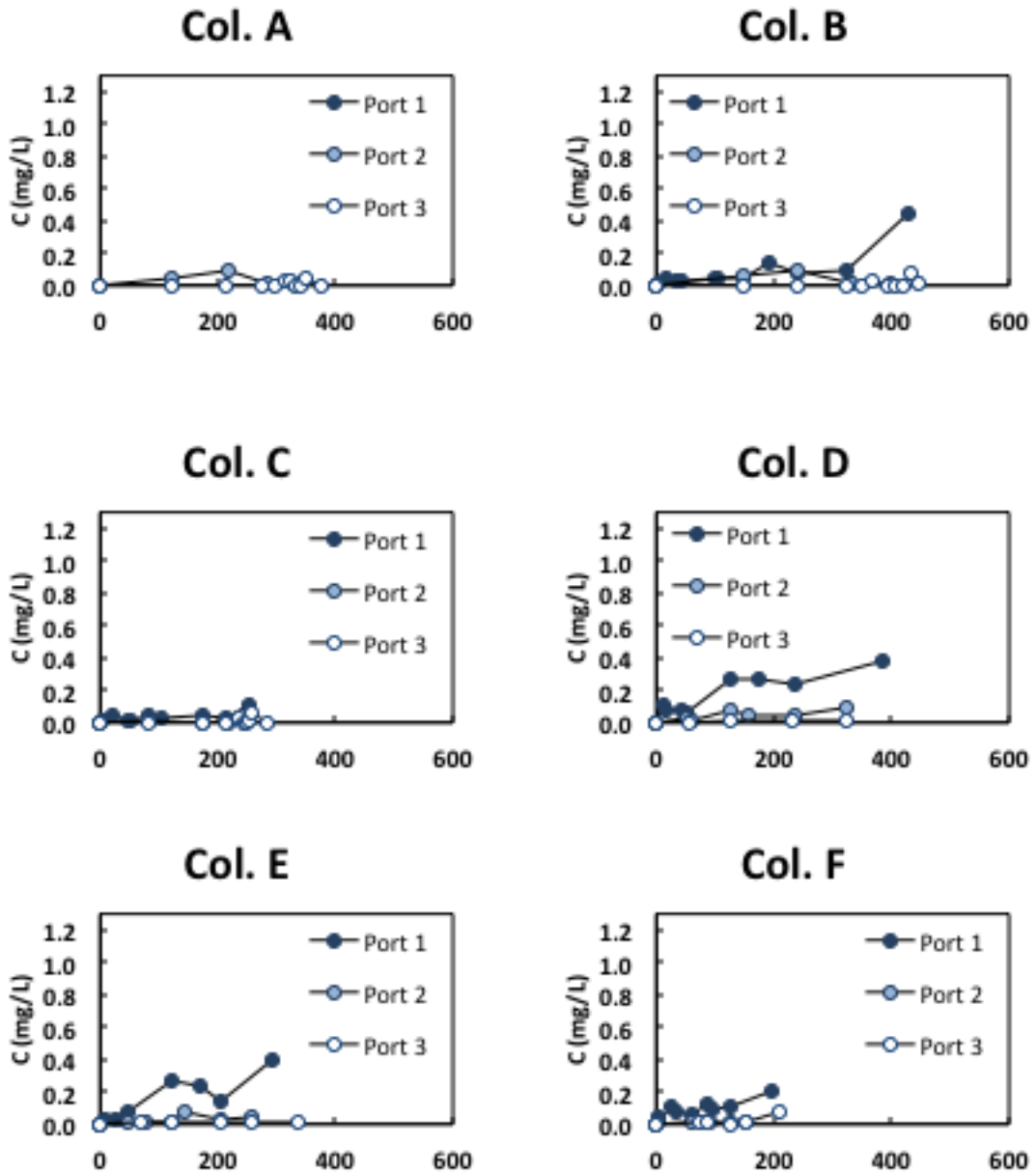


Figure 33. Cadmium data and Thomas Model fit for 15.24 cm of bioretention media.

B.2.2 Copper Figures



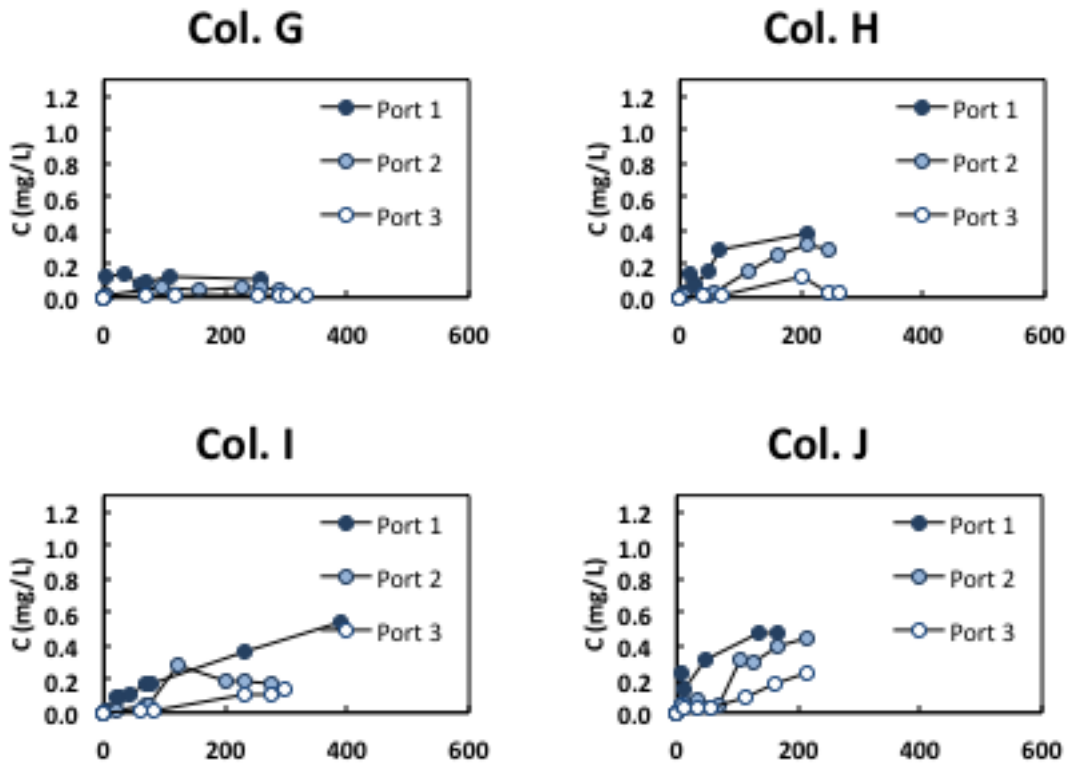
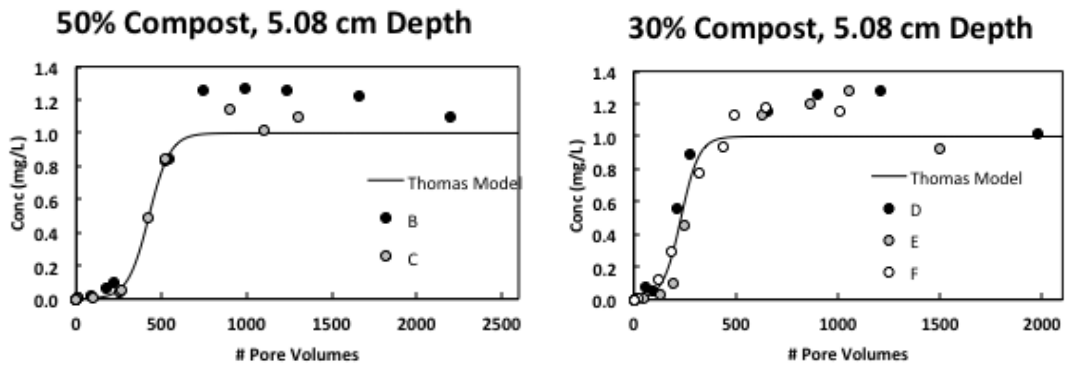


Figure 34. Dissolved Copper removal data from 0, 10, 30, and 50% compost columns. Columns A-C had 50% compost, Columns D-F had 30% compost, columns G-I had 10% compost, and column J had no compost added to the sand.

B.2.3 Zinc Figures



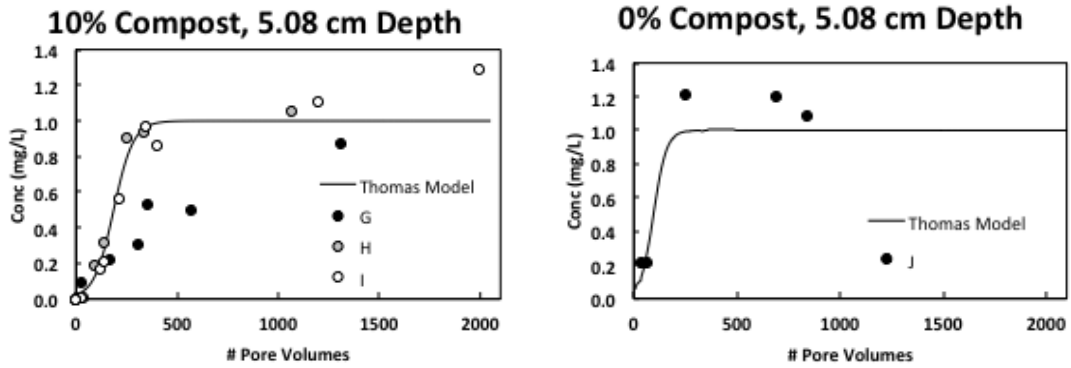


Figure 35. Zinc removal data and Thomas Model fits for 5.08 cm of bioretention media.

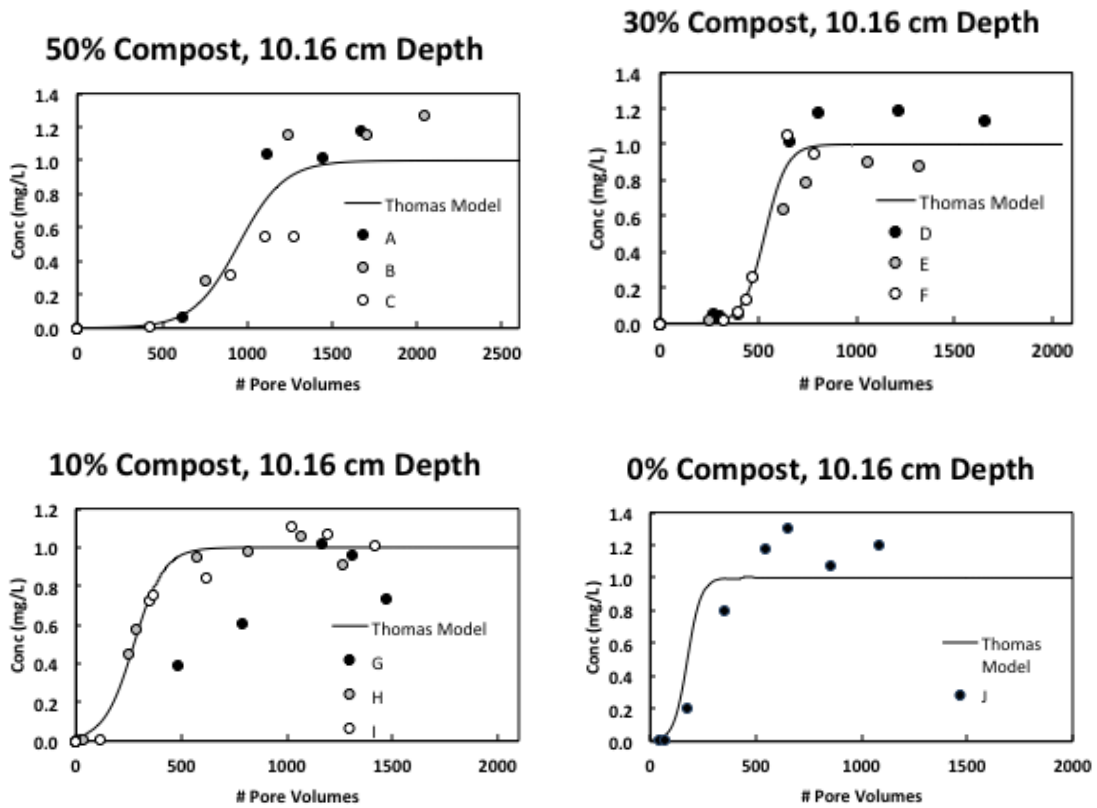


Figure 36. Zinc breakthrough data and Thomas Model fits for 10.16 cm of bioretention media.

