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Trace Metals in Stormwater: Alternative Best Management Practices

BY

Jennifer Mora

A research project report submitted in partial fulfillment
of the requirement for the degree of

MASTER OF SCIENCE
IN
CIVIL AND ENVIRONMENTAL ENGINEERING

Project Advisor:
Dr. Gwynn R. Johnson

Portland State University
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ABSTRACT

Heavy metals, such as copper (Cu) and zinc (Zn), are considered hazardous in natural waters due to their toxicity and non-biodegradability. The focus of this study is to use batch experiments to investigate the heavy metal (Cu and Zn) removal efficiency of perlite and Earthlite™ to improve in-situ filtration systems for stormwater catchment basins. Stormwater samples from two field sites in Portland, OR, chosen to represent a high-use commercial site and high-traffic urban road, were characterized to inform experimental design and compare to values found in literature. The Linear, Freundlich, and Langmuir isotherm models were used to describe equilibrium data and determine partitioning coefficients for single-metal batch studies. Both the Freundlich and Langmuir models fit most single metal batch systems, while Cu-Perlite, Zn-Perlite, and Zn-Earthlite™, were best fit by the Langmuir model, $R^2 = 0.9594; 0.9538; 0.9811$, respectively. Competitive adsorption behaviors for Cu and Zn were evaluated using a synthetic stormwater recipe where relative concentrations of Cu and Zn were maintained to be consistent with representative stormwater samples. Perlite showed a decrease in the sorption capacity of Cu and Zn in the presence of competing ions in solution. Earthlite™ showed no difference in the affinity for copper uptake between competitive and non-competitive batch experiments. Earthlite™ affinity for Zn decreased by two orders of magnitude in the competitive batch system. The results from this study will be applied to estimate filter lifetime for traditional and advanced stormwater filter systems. These results will inform experimental design in dynamic flow-through experiments using various filter media thereby improving filter design and implementation of stormwater best management practices.

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INTRODUCTION

Removal of heavy metals from stormwater effluent is an important research topic due to the increase in contamination of natural waters. Heavy metals, such as copper (Cu) and zinc (Zn), are not degradable and can bioaccumulate, adversely affecting the health and viability of salmon, a measure of water quality in the Pacific Northwest (Baldwin et al., 2003; Nason et al., 2011; Arabyarmohammadi et al., 2016). Of the many sources that contribute to metal loadings, including roofing, building siding, atmospheric deposition and oil leaks, brake pad wear is the biggest source of Cu and Zn in stormwater effluent (Nason et al., 2012). An example of the state of Oregon's regulatory requirements for stormwater treated effluent limits for TSS, Cu, and Zn are 100 mg L^{-1} , $22 \text{ } \mu\text{g L}^{-1}$, and $140 \text{ } \mu\text{g L}^{-1}$, respectively (EBS, personal communicate). It may be of interest to note, a study by Baldwin et al. (2002) placed the toxicity threshold for juvenile Coho salmon to be $2.3 - 3.0 \text{ } \mu\text{g L}^{-1}$, well below these treated effluent limits.

Of the different technologies used for removal of metals in solution, ion-exchange and adsorption mechanisms are proven to be highly effective and economical (Ghassabzadeh et al., 2010; Sari et al., 2007). Prefiltration systems, which consist of a customizable filter filled with filter media designed to target the pollutant of choice (Contech, 2017), are widely used in conjunction with pump and haul (e.g., the vacuum extraction, transport, and subsequent disposal of pollutants). The high costs associated with traditional pump and treat, in terms of disposal of removed solids, the energy cost, and large environmental footprint, motivate research on filter media to improve on-site filtration systems (EPA, 2009).

This study focuses on characterizing the performance of two filter media, perlite and Earthlite™. Perlite is a high porosity expanded volcanic rock that is economical and widely available (Ghassabzadeh et al., 2010) and is extensively used in stormwater catchment basins for removal of TSS, oil, and grease. Recent studies have shown perlite to have “fairly high” adsorption capacity for Cu (Ghassabzadeh et al., 2010) but few have examined heavy metal adsorption potential in a typical stormwater solution wherein the impact of competitive uptake may play a significant role in removal efficiencies. Deemed “an emerging and promising treatment technology,” biochars are increasingly investigated for removal of heavy metals in aqueous solutions (Park et al., 2015; Komkiene et al., 2016; Chen et al., 2011) though there is limited information available on the competitive adsorption of metals on biochars. Furthermore, the sorption potential of biochar is difficult to qualify given the variability in composition and type of organic material used as source materials. Earthlite™, a proprietary biochar made with hazelnuts, expanded shale, compost and oyster shells, is touted as ideal for removal of heavy metals due to its high porosity, high specific surface area and cation exchange capacity (Earthlite™, 2017).

Overall, the aim of this study is to investigate the heavy metal removal efficiency of perlite and Earthlite™ to improve in-situ filtration systems for stormwater catchment basins. The specific objectives are to: (1) characterize stormwater collected at various locations in Oregon to determine baseline concentrations for stormwater; (2) investigate the removal efficiency of perlite and Earthlite™ for copper and zinc; (3) determine the best-fit isotherm models to describe equilibrium data and estimate partitioning coefficients; and (4) evaluate the competitive adsorption behaviors of trace metals (copper and zinc) in perlite and Earthlite™.