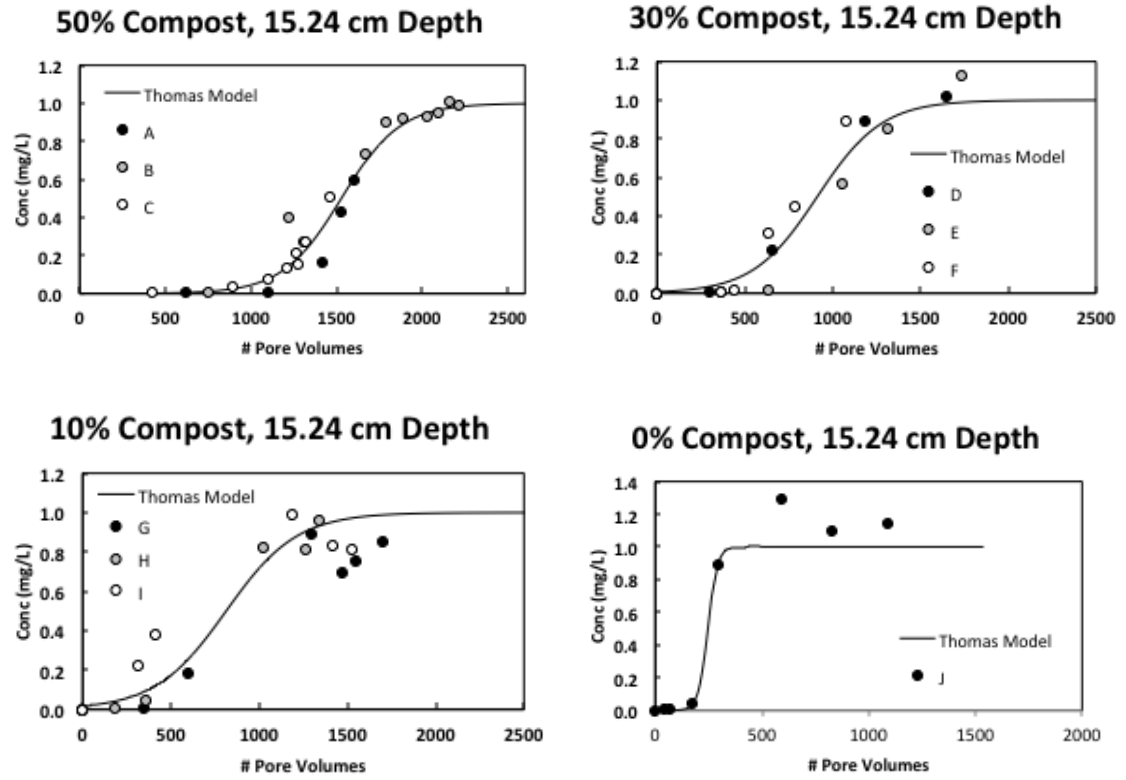


Figure 37. Zinc breakthrough data and Thomas Model fits for 15.24 cm of bioretention media.

B.3 Salt Tracer and Desorption Data

Table 24. Salt tracer and desorption data for Column A (50% compost).

Area = 20.27 cm²
 Length = 22.86 cm
 Dx = 0.24 cm²/min
 n = 0.75083
 Q = 7.26 mL/min

Time	Time Step	Sample	d V	Recorded Vol Vol (mL)	Corr. Vol (mL)	Cond	Conc (g/L)	Model Conc. (g/L)	Least Square
12:44 PM	0.00			100	100	0.26	0.01	0.00	0.00
12:51 PM	0.12			150	150	0.29	0.02	0.00	0.00
12:55 PM	0.18			180	180	0.27	0.01	0.00	0.00
12:59 PM	0.25			200	200	0.28	0.02	0.00	0.00
1:06 PM	0.37			250	250	0.51	0.13	0.06	0.01
1:10 PM	0.43	A02	11	280	280	0.82	0.28	0.15	0.02
1:13 PM	0.48	A03	11	290	301	1.06	0.39	0.24	0.02
1:16 PM	0.53	A04	11	300	322	1.22	0.47	0.36	0.01
1:19 PM	0.58	A05	11	310	343	1.44	0.57	0.47	0.01
1:22 PM	0.63	A06	11	320	364	1.6	0.65	0.59	0.00
1:26 PM	0.70			330	385	1.7	0.69	0.69	0.00
1:29 PM	0.75	A07	11	340	395	1.79	0.74	0.73	0.00
1:32 PM	0.80			350	416	1.89	0.78	0.80	0.00
1:35 PM	0.85			360	426	1.95	0.81	0.83	0.00
1:38 PM	0.90	A08	11	370	436	2.01	0.84	0.86	0.00
1:41 PM	0.95			380	457	2.07	0.87	0.90	0.00
1:45 PM	1.02			390	467	2.11	0.89	0.92	0.00
1:48 PM	1.07	A09	11	400	477	2.15	0.91	0.93	0.00
1:52 PM	1.13	A10	11	425	513	2.15	0.91	0.97	0.00
1:58 PM	1.23	A11	11	450	549	2.2	0.93	0.99	0.00
2:08 PM	1.40	A12	11	505	615	2.25	0.95	1.00	0.00
2:24 PM	1.67	A13	11	605	726	2.28	0.97	1.00	0.00
Sum =									0.08

Cd Cu Zn
 A00 0.806 0.007 1.311

A02 2.486 0.005 3.066

A08 5.828 0.008 5.326

Table 25. Salt tracer and desorption data for Column C (50% compost).

Area = 20.27 cm²
 Length = 22.86 cm
 Dx = 0.21255 cm²/min
 n = 0.77533
 Q = 6.56 mL/min

Time	Time Step	Sample	d V	Recorded Vol Vol (mL)	Corr. Vol (mL)	Cond	Conc (g/L)	Model Conc. (g/L)	Least Square
12:47 PM	0.00			100	100	0.28	0.02	0.00	0.00
12:58 PM	0.18			150	150	0.27	0.01	0.00	0.00
1:07 PM	0.33			200	200	0.33	0.04	0.00	0.00
1:17 PM	0.50	C02	11	250	250	0.54	0.14	0.04	0.01
1:25 PM	0.63	C03	11	280	291	0.92	0.32	0.16	0.03
1:27 PM	0.67	C04	11	290	312	1.08	0.40	0.25	0.02
1:30 PM	0.72	C05	11	300	333	1.4	0.55	0.36	0.04
1:33 PM	0.77			310	354	1.55	0.62	0.47	0.02
1:36 PM	0.82			320	364	1.67	0.68	0.52	0.02
1:39 PM	0.87	C06	11	330	374	1.82	0.75	0.58	0.03
1:42 PM	0.92			340	395	1.93	0.80	0.67	0.02
1:45 PM	0.97			350	405	2	0.84	0.72	0.01
1:48 PM	1.02	C07	11	360	415	2.07	0.87	0.75	0.01
1:53 PM	1.10	C08	11	380	446	2.14	0.90	0.85	0.00
1:56 PM	1.15	C09	11	390	467	2.18	0.92	0.89	0.00
2:00 PM	1.22	C10	11	400	488	2.21	0.94	0.93	0.00
2:09 PM	1.37	C11	11	450	549	2.26	0.96	0.98	0.00
2:20 PM	1.55	C12	11	500	610	2.3	0.98	0.99	0.00

Effluent Conc (mg/L)

Cd Cu Zn
 C00 0.400 0.007 0.761
 C01 0.299 0.004 0.590

C05 2.250 0.005 2.963

C09 2.672 0.006 2.932

C12 2.363 0.008 2.470

Table 26. Salt tracer and desorption data for Column E (30% Compost).

Area = 20.27 cm²
 Length = 22.86 cm
 Dx = 0.16828 cm²/min
 n = 0.75083
 Q = 8.02 mL/min

Time	Time Step	Sample	d V	Recorded Vol Vol (mL)	Corr. Vol (mL)	Conc (g/L)	Conc (g/L)	Model		Effluent Conc (mg/L)				
								Conc. (g/L)	Least Square	Cd	Cu	Zn		
1:13 PM	0.00			105	105	0.36	0.06	0.00	0.00					
1:19 PM	0.10			150	150	0.4	0.08	0.00	0.01					
1:22 PM	0.15	E04		175	175	0.39	0.07	0.00	0.01					
1:27 PM	0.23			200	200	0.37	0.06	0.00	0.00					
1:32 PM	0.32	E05	11	250	250	0.36	0.06	0.02	0.00					
1:35 PM	0.37	E06	11	280	291	0.42	0.09	0.14	0.00	E06	1.594	0.016	1.845	
1:38 PM	0.42	E07	11	290	312	0.7	0.22	0.26	0.00					
1:42 PM	0.48	E08	11	300	333	1.1	0.41	0.40	0.00					
1:45 PM	0.53	E09	11	310	354	1.41	0.56	0.54	0.00					
1:49 PM	0.60	E10	11	320	375	1.71	0.70	0.67	0.00					
1:52 PM	0.65	E11	11	330	396	1.94	0.81	0.78	0.00	E11	11.020	0.018	8.127	
1:55 PM	0.70	E12	11	340	417	2.07	0.87	0.86	0.00					
1:58 PM	0.75	E13	11	350	438	2.17	0.92	0.92	0.00					
2:02 PM	0.82	E14	11	360	459	2.32	0.99	0.95	0.00					
2:05 PM	0.87	E15	11	370	480	2.27	0.96	0.97	0.00	E15	8.923	0.025	6.276	
2:08 PM	0.92	E16	11	380	501	2.29	0.97	0.99	0.00					
2:11 PM	0.97	E17	11	390	522	2.29	0.97	0.99	0.00					
2:18 PM	1.08	E18	11	425	568	2.31	0.98	1.00	0.00	E18	7.007	0.022	4.945	
2:30 PM	1.28	E19	11	500	654	2.33	0.99	1.00	0.00					
2:46 PM	1.55	E20	11	600	765	2.34	1.00	1.00	0.00					
3:04 PM	1.85	E21	11	720	896	2.34	1.00	1.00	0.00					
3:16 PM	2.05	E22	11	800	987	2.35	1.00	1.00	0.00	E22	3.744	0.023	2.658	

Table 27. Salt tracer and desorption data for Column F (30% compost).

Area = 20.27 cm²
 Length = 22.86 cm
 Dx = 0.21255 cm²/min
 n = 0.77533
 Q = 10.50 mL/min

Time	Time Step	Sample	d V	Recorded Vol Vol (mL)	Corr. Vol (mL)	Conc (g/L)	Conc (g/L)	Model		Effluent Conc (mg/L)				
								Conc. (g/L)	Least Square	Cd	Cu	Zn		
1:23 PM	0.00			100	100	0.32	0.04	0.00	0.00					
1:30 PM	0.12			150	150	0.36	0.06	0.00	0.00					
1:35 PM	0.20			200	200	0.32	0.04	0.00	0.00					
1:40 PM	0.28			250	250	0.44	0.10	0.01	0.01	F03	0.867	0.008	1.192	
1:43 PM	0.33	F04	11	280	280	0.36	0.06	0.07	0.00					
1:46 PM	0.38	F05	11	300	311	0.48	0.11	0.19	0.01					
1:48 PM	0.42	F06	11	310	332	0.82	0.28	0.32	0.00	F06	3.293	0.007	3.221	
1:50 PM	0.45	F07	11	320	353	1.26	0.48	0.46	0.00					
1:53 PM	0.50	F08	11	330	374	1.59	0.64	0.60	0.00					
1:56 PM	0.55	F09	11	350	405	1.91	0.79	0.76	0.00					
1:58 PM	0.58	F10	11	360	426	2.06	0.86	0.85	0.00					
2:01 PM	0.63	F11	11	370	447	2.15	0.91	0.91	0.00					
2:03 PM	0.67	F12	11	380	468	2.22	0.94	0.94	0.00	F12	7.903	0.011	5.769	
2:05 PM	0.70	F13	11	390	489	2.28	0.97	0.97	0.00					
2:07 PM	0.73	F14	11	400	510	2.28	0.97	0.98	0.00					
2:11 PM	0.80	F15	11	420	541	2.29	0.97	0.99	0.00					
2:15 PM	0.87	F16	11	450	582	2.3	0.98	1.00	0.00					
2:21 PM	0.97	F17	11	500	643	2.31	0.98	1.00	0.00					
2:34 PM	1.18	F18	11	620	774	2.34	1.00	1.00	0.00	F18	3.796	0.014	2.819	
2:43 PM	1.33	F19	11	700	865	2.37	1.01	1.00	0.00					
3:03 PM	1.67	F20	11	880	1056	2.34	1.00	1.00	0.00					
3:16 PM	1.88	F21	11	1000	1187	2.35	1.00	1.00	0.00	F21	2.552	0.015	1.909	

Table 28. Salt tracer and desorption data for Column H (10% compost).

Area = 20.27 cm²
 Length = 22.86 cm
 Dx = 0.20914 cm²/min
 n = 0.70896
 Q = 8.31 mL/min

Time	Time Step	Sample	d V	Recorded Vol Vol (mL)	Corr. Vol (mL)	Cond	Conc (g/L)	Model		Effluent Conc (mg/L)			
								Conc. (g/L)	Least Square	Cd	Cu	Zn	
2:08 PM	0.00			105	105	0.38	0.07	0.00	0.00				
2:14 PM	0.10			150	150	0.25	0.01	0.00	0.00	H00	1.1	0.3	1.3
2:17 PM	0.15			175	175	0.31	0.03	0.00	0.00	H03	1.0	0.3	1.2
2:21 PM	0.22			200	200	0.33	0.04	0.00	0.00				
2:23 PM	0.25			220	220	0.28	0.02	0.01	0.00				
2:29 PM	0.35			250	250	0.31	0.03	0.06	0.00				
2:34 PM	0.43	H04	11	280	280	0.61	0.18	0.18	0.00				
2:37 PM	0.48	H05	11	290	301	0.72	0.23	0.31	0.01				
2:41 PM	0.55	H06	11	300	322	1.2	0.46	0.46	0.00	H06	6.2	0.5	5.3
2:44 PM	0.60	H07	11	310	343	1.59	0.64	0.60	0.00				
2:47 PM	0.65	H08	11	320	364	1.87	0.77	0.72	0.00				
2:50 PM	0.70	H09	11	330	385	2.04	0.85	0.81	0.00	H09	9.4	0.6	6.7
2:53 PM	0.75	H10	11	340	406	2.12	0.89	0.88	0.00				
2:56 PM	0.80	H11	11	350	427	2.17	0.92	0.93	0.00				
2:59 PM	0.85	H12	11	360	448	2.2	0.93	0.96	0.00				
3:02 PM	0.90	H13	11	370	469	2.22	0.94	0.98	0.00				
3:05 PM	0.95	H14	11	380	490	2.24	0.95	0.99	0.00				
3:09 PM	1.02	H15	11	400	521	2.25	0.95	1.00	0.00				
3:13 PM	1.08	H16	11	420	552	2.28	0.97	1.00	0.00	H16	5.1	0.5	3.6
3:17 PM	1.15	H17	11	440	583	2.26	0.96	1.00	0.00				
3:24 PM	1.27	H18	11	480	634	2.27	0.96	1.00	0.00				
3:38 PM	1.50	H19	11	580	745	2.28	0.97	1.00	0.00				
3:51 PM	1.72	H20	11	680	856	2.26	0.96	1.00	0.00	H20	3.2	0.4	2.3

Table 29. Salt tracer and desorption data for Column I (10% compost).

Area = 20.27 cm²
 Length = 22.86 cm
 Dx = 0.21863 cm²/min
 n = 0.71863
 Q = 7.50 mL/min

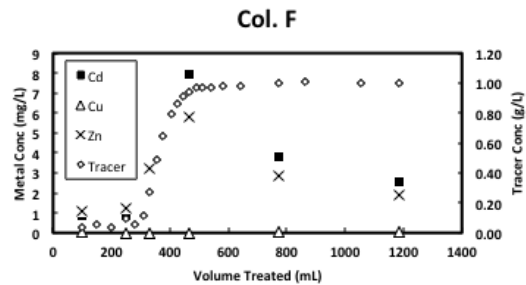
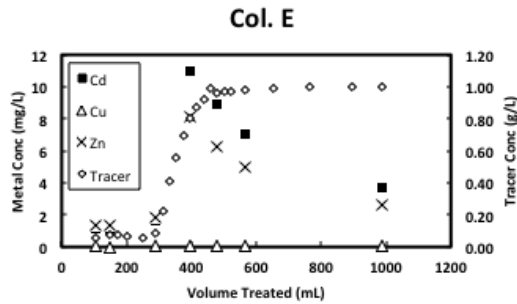
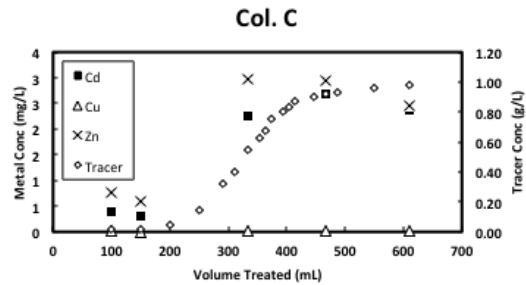
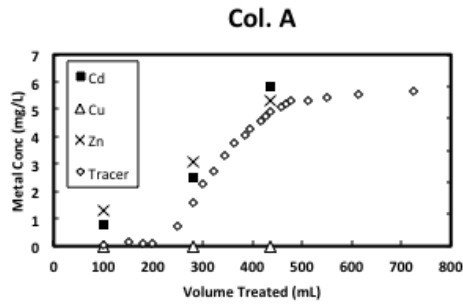
Time	Time Step	Sample	d V	Recorded Vol Vol (mL)	Corr. Vol (mL)	Cond	Conc (g/L)	Model		Effluent Conc (mg/L)			
								Conc. (g/L)	Least Square	Cd	Cu	Zn	
2:09 PM	0.00			100	100	0.31	0.03	0.00	0.00				
2:20 PM	0.18			150	150	0.25	0.01	0.00	0.00	I00	1.1	0.3	1.3
2:24 PM	0.25			175	175	0.31	0.03	0.00	0.00	I03	1.0	0.2	1.2
2:29 PM	0.33			200	200	0.32	0.04	0.00	0.00				
2:39 PM	0.50	I04	11	250	250	0.36	0.06	0.07	0.00				
2:45 PM	0.60	I05	11	280	291	0.59	0.17	0.24	0.01				
2:49 PM	0.67	I06	11	290	312	0.92	0.32	0.37	0.00				
2:50 PM	0.68	I07	11	300	333	1.32	0.51	0.50	0.00	I07	7.2	0.4	5.6
2:55 PM	0.77	I08	11	310	354	1.66	0.67	0.62	0.00				
2:59 PM	0.83	I09	11	320	375	1.92	0.80	0.73	0.00				
3:02 PM	0.88	I10	11	330	396	2.07	0.87	0.82	0.00				
3:05 PM	0.93	I11	11	340	417	2.15	0.91	0.88	0.00				
3:07 PM	0.97	I12	11	350	438	2.2	0.93	0.92	0.00				
3:10 PM	1.02	I13	11	360	459	2.22	0.94	0.95	0.00				
3:13 PM	1.07	I14	11	370	480	2.23	0.94	0.97	0.00				
3:16 PM	1.12	I15	11	380	501	2.25	0.95	0.98	0.00	I15	5.7	0.4	3.8
3:20 PM	1.18	I16	11	400	532	2.25	0.95	0.99	0.00				
3:25 PM	1.27	I17	11	420	563	2.28	0.97	1.00	0.00				
3:29 PM	1.33	I18	11	440	594	2.27	0.96	1.00	0.00				
3:36 PM	1.45	I19	11	480	645	2.3	0.98	1.00	0.00				
3:46 PM	1.62	I20	11	550	726	2.26	0.96	1.00	0.00				
4:00 PM	1.85	I21	11	645	832	2.26	0.96	1.00	0.00	I21	3.4	0.3	2.3

Table 30. Salt Tracer and desorption data for Column J (0% compost).

Area = 20.27 cm²
 Length = 22.86 cm
 Dx = 0.21863 cm²/min
 n = 0.79
 Q = 6.2314 mL/min

Time	Time Step	Sample	d V	Recorded Vol Vol (mL)	Corr. Vol (mL)	Conc	Conc (g/L)	Model Conc. (g/L)	Least Square
12:56 PM	0.00			100	100	0.25	0.01	0.00	0.00
1:01 PM	0.08			120	120	0.31	0.03	0.00	0.00
1:06 PM	0.17			140	140	0.37	0.06	0.00	0.00
1:09 PM	0.22	J04	11	160	160	0.39	0.07	0.00	0.01
1:15 PM	0.32			180	191	0.36	0.06	0.00	0.00
1:18 PM	0.37			210	221	0.32	0.04	0.01	0.00
1:22 PM	0.43			250	261	0.35	0.05	0.06	0.00
1:29 PM	0.55			280	291	0.24	0.00	0.15	0.02
1:36 PM	0.67			310	321	0.42	0.09	0.28	0.04
1:41 PM	0.75	J05	11	330	341	0.6	0.17	0.37	0.04
1:43 PM	0.78	J06	11	340	362	1.04	0.38	0.48	0.01
1:46 PM	0.83	J07	11	350	383	1.53	0.61	0.58	0.00
1:50 PM	0.90	J08	11	360	404	1.95	0.81	0.67	0.02
1:54 PM	0.97	J09	11	370	425	2.14	0.90	0.75	0.02
1:57 PM	1.02	J10	11	380	446	2.24	0.95	0.81	0.02
2:01 PM	1.08	J11	11	390	467	2.27	0.96	0.86	0.01
2:05 PM	1.15	J12	11	400	488	2.28	0.97	0.90	0.00
2:11 PM	1.25	J13	11	420	519	2.3	0.98	0.94	0.00
2:16 PM	1.33	J14	11	440	550	2.3	0.98	0.97	0.00
2:27 PM	1.52	J15	11	480	601	2.31	0.98	0.99	0.00
2:33 PM	1.62	J16	11	500	632	2.33	0.99	0.99	0.00
2:38 PM	1.70	J17	11	520	663	2.34	1.00	1.00	0.00
2:57 PM	2.02	J18	11	600	754	2.39	1.02	1.00	0.00