MATERIALS AND METHODS

Stormwater Sample Collection

Stormwater samples were collected and analyzed in this study from two field sites, TriMet MERLO and downtown Portland (PSU 4th Avenue and Harrison), each chosen for their high potential for heavy metal loadings based on their respective land use characteristics. Samples were collected from each site with the goal of characterizing stormwater effluent for “real world” environmental samples to inform future experimental design and compare to values found in literature.

TriMet MERLO, a garage facility and corporate headquarters for the greater Portland Metro bus service provider, was chosen to represent a high-use commercial site. Stormwater samples were collected from stormwater catchment basins at three locations on the TriMet MERLO site; specifically, the parking lot (A), bus route (B), and bus wash (C). Two of the locations, A and B (the parking lot and bus route, respectively), were of interest in terms of heavy metal concentrations considering the respective catchment basins had not been maintained for approximately 6 months, evidenced by the observed indicators of anoxic activity, strong odors of sulfur and methane. Sludge samples (as well as stormwater samples) were collected from these sites for testing and analysis. Grab samples of stormwater effluent were collected using 20 L polypropylene containers per Stormwater Methods and Procedures protocol 1060B. Specifically, the stormwater catchment basin was thoroughly mixed and a pre-rinsed bucket was used to collect a representative sample. The bucket sample was thoroughly mixed and funneled into a 20 L polypropylene container for transport and storage. Grab samples of sludge from sites A and B were collected and transported in plastic food-grade buckets for analysis in the lab.

The downtown Portland sampling location (PSU 4th Avenue and Harrison) is a busy intersection in downtown Portland, adjacent to a highway offramp and heavy use bus stop, chosen to represent a high traffic urban road. Grab samples, used to represent a “snapshot” in both time and space” (Standard Methods, 1060B), were collected using a 500-ml polypropylene bottle and 20-L polypropylene container for long-term storage and transport. Polypropylene bottles were used to collect samples due to suspected preferential sorption of metals onto glass surfaces suggested in the literature.

Grab samples for each site were thoroughly mixed and separated into discreet acid-washed sample containers upon arrival in the laboratory. Trace metal grade nitric acid was used to acid fix samples to pH<2 for long-term storage (<6 months) and sample preservation per Standard Methods for the Examination of Water and Wastewater 1060 A. The volume of acid necessary to achieve target pH<2 was determined by testing a sample of comparable total volume. The determined volume of acid was added to relevant samples to acid fix at pH<2 and recorded to account for dilution of original sample concentrations. Prior to acid fixing, the pH of environmental samples was measured using the Expandable IonAnalyzer EA920 at 25 °C. Sample pH was recorded to inform future experimental design and compare to values found in literature.

Sample Characterization and Digest Procedures

Samples were tested (with the assistance of researchers in our stormwater research group) for total solids (TS), total dissolved solids (TDS), and total suspended solids (TSS) per Standard Methods for the Examination of Water and Stormwater 2540 B-D (the concentrations for total dissolved solids (TDS) were below reproducible levels using this method and subsequently estimated by mass balance). Particles greater than 0.25 inches were removed from samples prior to filtration to promote sample homogeneity. The filtering apparatus used for this study consisted of a 300-ml Kimble Kontes LLC Glass funnel with a glass base (47 mm), a 2000-ml graduated flask and Air Admiral Cole Palmer Vacuum (Model No. P79202-00 115V).

Three discrete samples and a sample blank were tested for each of the four study sites. Total suspended solids (method 2540 D) were determined by filtering samples and measuring the solids remaining on the filter after drying in the oven at 105 °C. The mass of individual Millipore filters (1.2-µm particle retention) and aluminum weighing boats were recorded using a Mettler AJ100 analytical balance. Original sample containers were thoroughly shaken (approximately 10 seconds) to ensure discrete samples were homogeneous and representative. A small volume of nanopure water was used to pre-wet the filter prior to filtering the samples. Samples were poured into the filtering apparatus in a steady stream to ensure stability of the filter. Each filter was rinsed with three independent 10-ml aliquots of nanopure water in between samples and allowed to continue suction for 3 min after filtration to allow for removal of excess nanopure water. Filters were removed and placed in the pre-weighed aluminum weigh boats and dried at 105 °C in a VWR International 1350F convection oven for approximately one hour. After drying, samples were cooled and placed in a desiccator with White Drierite desiccant. Samples were dried, cooled, desiccated, and weighed until there was less than 4 percent difference between consecutive weights. Samples that did not meet this criterion were omitted from the results. Total suspended solids (TSS) were calculated using Equation 1 where A is the weight of the filter plus dried residue (mg) and B is the weight of the filter (mg).

$$TSS \left(\frac{mg}{L} \right) = \frac{(A-B) \times 1000}{sample\ volume(ml)} \quad (1)$$