Effluent Conc (mg/L)	Cd Cu Zn		
	Cd	Cu	Zn
J00	1.0	0.5	1.2
J03	0.9	0.4	1.0
J06	4.7	1.1	3.9
J12	4.7	0.9	3.2
J18	2.7	0.6	1.9



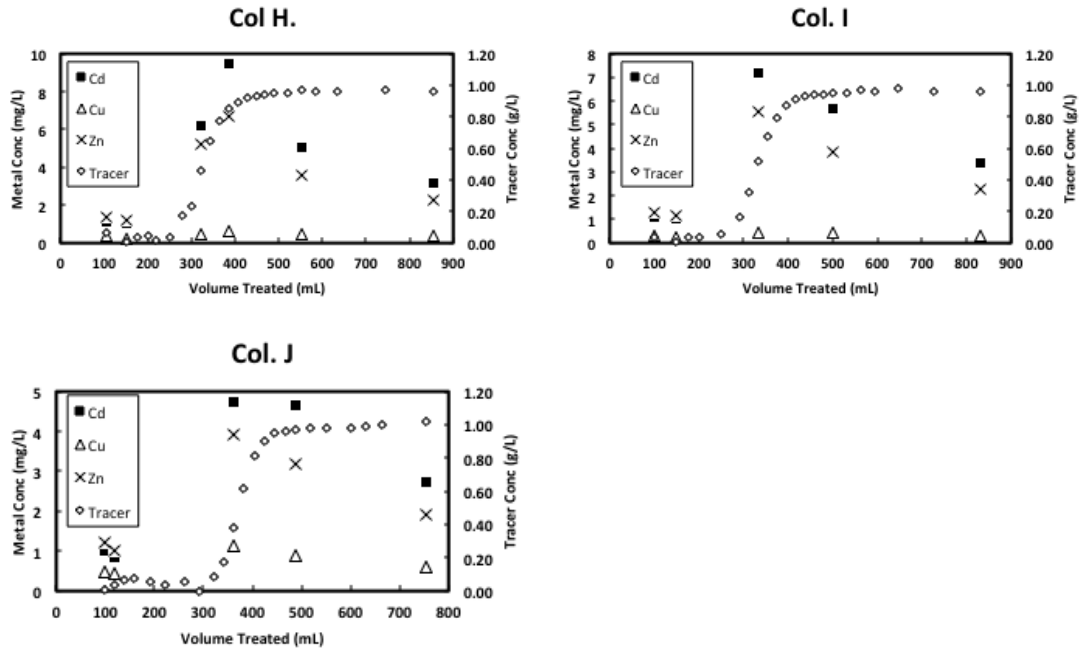


Figure 38. Salt tracer and desorption data for all columns. Salt concentration is plotted against the right axis and the metals concentration data is plotted on the left axis.

B.4 Column Study Data

The column headings are as follows, from left to right: specific metal removed, column replicate, compost fraction, port from which sample was drawn (5, 10, 15 cm depth), cumulative volume of water treated by each column, flow rate, bioretention media mass, mass of compost in the layer, mass of sand in the layer, mass of sand in the protective interlayers, and the concentration measured from each port.

Table 31. Column study data.

Metal	Column	Comp. [%]	Port	V _{eff} [L]	Q mL/min	Mass [g]	Comp [g]	Sand [g]	ms [g]	C [mg/L]
Cd	B	50	I	1.0	3.8	151.8	41.3	110.5	47.7	0.0
Cd	C	50	I	2.2	2.4	150.6	41.0	109.6	49.0	0.0
Cd	B	50	I	17.1	3.8	151.8	41.3	110.5	47.7	0.0
Cd	C	50	I	19.0	2.4	150.6	41.0	109.6	49.0	0.0
Cd	B	50	I	33.4	3.8	151.8	41.3	110.5	47.7	0.0
Cd	B	50	I	42.7	3.8	151.8	41.3	110.5	47.7	0.1
Cd	C	50	I	49.0	2.4	150.6	41.0	109.6	49.0	0.0
Cd	C	50	I	52.3	2.4	150.6	41.0	109.6	49.0	0.0
Cd	C	50	I	82.4	2.4	150.6	41.0	109.6	49.0	0.2
Cd	B	50	I	101.7	3.8	151.8	41.3	110.5	47.7	0.5
Cd	C	50	I	102.3	2.4	150.6	41.0	109.6	49.0	0.5
Cd	B	50	I	105.5	3.8	151.8	41.3	110.5	47.7	0.5
Cd	B	50	I	146.1	3.8	151.8	41.3	110.5	47.7	0.9
Cd	C	50	I	175.4	2.4	150.6	41.0	109.6	49.0	1.0
Cd	B	50	I	192.6	3.8	151.8	41.3	110.5	47.7	1.3
Cd	C	50	I	214.8	2.4	150.6	41.0	109.6	49.0	1.0
Cd	B	50	I	241.0	3.8	151.8	41.3	110.5	47.7	1.2
Cd	C	50	I	254.7	2.4	150.6	41.0	109.6	49.0	1.0
Cd	B	50	I	324.6	3.8	151.8	41.3	110.5	47.7	1.1
Cd	B	50	I	428.1	3.8	151.8	41.3	110.5	47.7	1.0
Cd	C	50	II	82.4	2.4	300.6	82.3	218.3	145.5	0.0
Cd	A	50	II	120.2	3.2	303.7	82.6	221.1	142.5	0.0
Cd	B	50	II	146.1	3.8	303.6	82.6	221.0	142.6	0.1
Cd	C	50	II	175.4	2.4	300.6	82.3	218.3	145.5	0.1
Cd	C	50	II	216.4	2.4	300.6	82.3	218.3	145.5	0.3
Cd	A	50	II	217.1	3.2	303.7	82.6	221.1	142.5	0.7
Cd	B	50	II	241.0	3.8	303.6	82.6	221.0	142.6	1.0
Cd	C	50	II	247.6	2.4	300.6	82.3	218.3	145.5	0.4
Cd	A	50	II	281.8	3.2	303.7	82.6	221.1	142.5	0.9
Cd	A	50	II	326.1	3.2	303.7	82.6	221.1	142.5	0.9
Cd	B	50	II	332.7	3.8	303.6	82.6	221.0	142.6	1.1
Cd	B	50	II	399.1	3.8	303.6	82.6	221.0	142.6	1.1
Cd	C	50	III	82.4	2.4	450.7	123.6	327.0	240.1	0.0
Cd	A	50	III	120.2	3.2	456.6	124.2	332.4	237.2	0.0
Cd	B	50	III	146.1	3.8	455.2	123.9	331.4	237.7	0.0
Cd	C	50	III	173.7	2.4	450.7	123.6	327.0	240.1	0.0

Cd	A	50	III	214.3	3.2	456.6	124.2	332.4	237.2	0.0
Cd	C	50	III	214.8	2.4	450.7	123.6	327.0	240.1	0.0
Cd	C	50	III	236.9	2.4	450.7	123.6	327.0	240.1	0.1
Cd	B	50	III	238.6	3.8	455.2	123.9	331.4	237.7	0.1
Cd	C	50	III	246.4	2.4	450.7	123.6	327.0	240.1	0.1
Cd	C	50	III	249.2	2.4	450.7	123.6	327.0	240.1	0.1
Cd	C	50	III	254.0	2.4	450.7	123.6	327.0	240.1	0.1
Cd	C	50	III	257.0	2.4	450.7	123.6	327.0	240.1	0.1
Cd	A	50	III	275.9	3.2	456.6	124.2	332.4	237.2	0.0
Cd	C	50	III	283.8	2.4	450.7	123.6	327.0	240.1	0.3
Cd	A	50	III	298.0	3.2	456.6	124.2	332.4	237.2	0.1
Cd	A	50	III	312.6	3.2	456.6	124.2	332.4	237.2	0.2
Cd	A	50	III	323.8	3.2	456.6	124.2	332.4	237.2	0.2
Cd	B	50	III	324.6	3.8	455.2	123.9	331.4	237.7	0.6
Cd	A	50	III	331.2	3.2	456.6	124.2	332.4	237.2	0.3
Cd	A	50	III	339.7	3.2	456.6	124.2	332.4	237.2	0.3
Cd	A	50	III	347.6	3.2	456.6	124.2	332.4	237.2	0.4
Cd	B	50	III	349.6	3.8	455.2	123.9	331.4	237.7	0.7
Cd	B	50	III	368.2	3.8	455.2	123.9	331.4	237.7	0.8
Cd	A	50	III	375.5	3.2	456.6	124.2	332.4	237.2	0.6
Cd	B	50	III	395.1	3.8	455.2	123.9	331.4	237.7	0.8
Cd	B	50	III	408.1	3.8	455.2	123.9	331.4	237.7	0.8
Cd	B	50	III	420.5	3.8	455.2	123.9	331.4	237.7	0.8
Cd	B	50	III	432.7	3.8	455.2	123.9	331.4	237.7	0.8
Cd	B	50	III	446.3	3.8	455.2	123.9	331.4	237.7	0.8
Cd	F	30	I	1.4	2.3	167.4	23.1	144.3	49.3	0.0
Cd	F	30	I	3.3	2.3	167.4	23.1	144.3	49.3	0.0
Cd	E	30	I	8.7	3.6	168.2	23.2	144.9	48.4	0.0
Cd	D	30	I	10.9	3.9	167.6	23.1	144.5	48.2	0.0
Cd	D	30	I	17.5	3.9	167.6	23.1	144.5	48.2	0.0
Cd	F	30	I	23.8	2.3	167.4	23.1	144.3	49.3	0.0
Cd	E	30	I	24.7	3.6	168.2	23.2	144.9	48.4	0.0
Cd	F	30	I	35.8	2.3	167.4	23.1	144.3	49.3	0.1
Cd	E	30	I	37.5	3.6	168.2	23.2	144.9	48.4	0.0
Cd	D	30	I	40.7	3.9	167.6	23.1	144.5	48.2	0.4
Cd	E	30	I	48.3	3.6	168.2	23.2	144.9	48.4	0.2
Cd	D	30	I	53.5	3.9	167.6	23.1	144.5	48.2	0.7
Cd	F	30	I	61.9	2.3	167.4	23.1	144.3	49.3	0.6
Cd	F	30	I	84.7	2.3	167.4	23.1	144.3	49.3	0.9
Cd	F	30	I	96.6	2.3	167.4	23.1	144.3	49.3	1.2
Cd	E	30	I	123.0	3.6	168.2	23.2	144.9	48.4	1.1
Cd	F	30	I	126.0	2.3	167.4	23.1	144.3	49.3	1.2
Cd	D	30	I	127.2	3.9	167.6	23.1	144.5	48.2	1.6
Cd	E	30	I	168.4	3.6	168.2	23.2	144.9	48.4	1.2
Cd	D	30	I	175.7	3.9	167.6	23.1	144.5	48.2	1.3
Cd	F	30	I	195.9	2.3	167.4	23.1	144.3	49.3	1.1
Cd	E	30	I	206.2	3.6	168.2	23.2	144.9	48.4	1.2
Cd	D	30	I	235.8	3.9	167.6	23.1	144.5	48.2	1.2
Cd	E	30	I	292.5	3.6	168.2	23.2	144.9	48.4	0.9

Cd	D	30	I	385.4	3.9	167.6	23.1	144.5	48.2	1.0
Cd	E	30	II	48.3	3.6	335.9	46.4	289.5	144.6	0.0
Cd	D	30	II	53.6	3.9	335.3	46.3	289.0	144.6	0.1
Cd	D	30	II	58.7	3.9	335.3	46.3	289.0	144.6	0.0
Cd	F	30	II	61.9	2.3	334.9	46.2	288.7	146.6	0.0
Cd	E	30	II	76.8	3.6	335.9	46.4	289.5	144.6	0.0
Cd	F	30	II	77.1	2.3	334.9	46.2	288.7	146.6	0.0
Cd	F	30	II	84.7	2.3	334.9	46.2	288.7	146.6	0.0
Cd	F	30	II	90.9	2.3	334.9	46.2	288.7	146.6	0.1
Cd	E	30	II	123.0	3.6	335.9	46.4	289.5	144.6	0.4
Cd	F	30	II	126.0	2.3	334.9	46.2	288.7	146.6	0.9
Cd	D	30	II	127.2	3.9	335.3	46.3	289.0	144.6	1.1
Cd	E	30	II	143.9	3.6	335.9	46.4	289.5	144.6	0.7
Cd	F	30	II	153.1	2.3	334.9	46.2	288.7	146.6	1.0
Cd	D	30	II	157.3	3.9	335.3	46.3	289.0	144.6	1.3
Cd	E	30	II	206.2	3.6	335.9	46.4	289.5	144.6	1.0
Cd	D	30	II	235.8	3.9	335.3	46.3	289.0	144.6	1.2
Cd	E	30	II	256.7	3.6	335.9	46.4	289.5	144.6	0.9
Cd	D	30	II	321.7	3.9	335.3	46.3	289.0	144.6	1.1
Cd	D	30	III	57.8	3.9	503.4	69.5	433.9	241.6	0.0
Cd	E	30	III	70.6	3.6	503.8	69.6	434.2	241.3	0.0
Cd	F	30	III	71.4	2.3	502.2	69.3	432.9	243.5	0.0
Cd	F	30	III	84.7	2.3	502.2	69.3	432.9	243.5	0.0
Cd	E	30	III	123.0	3.6	503.8	69.6	434.2	241.3	0.0
Cd	F	30	III	124.3	2.3	502.2	69.3	432.9	243.5	0.1
Cd	D	30	III	127.2	3.9	503.4	69.5	433.9	241.6	0.1
Cd	F	30	III	153.1	2.3	502.2	69.3	432.9	243.5	0.4
Cd	E	30	III	205.3	3.6	503.8	69.6	434.2	241.3	0.5
Cd	F	30	III	209.5	2.3	502.2	69.3	432.9	243.5	0.8
Cd	D	30	III	231.0	3.9	503.4	69.5	433.9	241.6	1.0
Cd	E	30	III	256.7	3.6	503.8	69.6	434.2	241.3	0.9
Cd	D	30	III	321.7	3.9	503.4	69.5	433.9	241.6	1.0
Cd	E	30	III	338.3	3.6	503.8	69.6	434.2	241.3	1.0
Cd	G	10	I	1.5	3.2	190.6	7.6	183.0	48.4	0.0
Cd	H	10	I	2.9	3.5	185.8	7.4	178.3	48.3	0.0
Cd	G	10	I	4.4	3.2	190.6	7.6	183.0	48.4	0.0
Cd	I	10	I	5.0	3.6	190.5	7.6	182.9	45.0	0.0
Cd	H	10	I	6.7	3.5	185.8	7.4	178.3	48.3	0.0
Cd	H	10	I	17.0	3.5	185.8	7.4	178.3	48.3	0.1
Cd	I	10	I	22.6	3.6	190.5	7.6	182.9	45.0	0.1
Cd	H	10	I	26.3	3.5	185.8	7.4	178.3	48.3	0.3
Cd	I	10	I	27.0	3.6	190.5	7.6	182.9	45.0	0.2
Cd	G	10	I	32.9	3.2	190.6	7.6	183.0	48.4	0.3
Cd	I	10	I	42.1	3.6	190.5	7.6	182.9	45.0	0.6
Cd	H	10	I	48.6	3.5	185.8	7.4	178.3	48.3	0.9
Cd	G	10	I	59.7	3.2	190.6	7.6	183.0	48.4	0.6
Cd	H	10	I	65.6	3.5	185.8	7.4	178.3	48.3	0.9
Cd	I	10	I	67.7	3.6	190.5	7.6	182.9	45.0	1.0
Cd	G	10	I	68.5	3.2	190.6	7.6	183.0	48.4	0.8

Cd	I	10	I	77.9	3.6	190.5	7.6	182.9	45.0	0.9
Cd	G	10	I	110.4	3.2	190.6	7.6	183.0	48.4	0.8
Cd	H	10	I	207.4	3.5	185.8	7.4	178.3	48.3	1.0
Cd	I	10	I	232.5	3.6	190.5	7.6	182.9	45.0	1.1
Cd	G	10	I	256.1	3.2	190.6	7.6	183.0	48.4	0.9
Cd	I	10	I	388.5	3.6	190.5	7.6	182.9	45.0	1.1
Cd	G	10	II	4.4	3.2	380.7	15.2	365.5	144.8	0.0
Cd	H	10	II	6.7	3.5	375.8	15.0	360.8	144.7	0.0
Cd	I	10	II	22.6	3.6	380.5	15.2	365.3	135.0	0.0
Cd	H	10	II	48.6	3.5	375.8	15.0	360.8	144.7	0.4
Cd	H	10	II	55.9	3.5	375.8	15.0	360.8	144.7	0.6
Cd	I	10	II	67.7	3.6	380.5	15.2	365.3	135.0	0.7
Cd	I	10	II	71.6	3.6	380.5	15.2	365.3	135.0	0.8
Cd	G	10	II	93.4	3.2	380.7	15.2	365.5	144.8	0.7
Cd	H	10	II	112.2	3.5	375.8	15.0	360.8	144.7	1.0
Cd	I	10	II	120.0	3.6	380.5	15.2	365.3	135.0	1.2
Cd	G	10	II	154.5	3.2	380.7	15.2	365.5	144.8	0.8
Cd	H	10	II	159.7	3.5	375.8	15.0	360.8	144.7	1.1
Cd	I	10	II	199.4	3.6	380.5	15.2	365.3	135.0	1.1
Cd	H	10	II	207.4	3.5	375.8	15.0	360.8	144.7	1.1
Cd	G	10	II	228.1	3.2	380.7	15.2	365.5	144.8	1.1
Cd	I	10	II	232.5	3.6	380.5	15.2	365.3	135.0	1.1
Cd	H	10	II	245.8	3.5	375.8	15.0	360.8	144.7	1.0
Cd	G	10	II	256.1	3.2	380.7	15.2	365.5	144.8	1.0
Cd	I	10	II	275.9	3.6	380.5	15.2	365.3	135.0	1.1
Cd	G	10	II	287.4	3.2	380.7	15.2	365.5	144.8	0.9
Cd	H	10	III	36.7	3.5	565.8	22.6	543.2	240.9	0.0
Cd	I	10	III	62.1	3.6	570.6	22.8	547.8	228.4	0.2
Cd	G	10	III	68.5	3.2	570.7	22.8	548.0	241.0	0.0
Cd	H	10	III	69.9	3.5	565.8	22.6	543.2	240.9	0.1
Cd	I	10	III	80.7	3.6	570.6	22.8	547.8	228.4	0.4
Cd	G	10	III	117.5	3.2	570.7	22.8	548.0	241.0	0.3
Cd	H	10	III	199.3	3.5	565.8	22.6	543.2	240.9	0.9
Cd	I	10	III	230.7	3.6	570.6	22.8	547.8	228.4	1.1
Cd	H	10	III	245.8	3.5	565.8	22.6	543.2	240.9	0.9
Cd	G	10	III	253.3	3.2	570.7	22.8	548.0	241.0	1.0
Cd	H	10	III	261.7	3.5	565.8	22.6	543.2	240.9	1.0
Cd	I	10	III	275.9	3.6	570.6	22.8	547.8	228.4	1.0
Cd	G	10	III	287.4	3.2	570.7	22.8	548.0	241.0	0.9
Cd	I	10	III	296.9	3.6	570.6	22.8	547.8	228.4	0.9
Cd	G	10	III	301.7	3.2	570.7	22.8	548.0	241.0	0.9
Cd	G	10	III	330.8	3.2	570.7	22.8	548.0	241.0	0.9
Cd	J	0	I	7.3	3.0	190.0	0.0	190.0	48.0	0.3
Cd	J	0	I	12.6	3.0	190.0	0.0	190.0	48.0	0.4
Cd	J	0	I	49.2	3.0	190.0	0.0	190.0	48.0	1.1
Cd	J	0	I	134.9	3.0	190.0	0.0	190.0	48.0	1.1
Cd	J	0	I	163.7	3.0	190.0	0.0	190.0	48.0	1.0
Cd	J	0	II	7.3	3.0	380.0	0.0	380.0	144.0	0.0
Cd	J	0	II	12.6	3.0	380.0	0.0	380.0	144.0	0.0

Cd	J	0	II	34.0	3.0	380.0	0.0	380.0	144.0	0.6
Cd	J	0	II	67.8	3.0	380.0	0.0	380.0	144.0	0.9
Cd	J	0	II	105.9	3.0	380.0	0.0	380.0	144.0	1.1
Cd	J	0	II	127.3	3.0	380.0	0.0	380.0	144.0	1.3
Cd	J	0	II	165.8	3.0	380.0	0.0	380.0	144.0	1.0
Cd	J	0	II	211.6	3.0	380.0	0.0	380.0	144.0	1.1
Cd	J	0	III	7.3	3.0	570.1	0.0	570.1	240.1	0.0
Cd	J	0	III	12.6	3.0	570.1	0.0	570.1	240.1	0.0
Cd	J	0	III	34.0	3.0	570.1	0.0	570.1	240.1	0.3
Cd	J	0	III	57.2	3.0	570.1	0.0	570.1	240.1	1.0
Cd	J	0	III	115.0	3.0	570.1	0.0	570.1	240.1	1.4
Cd	J	0	III	161.2	3.0	570.1	0.0	570.1	240.1	1.1
Cd	J	0	III	211.6	3.0	570.1	0.0	570.1	240.1	1.0
Cu	B	50	I	1.0	3.8	151.8	41.3	110.5	47.7	0.0
Cu	B	50	I	17.1	3.8	151.8	41.3	110.5	47.7	0.0
Cu	B	50	I	33.4	3.8	151.8	41.3	110.5	47.7	0.0
Cu	B	50	I	42.7	3.8	151.8	41.3	110.5	47.7	0.0
Cu	B	50	I	101.7	3.8	151.8	41.3	110.5	47.7	0.0
Cu	B	50	I	105.5	3.8	151.8	41.3	110.5	47.7	0.0
Cu	B	50	I	146.1	3.8	151.8	41.3	110.5	47.7	0.0
Cu	B	50	I	192.6	3.8	151.8	41.3	110.5	47.7	0.1
Cu	B	50	I	241.0	3.8	151.8	41.3	110.5	47.7	0.1
Cu	B	50	I	324.6	3.8	151.8	41.3	110.5	47.7	0.1
Cu	B	50	I	428.1	3.8	151.8	41.3	110.5	47.7	0.4
Cu	C	50	I	2.2	2.4	150.6	41.0	109.6	49.0	0.0
Cu	C	50	I	19.0	2.4	150.6	41.0	109.6	49.0	0.0
Cu	C	50	I	49.0	2.4	150.6	41.0	109.6	49.0	0.0
Cu	C	50	I	52.3	2.4	150.6	41.0	109.6	49.0	0.0
Cu	C	50	I	82.4	2.4	150.6	41.0	109.6	49.0	0.0
Cu	C	50	I	102.3	2.4	150.6	41.0	109.6	49.0	0.0
Cu	C	50	I	175.4	2.4	150.6	41.0	109.6	49.0	0.0
Cu	C	50	I	214.8	2.4	150.6	41.0	109.6	49.0	0.0
Cu	C	50	I	254.7	2.4	150.6	41.0	109.6	49.0	0.1
Cu	A	50	II	120.2	3.2	303.7	82.6	221.1	142.5	0.1
Cu	A	50	II	217.1	3.2	303.7	82.6	221.1	142.5	0.1
Cu	A	50	II	281.8	3.2	303.7	82.6	221.1	142.5	0.0
Cu	A	50	II	326.1	3.2	303.7	82.6	221.1	142.5	0.0
Cu	B	50	II	146.1	3.8	303.6	82.6	221.0	142.6	0.1
Cu	B	50	II	241.0	3.8	303.6	82.6	221.0	142.6	0.1
Cu	B	50	II	332.7	3.8	303.6	82.6	221.0	142.6	0.0
Cu	B	50	II	399.1	3.8	303.6	82.6	221.0	142.6	0.0
Cu	C	50	II	82.4	2.4	300.6	82.3	218.3	145.5	0.0
Cu	C	50	II	175.4	2.4	300.6	82.3	218.3	145.5	0.0
Cu	C	50	II	216.4	2.4	300.6	82.3	218.3	145.5	0.0
Cu	C	50	II	247.6	2.4	300.6	82.3	218.3	145.5	0.0
Cu	A	50	III	120.2	3.2	456.6	124.2	332.4	237.2	0.0
Cu	A	50	III	214.3	3.2	456.6	124.2	332.4	237.2	0.0
Cu	A	50	III	275.9	3.2	456.6	124.2	332.4	237.2	0.0