Total solids (method 2540 B) were determined by evaporating a blank and three well-mixed homogeneous discrete volumes of sample from each site in a beaker using a VWR International 1350F convection oven. Samples were dried at approximately 98 °C to avoid cross-contamination or mass loss due to splattering. Samples were dried, cooled, desiccated, and weighed until there was less than 4 percent difference between consecutive weights. Samples that did not meet this criterion were omitted from the results. Total solids were calculated using Equation 2 where A is the weight of the beaker plus dried residue (mg) and B is the weight of the beaker (mg).

$$TS \left(\frac{mg}{L} \right) = \frac{(A-B) \times 1000}{sample\ volume(ml)} \quad (2)$$

Total dissolved solids (method 2540 C) were determined by evaporating a composite sample of the filtrate from each study site in a VWR International 1350F convection oven at 180 °C. Each composite sample consisted of the filtrate, including rinse water used after filtration, of the discrete samples used in TSS analysis (described above) for each site. Samples were dried, cooled, desiccated, and weighed until there was less than 4 percent difference between consecutive weights. Samples that did not meet this criterion were omitted from the results. Total dissolved solids were calculated using Equation 3 where A is the weight of the beaker plus dried residue (mg) and B is the weight of the beaker (mg).

$$TDS \left(\frac{mg}{L} \right) = \frac{(A-B) \times 1000}{sample\ volume(ml)} \quad (3)$$

Samples were tested for total recoverable elements, defined as “all metals inorganically bound, both dissolved and particulate,” following Standard Methods 3030A, to fully characterize metal concentrations in stormwater samples. Three discrete samples from the PSU 4th Avenue and Harrison site (4A, 4B, and 4C) were tested, along with two synthetic stormwater samples (synTA and synTB) created using sludge collected from the TriMet Merlo field site (sludges TA5 and TB5, respectively). Synthetic stormwater samples were created by blending a subsample of the respective sludge (TA5 from TriMet Merlo Parking Lot or TB5 from Trimet Merlo Bus Route) with a measured volume of synthetic rainwater (described below), targeting the measured total solids from the respective field site’s stormwater samples (357 mg L⁻¹ and 128 mg L⁻¹ for the parking lot and the bus route, respectively).

Acid preserved sample aliquots (200 ml) were transferred to a 250 ml Griffin beaker where 4 ml of (1:1) nitric acid:water and 2 ml of (1:1) HCl:water were added to each sample. The samples were evaporated on a hot plate set to approximately 85 °C until the sample volume was reduced to 20 ml and then allowed to gently reflux for 30 min. Upon cooling, the samples were quantitatively transferred to a 50 ml volumetric flask, brought to volume using nanopure water, and analyzed for total recoverable metals using Shimadzu Atomic Absorption Spectrophotometer AA-7000. Samples that exceeded the linear range were diluted with nanopure water and reanalyzed.

Filter Media Characterization: Particle Size Analysis

A particle size analysis was completed with help from our stormwater research group for the filter media of interest per ASTM C136-01 Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates and ASTM D2487-10 Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System). ASHTO E-11 sieves ¼”, 4, 6, 10, 40 and 200 (6.3 mm, 4.75 mm, 3.35 mm, 2.00 mm, 0.425 mm and 0.075 mm, respectively) were used to define the particle size distribution. A 250-ml beaker was used as the standard volume of measure to compare particle sizes between perlite and Earthlite™. The samples were shaken on a mechanical sieve shaker for 5 min to minimize formation of fine particles through degradation of perlite. The percentages passing, based on the total mass of the initial sample, were calculated to determine the sample particle size distribution.

Synthetic Rainwater

A synthetic rainwater solution recipe was derived by our stormwater research group from published studies by Jung and Werby (Jung, 1958; Jung et al., 1958) based on concentrations of inorganic ions in rainwater across the United States. The studies focused on ammonium, calcium, potassium, sodium, chloride, nitrate, and sulfate as ions of interest. Data for Portland, Oregon, was extrapolated from maps of ion concentration in rainwater. A stock solution of 1000x rainwater (see Table 1) was made using lab grade reagents and nanopure water. Nanopure water was mixed on a IKA-Vibrax-VXR orbital shaker at a speed sufficient to break the surface of the water and air-equilibrate for approximately 12 hours prior to use in the rainwater solution. 1X rainwater solutions were made by diluting the 1000x Rainwater stock using air-equilibrated nanopure water. A charge balance of the extrapolated concentrations resulted in concentrations for most ions, except for sodium and nitrate, to be within 10 percent error from reported concentrations for Portland, OR (Table 2). Concentrations for sodium and nitrate were adjusted from reported values to improve solubility of ions in solution. The rainwater recipe balanced at a pH of 5.6.

Table 1. Stock solution recipe of synthetic rainwater.