Cu	A	50	III	298.0	3.2	456.6	124.2	332.4	237.2	0.0
Cu	A	50	III	312.6	3.2	456.6	124.2	332.4	237.2	0.0
Cu	A	50	III	323.8	3.2	456.6	124.2	332.4	237.2	0.0
Cu	A	50	III	331.2	3.2	456.6	124.2	332.4	237.2	0.0
Cu	A	50	III	339.7	3.2	456.6	124.2	332.4	237.2	0.0
Cu	A	50	III	347.6	3.2	456.6	124.2	332.4	237.2	0.0
Cu	A	50	III	375.5	3.2	456.6	124.2	332.4	237.2	0.0
Cu	B	50	III	146.1	3.8	455.2	123.9	331.4	237.7	0.0
Cu	B	50	III	238.6	3.8	455.2	123.9	331.4	237.7	0.0
Cu	B	50	III	324.6	3.8	455.2	123.9	331.4	237.7	0.0
Cu	B	50	III	349.6	3.8	455.2	123.9	331.4	237.7	0.0
Cu	B	50	III	368.2	3.8	455.2	123.9	331.4	237.7	0.0
Cu	B	50	III	395.1	3.8	455.2	123.9	331.4	237.7	0.0
Cu	B	50	III	408.1	3.8	455.2	123.9	331.4	237.7	0.0
Cu	B	50	III	420.5	3.8	455.2	123.9	331.4	237.7	0.0
Cu	B	50	III	432.7	3.8	455.2	123.9	331.4	237.7	0.1
Cu	B	50	III	446.3	3.8	455.2	123.9	331.4	237.7	0.0
Cu	C	50	III	82.4	2.4	450.7	123.6	327.0	240.1	0.0
Cu	C	50	III	173.7	2.4	450.7	123.6	327.0	240.1	0.0
Cu	C	50	III	214.8	2.4	450.7	123.6	327.0	240.1	0.0
Cu	C	50	III	236.9	2.4	450.7	123.6	327.0	240.1	0.0
Cu	C	50	III	246.4	2.4	450.7	123.6	327.0	240.1	0.0
Cu	C	50	III	249.2	2.4	450.7	123.6	327.0	240.1	0.0
Cu	C	50	III	254.0	2.4	450.7	123.6	327.0	240.1	0.0
Cu	C	50	III	257.0	2.4	450.7	123.6	327.0	240.1	0.1
Cu	C	50	III	283.8	2.4	450.7	123.6	327.0	240.1	0.0
Cu	D	30	I	10.9	3.9	167.6	23.1	144.5	48.2	0.1
Cu	D	30	I	17.5	3.9	167.6	23.1	144.5	48.2	0.1
Cu	D	30	I	40.7	3.9	167.6	23.1	144.5	48.2	0.1
Cu	D	30	I	53.5	3.9	167.6	23.1	144.5	48.2	0.1
Cu	D	30	I	127.2	3.9	167.6	23.1	144.5	48.2	0.3
Cu	D	30	I	175.7	3.9	167.6	23.1	144.5	48.2	0.3
Cu	D	30	I	235.8	3.9	167.6	23.1	144.5	48.2	0.2
Cu	D	30	I	385.4	3.9	167.6	23.1	144.5	48.2	0.4
Cu	E	30	I	8.7	3.6	168.2	23.2	144.9	48.4	0.0
Cu	E	30	I	24.7	3.6	168.2	23.2	144.9	48.4	0.0
Cu	E	30	I	37.5	3.6	168.2	23.2	144.9	48.4	0.0
Cu	E	30	I	48.3	3.6	168.2	23.2	144.9	48.4	0.1
Cu	E	30	I	123.0	3.6	168.2	23.2	144.9	48.4	0.3
Cu	E	30	I	168.4	3.6	168.2	23.2	144.9	48.4	0.2
Cu	E	30	I	206.2	3.6	168.2	23.2	144.9	48.4	0.1
Cu	E	30	I	292.5	3.6	168.2	23.2	144.9	48.4	0.4
Cu	F	30	I	1.4	2.3	167.4	23.1	144.3	49.3	0.0
Cu	F	30	I	3.3	2.3	167.4	23.1	144.3	49.3	0.0
Cu	F	30	I	23.8	2.3	167.4	23.1	144.3	49.3	0.1
Cu	F	30	I	35.8	2.3	167.4	23.1	144.3	49.3	0.1
Cu	F	30	I	61.9	2.3	167.4	23.1	144.3	49.3	0.1
Cu	F	30	I	84.7	2.3	167.4	23.1	144.3	49.3	0.1
Cu	F	30	I	96.6	2.3	167.4	23.1	144.3	49.3	0.1

Cu	F	30	I	126.0	2.3	167.4	23.1	144.3	49.3	0.1
Cu	F	30	I	195.9	2.3	167.4	23.1	144.3	49.3	0.2
Cu	D	30	II	53.6	3.9	335.3	46.3	289.0	144.6	0.0
Cu	D	30	II	58.7	3.9	335.3	46.3	289.0	144.6	0.0
Cu	D	30	II	127.2	3.9	335.3	46.3	289.0	144.6	0.1
Cu	D	30	II	157.3	3.9	335.3	46.3	289.0	144.6	0.0
Cu	D	30	II	235.8	3.9	335.3	46.3	289.0	144.6	0.1
Cu	D	30	II	321.7	3.9	335.3	46.3	289.0	144.6	0.1
Cu	E	30	II	48.3	3.6	335.9	46.4	289.5	144.6	0.0
Cu	E	30	II	76.8	3.6	335.9	46.4	289.5	144.6	0.0
Cu	E	30	II	123.0	3.6	335.9	46.4	289.5	144.6	0.0
Cu	E	30	II	143.9	3.6	335.9	46.4	289.5	144.6	0.1
Cu	E	30	II	206.2	3.6	335.9	46.4	289.5	144.6	0.0
Cu	E	30	II	256.7	3.6	335.9	46.4	289.5	144.6	0.0
Cu	F	30	II	61.9	2.3	334.9	46.2	288.7	146.6	0.0
Cu	F	30	II	77.1	2.3	334.9	46.2	288.7	146.6	0.0
Cu	F	30	II	84.7	2.3	334.9	46.2	288.7	146.6	0.0
Cu	F	30	II	90.9	2.3	334.9	46.2	288.7	146.6	0.0
Cu	F	30	II	126.0	2.3	334.9	46.2	288.7	146.6	0.0
Cu	F	30	II	153.1	2.3	334.9	46.2	288.7	146.6	0.0
Cu	D	30	III	57.8	3.9	503.4	69.5	433.9	241.6	0.0
Cu	D	30	III	127.2	3.9	503.4	69.5	433.9	241.6	0.0
Cu	D	30	III	231.0	3.9	503.4	69.5	433.9	241.6	0.0
Cu	D	30	III	321.7	3.9	503.4	69.5	433.9	241.6	0.0
Cu	E	30	III	70.6	3.6	503.8	69.6	434.2	241.3	0.0
Cu	E	30	III	123.0	3.6	503.8	69.6	434.2	241.3	0.0
Cu	E	30	III	205.3	3.6	503.8	69.6	434.2	241.3	0.0
Cu	E	30	III	256.7	3.6	503.8	69.6	434.2	241.3	0.0
Cu	E	30	III	338.3	3.6	503.8	69.6	434.2	241.3	0.0
Cu	F	30	III	71.4	2.3	502.2	69.3	432.9	243.5	0.0
Cu	F	30	III	84.7	2.3	502.2	69.3	432.9	243.5	0.0
Cu	F	30	III	124.3	2.3	502.2	69.3	432.9	243.5	0.0
Cu	F	30	III	153.1	2.3	502.2	69.3	432.9	243.5	0.0
Cu	F	30	III	209.5	2.3	502.2	69.3	432.9	243.5	0.1
Cu	G	10	I	1.5	3.2	190.6	7.6	183.0	48.4	0.0
Cu	G	10	I	4.4	3.2	190.6	7.6	183.0	48.4	0.1
Cu	G	10	I	32.9	3.2	190.6	7.6	183.0	48.4	0.1
Cu	G	10	I	59.7	3.2	190.6	7.6	183.0	48.4	0.1
Cu	G	10	I	68.5	3.2	190.6	7.6	183.0	48.4	0.1
Cu	G	10	I	110.4	3.2	190.6	7.6	183.0	48.4	0.1
Cu	G	10	I	256.1	3.2	190.6	7.6	183.0	48.4	0.1
Cu	H	10	I	2.9	3.5	185.8	7.4	178.3	48.3	0.0
Cu	H	10	I	6.7	3.5	185.8	7.4	178.3	48.3	0.0
Cu	H	10	I	17.0	3.5	185.8	7.4	178.3	48.3	0.1
Cu	H	10	I	26.3	3.5	185.8	7.4	178.3	48.3	0.1
Cu	H	10	I	48.6	3.5	185.8	7.4	178.3	48.3	0.2
Cu	H	10	I	65.6	3.5	185.8	7.4	178.3	48.3	0.3
Cu	H	10	I	207.4	3.5	185.8	7.4	178.3	48.3	0.4
Cu	I	10	I	5.0	3.6	190.5	7.6	182.9	45.0	0.0

Cu	I	10	I	22.6	3.6	190.5	7.6	182.9	45.0	0.1
Cu	I	10	I	27.0	3.6	190.5	7.6	182.9	45.0	0.1
Cu	I	10	I	42.1	3.6	190.5	7.6	182.9	45.0	0.1
Cu	I	10	I	67.7	3.6	190.5	7.6	182.9	45.0	0.2
Cu	I	10	I	77.9	3.6	190.5	7.6	182.9	45.0	0.2
Cu	I	10	I	232.5	3.6	190.5	7.6	182.9	45.0	0.4
Cu	I	10	I	388.5	3.6	190.5	7.6	182.9	45.0	0.5
Cu	G	10	II	4.4	3.2	380.7	15.2	365.5	144.8	0.0
Cu	G	10	II	93.4	3.2	380.7	15.2	365.5	144.8	0.1
Cu	G	10	II	154.5	3.2	380.7	15.2	365.5	144.8	0.0
Cu	G	10	II	228.1	3.2	380.7	15.2	365.5	144.8	0.1
Cu	G	10	II	256.1	3.2	380.7	15.2	365.5	144.8	0.1
Cu	G	10	II	287.4	3.2	380.7	15.2	365.5	144.8	0.1
Cu	H	10	II	6.7	3.5	375.8	15.0	360.8	144.7	0.0
Cu	H	10	II	48.6	3.5	375.8	15.0	360.8	144.7	0.0
Cu	H	10	II	55.9	3.5	375.8	15.0	360.8	144.7	0.0
Cu	H	10	II	112.2	3.5	375.8	15.0	360.8	144.7	0.1
Cu	H	10	II	159.7	3.5	375.8	15.0	360.8	144.7	0.3
Cu	H	10	II	207.4	3.5	375.8	15.0	360.8	144.7	0.3
Cu	H	10	II	245.8	3.5	375.8	15.0	360.8	144.7	0.3
Cu	I	10	II	22.6	3.6	380.5	15.2	365.3	135.0	0.0
Cu	I	10	II	67.7	3.6	380.5	15.2	365.3	135.0	0.0
Cu	I	10	II	71.6	3.6	380.5	15.2	365.3	135.0	0.0
Cu	I	10	II	120.0	3.6	380.5	15.2	365.3	135.0	0.3
Cu	I	10	II	199.4	3.6	380.5	15.2	365.3	135.0	0.2
Cu	I	10	II	232.5	3.6	380.5	15.2	365.3	135.0	0.2
Cu	I	10	II	275.9	3.6	380.5	15.2	365.3	135.0	0.2
Cu	G	10	III	68.5	3.2	570.7	22.8	548.0	241.0	0.0
Cu	G	10	III	117.5	3.2	570.7	22.8	548.0	241.0	0.0
Cu	G	10	III	253.3	3.2	570.7	22.8	548.0	241.0	0.0
Cu	G	10	III	287.4	3.2	570.7	22.8	548.0	241.0	0.0
Cu	G	10	III	301.7	3.2	570.7	22.8	548.0	241.0	0.0
Cu	G	10	III	330.8	3.2	570.7	22.8	548.0	241.0	0.0
Cu	H	10	III	36.7	3.5	565.8	22.6	543.2	240.9	0.0
Cu	H	10	III	69.9	3.5	565.8	22.6	543.2	240.9	0.0
Cu	H	10	III	199.3	3.5	565.8	22.6	543.2	240.9	0.1
Cu	H	10	III	245.8	3.5	565.8	22.6	543.2	240.9	0.0
Cu	H	10	III	261.7	3.5	565.8	22.6	543.2	240.9	0.0
Cu	I	10	III	62.1	3.6	570.6	22.8	547.8	228.4	0.0
Cu	I	10	III	80.7	3.6	570.6	22.8	547.8	228.4	0.0
Cu	I	10	III	230.7	3.6	570.6	22.8	547.8	228.4	0.1
Cu	I	10	III	275.9	3.6	570.6	22.8	547.8	228.4	0.1
Cu	I	10	III	296.9	3.6	570.6	22.8	547.8	228.4	0.1
Cu	J	0	I	7.3	3.0	190.0	0.0	190.0	48.0	0.2
Cu	J	0	I	12.6	3.0	190.0	0.0	190.0	48.0	0.1
Cu	J	0	I	49.2	3.0	190.0	0.0	190.0	48.0	0.3
Cu	J	0	I	134.9	3.0	190.0	0.0	190.0	48.0	0.5
Cu	J	0	I	163.7	3.0	190.0	0.0	190.0	48.0	0.5
Cu	J	0	II	7.3	3.0	380.0	0.0	380.0	144.0	0.0

Cu	J	0	II	12.6	3.0	380.0	0.0	380.0	144.0	0.1
Cu	J	0	II	34.0	3.0	380.0	0.0	380.0	144.0	0.1
Cu	J	0	II	67.8	3.0	380.0	0.0	380.0	144.0	0.0
Cu	J	0	II	105.9	3.0	380.0	0.0	380.0	144.0	0.3
Cu	J	0	II	127.3	3.0	380.0	0.0	380.0	144.0	0.3
Cu	J	0	II	165.8	3.0	380.0	0.0	380.0	144.0	0.4
Cu	J	0	II	211.6	3.0	380.0	0.0	380.0	144.0	0.4
Cu	J	0	III	7.3	3.0	570.1	0.0	570.1	240.1	0.0
Cu	J	0	III	12.6	3.0	570.1	0.0	570.1	240.1	0.0
Cu	J	0	III	34.0	3.0	570.1	0.0	570.1	240.1	0.0
Cu	J	0	III	57.2	3.0	570.1	0.0	570.1	240.1	0.0
Cu	J	0	III	115.0	3.0	570.1	0.0	570.1	240.1	0.1
Cu	J	0	III	161.2	3.0	570.1	0.0	570.1	240.1	0.2
Cu	J	0	III	211.6	3.0	570.1	0.0	570.1	240.1	0.2
Zn	B	50	I	1.0	3.8	151.8	41.3	110.5	47.7	0.0
Zn	B	50	I	17.1	3.8	151.8	41.3	110.5	47.7	0.0
Zn	B	50	I	33.4	3.8	151.8	41.3	110.5	47.7	0.1
Zn	B	50	I	42.7	3.8	151.8	41.3	110.5	47.7	0.1
Zn	B	50	I	101.7	3.8	151.8	41.3	110.5	47.7	0.8
Zn	B	50	I	105.5	3.8	151.8	41.3	110.5	47.7	0.9
Zn	B	50	I	146.1	3.8	151.8	41.3	110.5	47.7	1.3
Zn	B	50	I	192.6	3.8	151.8	41.3	110.5	47.7	1.3
Zn	B	50	I	241.0	3.8	151.8	41.3	110.5	47.7	1.3
Zn	B	50	I	324.6	3.8	151.8	41.3	110.5	47.7	1.2
Zn	B	50	I	428.1	3.8	151.8	41.3	110.5	47.7	1.1
Zn	C	50	I	2.2	2.4	150.6	41.0	109.6	49.0	0.0
Zn	C	50	I	19.0	2.4	150.6	41.0	109.6	49.0	0.0
Zn	C	50	I	49.0	2.4	150.6	41.0	109.6	49.0	0.0
Zn	C	50	I	52.3	2.4	150.6	41.0	109.6	49.0	0.1
Zn	C	50	I	82.4	2.4	150.6	41.0	109.6	49.0	0.5
Zn	C	50	I	102.3	2.4	150.6	41.0	109.6	49.0	0.8
Zn	C	50	I	175.4	2.4	150.6	41.0	109.6	49.0	1.1
Zn	C	50	I	214.8	2.4	150.6	41.0	109.6	49.0	1.0
Zn	C	50	I	254.7	2.4	150.6	41.0	109.6	49.0	1.1
Zn	A	50	II	120.2	3.2	303.7	82.6	221.1	142.5	0.1
Zn	A	50	II	217.1	3.2	303.7	82.6	221.1	142.5	1.0
Zn	A	50	II	281.8	3.2	303.7	82.6	221.1	142.5	1.0
Zn	A	50	II	326.1	3.2	303.7	82.6	221.1	142.5	1.2
Zn	B	50	II	146.1	3.8	303.6	82.6	221.0	142.6	0.3
Zn	B	50	II	241.0	3.8	303.6	82.6	221.0	142.6	1.2
Zn	B	50	II	332.7	3.8	303.6	82.6	221.0	142.6	1.2
Zn	B	50	II	399.1	3.8	303.6	82.6	221.0	142.6	1.3
Zn	C	50	II	82.4	2.4	300.6	82.3	218.3	145.5	0.0
Zn	C	50	II	175.4	2.4	300.6	82.3	218.3	145.5	0.3
Zn	C	50	II	216.4	2.4	300.6	82.3	218.3	145.5	0.6
Zn	C	50	II	247.6	2.4	300.6	82.3	218.3	145.5	0.5
Zn	A	50	III	120.2	3.2	456.6	124.2	332.4	237.2	0.0
Zn	A	50	III	214.3	3.2	456.6	124.2	332.4	237.2	0.0

Zn	A	50	III	275.9	3.2	456.6	124.2	332.4	237.2	0.2
Zn	A	50	III	298.0	3.2	456.6	124.2	332.4	237.2	0.4
Zn	A	50	III	312.6	3.2	456.6	124.2	332.4	237.2	0.6
Zn	A	50	III	323.8	3.2	456.6	124.2	332.4	237.2	0.7
Zn	A	50	III	331.2	3.2	456.6	124.2	332.4	237.2	0.7
Zn	A	50	III	339.7	3.2	456.6	124.2	332.4	237.2	0.8
Zn	A	50	III	347.6	3.2	456.6	124.2	332.4	237.2	0.7
Zn	A	50	III	375.5	3.2	456.6	124.2	332.4	237.2	1.0
Zn	B	50	III	146.1	3.8	455.2	123.9	331.4	237.7	0.0
Zn	B	50	III	238.6	3.8	455.2	123.9	331.4	237.7	0.4
Zn	B	50	III	324.6	3.8	455.2	123.9	331.4	237.7	0.7
Zn	B	50	III	349.6	3.8	455.2	123.9	331.4	237.7	0.9
Zn	B	50	III	368.2	3.8	455.2	123.9	331.4	237.7	0.9
Zn	B	50	III	395.1	3.8	455.2	123.9	331.4	237.7	0.9
Zn	B	50	III	408.1	3.8	455.2	123.9	331.4	237.7	1.0
Zn	B	50	III	420.5	3.8	455.2	123.9	331.4	237.7	1.0
Zn	B	50	III	432.7	3.8	455.2	123.9	331.4	237.7	1.0
Zn	B	50	III	446.3	3.8	455.2	123.9	331.4	237.7	1.0
Zn	C	50	III	82.4	2.4	450.7	123.6	327.0	240.1	0.0
Zn	C	50	III	173.7	2.4	450.7	123.6	327.0	240.1	0.0
Zn	C	50	III	214.8	2.4	450.7	123.6	327.0	240.1	0.1
Zn	C	50	III	236.9	2.4	450.7	123.6	327.0	240.1	0.1
Zn	C	50	III	246.4	2.4	450.7	123.6	327.0	240.1	0.2
Zn	C	50	III	249.2	2.4	450.7	123.6	327.0	240.1	0.2
Zn	C	50	III	254.0	2.4	450.7	123.6	327.0	240.1	0.3
Zn	C	50	III	257.0	2.4	450.7	123.6	327.0	240.1	0.3
Zn	C	50	III	283.8	2.4	450.7	123.6	327.0	240.1	0.5
Zn	D	30	I	10.9	3.9	167.6	23.1	144.5	48.2	0.1
Zn	D	30	I	17.5	3.9	167.6	23.1	144.5	48.2	0.1
Zn	D	30	I	40.7	3.9	167.6	23.1	144.5	48.2	0.6
Zn	D	30	I	53.5	3.9	167.6	23.1	144.5	48.2	0.9
Zn	D	30	I	127.2	3.9	167.6	23.1	144.5	48.2	1.2
Zn	D	30	I	175.7	3.9	167.6	23.1	144.5	48.2	1.3
Zn	D	30	I	235.8	3.9	167.6	23.1	144.5	48.2	1.3
Zn	D	30	I	385.4	3.9	167.6	23.1	144.5	48.2	1.0
Zn	E	30	I	8.7	3.6	168.2	23.2	144.9	48.4	0.0
Zn	E	30	I	24.7	3.6	168.2	23.2	144.9	48.4	0.0
Zn	E	30	I	37.5	3.6	168.2	23.2	144.9	48.4	0.1
Zn	E	30	I	48.3	3.6	168.2	23.2	144.9	48.4	0.5
Zn	E	30	I	123.0	3.6	168.2	23.2	144.9	48.4	1.1
Zn	E	30	I	168.4	3.6	168.2	23.2	144.9	48.4	1.2
Zn	E	30	I	206.2	3.6	168.2	23.2	144.9	48.4	1.3
Zn	E	30	I	292.5	3.6	168.2	23.2	144.9	48.4	0.9
Zn	F	30	I	1.4	2.3	167.4	23.1	144.3	49.3	0.0
Zn	F	30	I	3.3	2.3	167.4	23.1	144.3	49.3	0.0
Zn	F	30	I	23.8	2.3	167.4	23.1	144.3	49.3	0.1
Zn	F	30	I	35.8	2.3	167.4	23.1	144.3	49.3	0.3
Zn	F	30	I	61.9	2.3	167.4	23.1	144.3	49.3	0.8
Zn	F	30	I	84.7	2.3	167.4	23.1	144.3	49.3	0.9