Available Chemicals	1000x Solution in 3 Liter						
	Ammonium Sulfate	Sodium Sulfate	Potassium Sulfate	Potassium Chloride	Calcium Nitrate	Sodium Nitrate	Calcium Chloride Dihydrate
Formula	(NH ₄) ₂ SO ₄	Na ₂ SO ₄	K ₂ SO ₄	KCl	Ca(NO ₃) ₂ 4H ₂ O	NaNO ₃	CaCl ₂ 2H ₂ O
FW (g)	132.14	142	174.27	74.55	236.15	84.99	147.01
Equivalents	2.00E+00	2.00E+00	2.00E+00	2.00E+00	2.00E+00	2.00E+00	2.00E+00
Equivalent weight (g)	6.61E+01	7.10E+01	8.71E+01	7.46E+01	1.18E+02	8.50E+01	7.35E+01
Solubility in 100g H ₂ O	76.4 g/100 g			35.5 g			
mols in 1 gram	7.57E-03	7.04E-03	5.74E-03	1.34E-02	4.23E-03	1.18E-02	6.80E-03
x grams	0.6688	2.1091	0	0.3696	0	0.2495	2.0909
Normality	0.0101	0.0297	0	0.005	0	0.0029	0.0284
mols in x gram	5.06E-03	1.49E-02	0.00E+00	4.96E-03	0.00E+00	2.94E-03	1.42E-02
							0.00E+00

Table 2. Ion concentrations in synthetic rainwater compared to those reported in the literature.

Cations	Formula	MW (g)	Junge Conc	Actual Concentration	Actual Concentration	Actual Concentration	% Error from Junge
		(g)	(mg L ⁻¹)	(eq L ⁻¹)	(mg L ⁻¹)	(mmol L ⁻¹)	
Ammonium	NH ₄ ⁺	18	0.06	3.37E-06	0.061	0.003374	1.2
Calcium	Ca ⁺⁺	40.08	0.19	9.48E-06	0.19	0.004741	0
Potassium	K ⁺	39.1	0.06	1.65E-06	0.065	0.001653	7.7
Sodium	Na ⁺	22.99	0.48	1.09E-05	0.25	0.01088	47.9
Hydrogen	H ⁺	1.0079		6.31E-07			
Anions							
Chloride	Cl ⁻	35.45	0.41	1.11E-05	0.395	0.011134	3.7
Nitrate	NO ₃ ⁻	62	0.0975	9.79E-07	0.061	0.000979	37.8
Sulfate	SO ₄ ⁻⁻	96.06	0.67	1.33E-05	0.638	0.006638	4.8
Hydroxide	OH ⁻			1.58E-08			

Analytical Procedures

A Mettler AJ100 (range 0.0001 – 105 g) was used for stock standard solutions and early experiments. A Mettler PJ3600 Delta Range analytical balance (0.01 – 3000 g) was used for masses that exceeded the Mettler AJ100 range. The Ohaus Adventurer AX 324 analytical balance (range 0.0001 – 320 g) was used for standards, sample dilutions, and mass in evaporative extractions. An Expandable ionAnalyzer EA920 (range 2.00 – 14.00 +/- 0.5) and Hanna Instrument HI 98190 pH/ORP meter (range - 2.000 – 20.0000 +/- 0.1 pH accuracy at 25 degrees C) were used to measure pH. The Shimadzu Atomic Absorption Spectrophotometer AA-7700 was used for analysis of trace metal concentrations in stormwater samples. The instrument was calibrated by conducting a line search/beam balance operation using the high standard concentration of the respective analyte range (8 mg L⁻¹ for Cu and 2 mg L⁻¹ for Zn). Burner height was set to 7 mm per specifications in the Shimadzu Atomic Absorption Spectrophotometer AA-7000 Series Instruction Manual. Analysis was completed using a hollow cathode and deuterium lamp, for analysis of atomic absorption plus background and background, respectively. Rinse water blanks were adjusted (pH and background ion concentrations) to match tested sample matrix. A Central Scientific CAT No 16674 115V hot plate was used for sample digests. An IKA-VIBRAX-VXR orbital shaker was used to air-equilibrate nanopure water and thoroughly mix rainwater solutions. A Lab-line orbit shaker bath, Model 3540, was used for batch experiment procedures and a Barnstead NANOpure-DiamondTM system (Model No. D11901) was used to filter and purify nanopure water used in the experiments.

Evaporative Concentrating

Sample concentrations below AAS instrument detection limits were reduced in volume by evaporation in a VWR International 1350F convection oven at 105 °C. Sample bottles were weighed using Ohaus Adventurer AX324 analytical balance, in addition to pre- and post-evaporation masses, to calculate sample concentrations. Due to formation of precipitates upon evaporation, samples were acidified by addition of trace metal grade nitric acid to pH<2. The volume of acid necessary to achieve target pH<2 was determined by testing a sample of comparable total volume. The determined volume of acid was added to relevant samples to acid fix at pH<2 and recorded to account for dilution of original sample concentrations. Acidified samples reflect free metal ion concentrations and are marked accordingly.