Zn	F	30	I	96.6	2.3	167.4	23.1	144.3	49.3	1.1
Zn	F	30	I	126.0	2.3	167.4	23.1	144.3	49.3	1.2
Zn	F	30	I	195.9	2.3	167.4	23.1	144.3	49.3	1.2
Zn	D	30	II	53.6	3.9	335.3	46.3	289.0	144.6	0.1
Zn	D	30	II	58.7	3.9	335.3	46.3	289.0	144.6	0.0
Zn	D	30	II	127.2	3.9	335.3	46.3	289.0	144.6	1.0
Zn	D	30	II	157.3	3.9	335.3	46.3	289.0	144.6	1.2
Zn	D	30	II	235.8	3.9	335.3	46.3	289.0	144.6	1.2
Zn	D	30	II	321.7	3.9	335.3	46.3	289.0	144.6	1.1
Zn	E	30	II	48.3	3.6	335.9	46.4	289.5	144.6	0.0
Zn	E	30	II	76.8	3.6	335.9	46.4	289.5	144.6	0.1
Zn	E	30	II	123.0	3.6	335.9	46.4	289.5	144.6	0.6
Zn	E	30	II	143.9	3.6	335.9	46.4	289.5	144.6	0.8
Zn	E	30	II	206.2	3.6	335.9	46.4	289.5	144.6	0.9
Zn	E	30	II	256.7	3.6	335.9	46.4	289.5	144.6	0.9
Zn	F	30	II	61.9	2.3	334.9	46.2	288.7	146.6	0.0
Zn	F	30	II	77.1	2.3	334.9	46.2	288.7	146.6	0.1
Zn	F	30	II	84.7	2.3	334.9	46.2	288.7	146.6	0.1
Zn	F	30	II	90.9	2.3	334.9	46.2	288.7	146.6	0.3
Zn	F	30	II	126.0	2.3	334.9	46.2	288.7	146.6	1.1
Zn	F	30	II	153.1	2.3	334.9	46.2	288.7	146.6	0.9
Zn	D	30	III	57.8	3.9	503.4	69.5	433.9	241.6	0.0
Zn	D	30	III	127.2	3.9	503.4	69.5	433.9	241.6	0.2
Zn	D	30	III	231.0	3.9	503.4	69.5	433.9	241.6	0.9
Zn	D	30	III	321.7	3.9	503.4	69.5	433.9	241.6	1.0
Zn	E	30	III	70.6	3.6	503.8	69.6	434.2	241.3	0.0
Zn	E	30	III	123.0	3.6	503.8	69.6	434.2	241.3	0.0
Zn	E	30	III	205.3	3.6	503.8	69.6	434.2	241.3	0.6
Zn	E	30	III	256.7	3.6	503.8	69.6	434.2	241.3	0.9
Zn	E	30	III	338.3	3.6	503.8	69.6	434.2	241.3	1.1
Zn	F	30	III	71.4	2.3	502.2	69.3	432.9	243.5	0.0
Zn	F	30	III	84.7	2.3	502.2	69.3	432.9	243.5	0.0
Zn	F	30	III	124.3	2.3	502.2	69.3	432.9	243.5	0.3
Zn	F	30	III	153.1	2.3	502.2	69.3	432.9	243.5	0.4
Zn	F	30	III	209.5	2.3	502.2	69.3	432.9	243.5	0.9
Zn	G	10	I	1.5	3.2	190.6	7.6	183.0	48.4	0.0
Zn	G	10	I	4.4	3.2	190.6	7.6	183.0	48.4	0.1
Zn	G	10	I	32.9	3.2	190.6	7.6	183.0	48.4	0.2
Zn	G	10	I	59.7	3.2	190.6	7.6	183.0	48.4	0.3
Zn	G	10	I	68.5	3.2	190.6	7.6	183.0	48.4	0.5
Zn	G	10	I	110.4	3.2	190.6	7.6	183.0	48.4	0.5
Zn	G	10	I	256.1	3.2	190.6	7.6	183.0	48.4	0.9
Zn	H	10	I	2.9	3.5	185.8	7.4	178.3	48.3	0.0
Zn	H	10	I	6.7	3.5	185.8	7.4	178.3	48.3	0.0
Zn	H	10	I	17.0	3.5	185.8	7.4	178.3	48.3	0.2
Zn	H	10	I	26.3	3.5	185.8	7.4	178.3	48.3	0.3
Zn	H	10	I	48.6	3.5	185.8	7.4	178.3	48.3	0.9
Zn	H	10	I	65.6	3.5	185.8	7.4	178.3	48.3	0.9
Zn	H	10	I	207.4	3.5	185.8	7.4	178.3	48.3	1.1

Zn	I	10	I	5.0	3.6	190.5	7.6	182.9	45.0	0.0
Zn	I	10	I	22.6	3.6	190.5	7.6	182.9	45.0	0.2
Zn	I	10	I	27.0	3.6	190.5	7.6	182.9	45.0	0.2
Zn	I	10	I	42.1	3.6	190.5	7.6	182.9	45.0	0.6
Zn	I	10	I	67.7	3.6	190.5	7.6	182.9	45.0	1.0
Zn	I	10	I	77.9	3.6	190.5	7.6	182.9	45.0	0.9
Zn	I	10	I	232.5	3.6	190.5	7.6	182.9	45.0	1.1
Zn	I	10	I	388.5	3.6	190.5	7.6	182.9	45.0	1.3
Zn	G	10	II	4.4	3.2	380.7	15.2	365.5	144.8	0.0
Zn	G	10	II	93.4	3.2	380.7	15.2	365.5	144.8	0.4
Zn	G	10	II	154.5	3.2	380.7	15.2	365.5	144.8	0.6
Zn	G	10	II	228.1	3.2	380.7	15.2	365.5	144.8	1.0
Zn	G	10	II	256.1	3.2	380.7	15.2	365.5	144.8	1.0
Zn	G	10	II	287.4	3.2	380.7	15.2	365.5	144.8	0.7
Zn	H	10	II	6.7	3.5	375.8	15.0	360.8	144.7	0.0
Zn	H	10	II	48.6	3.5	375.8	15.0	360.8	144.7	0.5
Zn	H	10	II	55.9	3.5	375.8	15.0	360.8	144.7	0.6
Zn	H	10	II	112.2	3.5	375.8	15.0	360.8	144.7	0.9
Zn	H	10	II	159.7	3.5	375.8	15.0	360.8	144.7	1.0
Zn	H	10	II	207.4	3.5	375.8	15.0	360.8	144.7	1.1
Zn	H	10	II	245.8	3.5	375.8	15.0	360.8	144.7	0.9
Zn	I	10	II	22.6	3.6	380.5	15.2	365.3	135.0	0.0
Zn	I	10	II	67.7	3.6	380.5	15.2	365.3	135.0	0.7
Zn	I	10	II	71.6	3.6	380.5	15.2	365.3	135.0	0.8
Zn	I	10	II	120.0	3.6	380.5	15.2	365.3	135.0	0.8
Zn	I	10	II	199.4	3.6	380.5	15.2	365.3	135.0	1.1
Zn	I	10	II	232.5	3.6	380.5	15.2	365.3	135.0	1.1
Zn	I	10	II	275.9	3.6	380.5	15.2	365.3	135.0	1.0
Zn	G	10	III	68.5	3.2	570.7	22.8	548.0	241.0	0.0
Zn	G	10	III	117.5	3.2	570.7	22.8	548.0	241.0	0.2
Zn	G	10	III	253.3	3.2	570.7	22.8	548.0	241.0	0.9
Zn	G	10	III	287.4	3.2	570.7	22.8	548.0	241.0	0.7
Zn	G	10	III	301.7	3.2	570.7	22.8	548.0	241.0	0.8
Zn	G	10	III	330.8	3.2	570.7	22.8	548.0	241.0	0.9
Zn	H	10	III	36.7	3.5	565.8	22.6	543.2	240.9	0.0
Zn	H	10	III	69.9	3.5	565.8	22.6	543.2	240.9	0.0
Zn	H	10	III	199.3	3.5	565.8	22.6	543.2	240.9	0.8
Zn	H	10	III	245.8	3.5	565.8	22.6	543.2	240.9	0.8
Zn	H	10	III	261.7	3.5	565.8	22.6	543.2	240.9	1.0
Zn	I	10	III	62.1	3.6	570.6	22.8	547.8	228.4	0.2
Zn	I	10	III	80.7	3.6	570.6	22.8	547.8	228.4	0.4
Zn	I	10	III	230.7	3.6	570.6	22.8	547.8	228.4	1.0
Zn	I	10	III	275.9	3.6	570.6	22.8	547.8	228.4	0.8
Zn	I	10	III	296.9	3.6	570.6	22.8	547.8	228.4	0.8
Zn	J	0	I	7.3	3.0	190.0	0.0	190.0	48.0	0.2
Zn	J	0	I	12.6	3.0	190.0	0.0	190.0	48.0	0.2
Zn	J	0	I	49.2	3.0	190.0	0.0	190.0	48.0	1.2
Zn	J	0	I	134.9	3.0	190.0	0.0	190.0	48.0	1.2
Zn	J	0	I	163.7	3.0	190.0	0.0	190.0	48.0	1.1

Zn	J	0	II	7.3	3.0	380.0	0.0	380.0	144.0	0.0
Zn	J	0	II	12.6	3.0	380.0	0.0	380.0	144.0	0.0
Zn	J	0	II	34.0	3.0	380.0	0.0	380.0	144.0	0.2
Zn	J	0	II	67.8	3.0	380.0	0.0	380.0	144.0	0.8
Zn	J	0	II	105.9	3.0	380.0	0.0	380.0	144.0	1.2
Zn	J	0	II	127.3	3.0	380.0	0.0	380.0	144.0	1.3
Zn	J	0	II	165.8	3.0	380.0	0.0	380.0	144.0	1.1
Zn	J	0	II	211.6	3.0	380.0	0.0	380.0	144.0	1.2
Zn	J	0	III	7.3	3.0	570.1	0.0	570.1	240.1	0.0
Zn	J	0	III	12.6	3.0	570.1	0.0	570.1	240.1	0.0
Zn	J	0	III	34.0	3.0	570.1	0.0	570.1	240.1	0.0
Zn	J	0	III	57.2	3.0	570.1	0.0	570.1	240.1	0.9
Zn	J	0	III	115.0	3.0	570.1	0.0	570.1	240.1	1.3
Zn	J	0	III	161.2	3.0	570.1	0.0	570.1	240.1	1.1
Zn	J	0	III	211.6	3.0	570.1	0.0	570.1	240.1	1.1