Standardization and QA/QC

Stock standard solutions (500 and 1000 mg L⁻¹) were made using the relevant mass of Cu (CuCl₂*2H₂O) and Zn (ZnCl₂) metal salts in a 2% nitric acid solution using trace metal grade acid and nanopure water. The linear range of the Shimadzu AAS instrument was established and tested regularly using a nine-point calibration procedure. The calibration standards were used to qualify the high, mid,

and lower limits of the linear range for each target analyte. The linear range determined for Cu and Zn equaled 0.1 – 8 mg L⁻¹ and 0.1 – 2 mg L⁻¹, respectively.

A lab reagent blank (LRB), multiple lab fortified blanks (Cu/Zn, Cu-H, Cu-L, Zn-H, Zn-L), and a lab fortified matrix (4B*), a sample duplicate spiked with a known concentration using 500 mg L⁻¹ stock solution, were processed with each batch of digest samples to test for quality control. The percent recovery was calculated for each analyte to determine the accuracy of the procedure using Equation 4 where *R* is percent recovery, *LFB* is the lab fortified blank, *LRB* is the laboratory reagent blank and *s* is the concentration equivalent of analyte added to fortify the LFB solution. The percent recovery of the analyte should fall within 85 – 115%. Experimentally derived concentrations were compared to ALS lab tested samples for validation.

$$R = \frac{LFB - LRB}{s} \times 100 \quad (4)$$

Batch Procedures

Batch experiments were used to qualify the adsorption of heavy metals, Cu and Zn, onto perlite and Earthlite™ filter media. The experimental design is consistent with the constant soil:solution method detailed in protocol EPA 530/SW-87/006 F (EPA Batch Type Procedures for Estimating Soil Adsorption of Chemicals).

Filter media were prepared for batch testing based on physical characteristics and measured particle size distributions. Perlite particles passing through ASHTO E-11 sieve # 10 (2 mm) and retained on sieve #40 (0.425 microns) were used throughout these experiments. A grab sample of Earthlite™ was collected from the source bag (Sunmark Environmental Services) after thoroughly mixing and used as received for particle size analysis and batch testing.

Six discrete aqueous-phase concentrations (*C*₀) were used in “single metal” batch experiments (approximately 1, 10, 25, 50, 75, and 100 mg L⁻¹). These initial concentrations were created by diluting a 1000 mg L⁻¹ stock using synthetic rainwater. Competitive sorption batch experiments (i.e., “multiple metal” batch experiments) were designed using a synthetic stormwater recipe reflecting relative concentrations of Cu and Zn as measured in the stormwaters collected for this study (TriMet MERLO and PSU 4th Avenue and Harrison). The initial concentrations (approximately 10/25, 25/62.5, 50/125 mg L⁻¹ Cu/Zn, respectively) were diluted from 1000 mg L⁻¹ stock synthetic rainwater. Each solution was adjusted to pH 6.2 - 6.4 using trace metal grade HNO₃ or NaOH reflecting the average pH of stormwater collected in this study. The volume added to adjust sample pH were recorded to account for dilution of original sample concentrations.

All batch experiments in this study were based on a 1:10 soil:solution ratio. Five discrete samples, in addition to a positive and negative control, were run for each *C*₀ concentration. Each acid-washed polypropylene bottle was weighed before addition of the filter media (10 g) and pH-adjusted *C*₀ solution (100 g). The negative control, testing for background conditions or contaminated media, consisted of only synthetic rainwater and media. The positive control, testing for mass loss through adsorption to the bottles and overall stability of the target metal with the synthetic rainwater solution, consisted of filter media in a solution of synthetic rainwater and respective target metal.

Samples were set to mix at room temperature in an orbital shaker at approximately 75 rpm for 24 hours to achieve chemical equilibrium. Per EPA 530/SW-86/006-F, “the equilibration time should be the minimum amount of time needed to establish a rate of change of the solute concentration in solution equal

or less than 5% per 24-hour interval” (EPA, 1992). The final mass of each bottle was recorded before and after the 24-hour equilibration time to account for mass loss in the system.

Following the 24 hour equilibration time, samples were allowed to settle gravimetrically for 1-2 hours, samples were filtered using Whatman 40 filters, and the eluent pH was recorded to account for changes in the sample matrix prior to analysis using Shimadzu Atomic Absorption Spectrophotometer AA-7000 (AA-Flame). Samples that exceeded the linear range of the AA-Flame were diluted with pH-adjusted (6.2 – 6.4) nanopure water and reanalyzed. The amount of solute adsorbed per mass of adsorbent (S) was calculated by mass balance using Equation 5.

$$S = \frac{C_o - C_{EQ}}{m} * (V) \quad (5)$$

where S is the sorbed-phase concentration (mass of solute sorbed relative to mass of sorbent, $\mu\text{g g}^{-1}$), C_o is the analytically determined initial solute concentration in solution (mg L^{-1}), C_{EQ} is the final, aqueous-phase equilibrium concentration of the solute (mg L^{-1}), and V equals the volume of solution (mL). The resulting percent change in concentration measured after equilibrating for approximately 24 hours was calculated using Equation 6.

$$\% \Delta C = \frac{C_i - C_{EQ}}{C_i} * 100 \quad (6)$$

where $\% \Delta C$ equals the percent change in solute concentration, C_i is the analytically determined initial solute concentration in solution (mg L^{-1}), and C_{EQ} is as described previously.

Data Analysis

Adsorption isotherms were used to describe equilibrium data as a “graphic representation showing the amount of adsorbent as a function of the equilibrium concentrations of the solute” (EPA, 1992). This study compares measured results of batch sorption experiments using the Langmuir, the Freundlich, and the Linear isotherm models to describe equilibrium data and determine partitioning coefficients. The Langmuir (defined in Equation 8) and Freundlich (defined in Equation 9) models were linearized to facilitate analysis as shown below. The coefficient of determination (R^2) was calculated for each modeled equation to determine goodness of fit.

The traditional Langmuir sorption isotherm wherein there is an assumed maximum amount of available sorption sites on a given adsorbent is defined by Equation 8a.

$$S = \frac{K_L M C_{EQ}}{(1 + K_L C_{EQ})} \quad (8a)$$

where S represents the concentration of sorbate per mass of adsorbent (mg g^{-1}), K_L is called the Langmuir constant and is often related to the capacity or affinity of the adsorbent (L mg^{-1}), M represents the adsorption maximum of the adsorbent ($\mu\text{g g}^{-1}$), and C_{EQ} equals the measured equilibrium concentration of solute in solution (mg L^{-1}). The traditional linearized Langmuir isotherm is shown in Equation 8b.

$$\frac{C_{EQ}}{S} = \frac{1}{K_L M} + \frac{C_{EQ}}{M} \quad (8b)$$

where a plot of the relative concentration, C_{EQ}/S , versus C_{EQ} will yield a straight line if the Langmuir isotherm models the measured sorption data with a slope equal to $1/M$ and a y-intercept equal to $1/K_L M$.

The Freundlich sorption isotherm is an empirical relationship wherein it is assumed that the sorbent is composed of many different sorption sites (i.e., heterogeneous in nature) all having different sorption/binding energies. The model is defined by Equation 9a.

$$S = K_f C_{EQ}^n \quad (9a)$$

where S and C_{EQ} are as defined above, K_f is the Freundlich constant, related to the capacity or affinity of the adsorbent, and n equals the Freundlich exponent, an indicator of the diversity of adsorption binding energies for the heterogeneous sorbent. The linearized Freundlich is shown in Equation 9b.

$$\log(S) = \log K_f + n \log C_{EQ} \quad (9b)$$

where a log-log plot of the sorbed-phase concentration versus the measured equilibrium aqueous-phase concentration of solute will yield a straight line if the Freundlich model effectively describes the sorbent's uptake of solute with a slope equal to n and a y-intercept equal to $\log K_f$.

RESULTS

Stormwater Sample Characterization

Table 3 shows concentrations of pH, TSS, dissolved organic carbon (DOC), and trace metals as reported in the literature. Published values were based on the median range of heavy metal concentrations, DOC, and pH from samples collected at 22 sites throughout Oregon, 5 of which were in Portland (Nason et al., 2012). The higher median range for concentration of metals and dissolved organic carbon in Portland as compared to Oregon may be explained by Portland's higher population density relative to the other sites included in the study (e.g., Corvallis, Wemme, and Bend).

Table 3. Concentrations of heavy metals, TSS, and pH as reported for Oregon and Portland.

	Davis et al., 2000		Nason et al., 2012	
Water Quality	Total metal loadings		Median range for 22 sites in OR***	Median range for 5 sites in Portland, OR***
	(mg m ⁻² -yr)	(mg m ⁻² -day)	(mg L ⁻¹)	(mg L ⁻¹)
pH	--	--	6.76 - 6.92	6.24 - 7.15
TSS	--	--	26.1 - 163	23.1 - 118
DOC	--	--	2.5 - 7	5.88 - 9.97
Copper	24.3	0.0666	0.00908 - 0.0409	0.0368 - 0.0609
Zinc	216	0.5918	0.0586 - 0.162	0.106 - 0.219
Lead	0.22	0.0006	0.00686 - 0.018	0.011 - 0.0313
Cadmium	18	0.0493	BRL - 0.00068	0.037 - 0.074
			***Highway storm water runoff	

The average concentrations of total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS) measured from stormwater samples collected in this study at TriMet MERLO and in downtown Portland (PSU 4th and Harrison) are reported in Table 4. TSS levels in all samples, except for the TriMet MERLO parking lot (A), were within range of expected TSS concentrations in Oregon as compared to published reports (Nason et al., 2012; Davis et al., 2000). Specifically, measured TSS values (30.0 – 108 mg L⁻¹) for TriMet MERLO B, C and downtown Portland samples were consistent with published concentrations (23.1 – 118 mg L⁻¹) for highway runoff in Portland. TSS for the TriMet parking lot (A) samples was considerably higher than highway runoff samples and consistent with expectations given the conditions of the catchment basin, not maintained for 6 months, and the specific land use characteristics of the site. The automobile density, brakes, tires, and oil residue from a parking lot are all sources of heavy metals and TSS that can contribute to elevated concentrations compared to highway stormwater runoff.

Table 4. Measured TS, TSS, and TDS for stormwater collected in this study.

Site ID	Sample ID	TS	TSS	TDS
		(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)
Trimet MERLO	A	357 ± 2.4	326 ± 11	BDL
	B	128 ± 1.2	95.6 ± 0.3	58.0
	C	121 ± 0.65	30.0 ± 0.5	80.6
PSU 4th & Harrison	Millipore	90.6 ± 8.8	108 ± 1.9	66.3
	Whatman	138 ± 5.8	105 ± 1.1	

Summary results for the total recoverable metal concentrations, in mg L⁻¹, and percent recovery using EPA Digest 200.8 are shown in Table 3. Results from representative samples analyzed by ALS Environmental (a NELAP certified lab located in Kelso, WA) are also included for comparison in Table 5. Positive and negative controls were within the percent recovery limits (85 < %R < 115) established by the EPA protocol. The only internal control to approach the percent recovery limit (%R = 115.58) was the lab fortified matrix, 4B*. The quality of the digest procedure was not compromised considering sample 4B* is made up of the 4B sample matrix spiked with a known concentration of target metal, 5 and 2 mg L⁻¹ of Cu and Zn, respectively. As such, the percent difference reflects both the original sample concentration and the added concentration. A corrected percent difference for this value, accounting for the initial concentration, is 96.29% and 106.22% for Cu and Zn, respectively. These values are within the percent recovery limits for this procedure.

The results of total metals measured for three discreet subsamples collected in downtown Portland (PSU 4th and Harrison) were consistent in magnitude for both copper and zinc. Concentrations for this site ranged from approximately 20 - 30 µg L⁻¹ for Cu and 120 – 200 µg L⁻¹ for Zn. The detected total metal concentrations are consistent with those expected highway runoff heavy metal concentrations as reported in the literature (36.8 – 60.9 µg-Cu L⁻¹; 106 – 219 µg-Zn L⁻¹) in Portland, OR (Nason et al.,

2012). A comparison of the experimental concentrations to independent ALS Environmental lab results was designed to further validate the digest procedure reported in this study and to facilitate a comparison of synthetic stormwater solutions created by mixing volumes of sludge (collected at TriMet MERLO sampling stations) with synthetic rainwater.

Measured trace metal concentrations for synthetic stormwater samples created by mixing a measured volume of sludge (either sludge TA or TB, collected at TriMet MERLO parking lot (A) or at the bus route (B)) shows some variability in the total metals in solution depending on the sludge source (either A or B, for example). These results are as expected considering the variable total metal concentrations detected in those discrete sludge samples collected at the field sites. For example, the average concentration of total copper equaled approximately 50 and 130 mg kg⁻¹ for sludge A and B, respectively. Similarly, the average concentration of total zinc equaled approximately 220 and 1100 mg kg⁻¹ for sludge A and B, respectively. Mean concentrations of total recoverable metals and standard error for the samples analyzed in this study compared to those analyzed by an independent, certified laboratory show reproducibility in the methods and confidence in the results (see Table 6). As described above, the mean concentrations for the synthetic stormwater samples are reflective of the variability inherent in making a stormwater solution from sludge samples.

Particle Size Distribution

The particle size analysis data for perlite and Earthlite™ is shown in Figure 1. The weighted average particle size (D50) for perlite equaled 4.1 mm compared to 3 mm for Earthlite™. The effective size (D10), particle diameter corresponding to 10 percent finer, for perlite and Earthlite™ equaled 2.4 mm and 0.9 mm, respectively. The calculated uniformity coefficient value (D60/D10) for perlite, 2.3, is indicative of a poorly graded, uniform media where the particles are generally the same size. Conversely, Earthlite™ has a calculated uniformity coefficient, 5, that qualifies it as well graded or indicative of particle sizes that are distributed over a wide range. This experiment served to inform experimental design for batch experiments. Due to the wide availability, potential variability in perlite by vendor, and the interest in using the batch results to inform future column studies, a specific particle range (0.045 microns – 2 mm) was used for perlite batch experiments. Given the wide range of particle sizes in Earthlite™, a representative sample was used to fully qualify sorption behavior of this media.

Table 5. Total recoverable metals for collected stormwater and synthetic stormwater.

		Total Copper (µg L ⁻¹)		Total Zinc (µg L ⁻¹)		
Site ID	Sample ID	C _(ALS)	C _(PSU)	C _(ALS)	C _(PSU)	
TriMet MERLO	SynSW-TA1	22.2		93.8		
	SynSW-TA2	5.60		17.8		
	SynSW-TB1	25.1		206		
	SynSW-TB2	14.4		110.		
	A1	16.3		73.6		
	A2	21.1		96.1		
	B1	13.8		132		
	B2	8.75		89.7		
PSU 4th & Harrison	Subsample A	33.7		200.		
	Subsample B	31.1		181		
	Subsample C	32.0		181		
	Average	20.4	32.3	123	187	
Controls	Sample ID	Target (mg L ⁻¹)		Spiked	Measured C _(PSU)	%Recovery*
	4B*	Cu	5	4.85	4.70	96.90
		Zn	2	1.93	2.23	115.00
	Cu, Zn	Cu	5	4.77	4.60	96.50
		Zn	2	1.89	2.16	114.00
	Cu-H	5		4.97	4.68	94.20
		0.5		0.50	0.49	97.30
	Zn-H	2		1.92	2.11	110.
		0.5		0.48	0.54	112.00
	Blank	Cu	N/A	0.00	0.01	N/A
Zn		N/A	0.00	0.03	N/A	

*Percent Recovery limits per EPA 200.8: $85 < \%R < 115$

Table 6. Average concentrations of trace metals in stormwater samples.

	C_{MEAN} ($\mu\text{g g}^{-1}$)	
	Cu	Zn
PSU 4th & Harrison	32.3 +/- 0.78	187.40 +/- 6.52
PSU 4th & Harrison / ALS	27.51 +/- 2.95	161.64 +/- 16.2
TA / ALS	11.13 +/- 5.67	43.12 +/- 25.78
TB / ALS	17.98 +/- 3.54	142.09 +/- 32.27

Figure 1. Particle size distribution for Perlite and Earthlite™ with relative percentage of particles passing through based on particle size.

Filter Media Efficiency and Modeling

Batch experiments served to inform the relationship between heavy metal concentrations and the removal efficiency of the various filter media. The mean equilibrium concentrations of copper measured in solution, sorption determined by mass balance, and the resulting percent change in concentration per measured initial aqueous-phase concentration of copper are presented in Table 7. Similar results for zinc are presented in Table 8. The batch data for the five discrete aqueous samples tested at each concentration show these results to be reproducible as indicated by the magnitudes of the standard square error reported accordingly (see Tables 7 and 8). The measured initial concentrations of the trace metals are based on measured concentrations in solution and reflect mass loss through formation of precipitates,

for example, given that samples are filtered prior to analysis. As such, equilibrium concentrations for non-acidified samples reflect total dissolved metal ions.

Table 7. Summary of mean sorption, equilibrium concentrations, and filter removal efficiency (% concentration change) for Copper.

Single Metal Batch Experiments								
Sample ID	COPPER-PERLITE				COPPER-Earthlite™ **			
	C _{EQ} (mg L ⁻¹)		S (µg g ⁻¹)	% ΔConc.	C _{EQ} (mg L ⁻¹)		S (µg g ⁻¹)	% ΔConc.
	mean	std error			mean	std error		
1	0.085	0.0063	3.2	79	0.010	0.0034	4.0	97
10	0.51	0.072	80	94	0.026	0.0021	62	99.6
25	8.3	1.5	90	52	0.057	0.0025	240	99.8
50	38	0.82	87	18	0.090	0.0044	490	99.8
75	43	0.31	76	15	0.14	0.0038	710	99.8
100	67	0.43	88	12	0.16	0.0048	900	99.8
Competitive (Multiple Metal) Batch Experiments								
Sample ID	COPPER-PERLITE				COPPER-Earthlite™ **			
	C _{EQ} (mg L ⁻¹)		S (µg g ⁻¹)	% ΔConc.	C _{EQ} (mg L ⁻¹)		S (µg g ⁻¹)	% ΔConc.
	mean	std error			mean	std error		
Cu / Zn								
10 / 25	1.6	0.070	23	59	0.022	0.0020	57	99.6
25 / 62.5	17	0.50	53	24	0.047	0.0031	240	99.8
50 / 125	41	0.39	54	12	0.086	0.0068	440	99.8
**Equilibrium concentrations based on free metal ions.								

Sorption magnitudes increased as concentrations increased until sorption reached a maximum capacity at higher concentrations where sorption magnitudes stabilized for all single-metal batch experiments (except for Cu-Earthlite™). This trending behavior is consistent with the traditional Langmuir sorption isotherm wherein there is an assumed maximum amount of available sorption sites on a given adsorbent. The adsorption maximum of the adsorbent, *M*, derived by the Langmuir model for Cu-Perlite, Zn-Perlite and Zn-Earthlite was 85.30, 49.18, and 1064.63 µg g⁻¹, respectively. The difference in magnitudes of the adsorption maximum between Cu and Zn indicates perlite has a higher adsorption capacity for Cu as compared to Zn under these conditions. Sorption for the Copper-Earthlite™ batch was so effective that equilibrium concentrations exceeded the instrument lower detection limits and samples required evaporative concentrating for analytical detection. Due to formation of precipitates upon evaporation, samples were acidified and equilibrium concentrations and subsequent calculations reflect total metals in solution, which consist of total dissolved metals and total suspended metals (total dissolved metals reported in all other batch experimental results). The sorption values for these experiments are conservative considering non-acidified equilibrium concentrations would be lower, thus resulting in higher sorption values.

Table 8. Summary of mean sorption, equilibrium concentrations, and filter removal efficiency (% concentration change) for Zinc.

Single Metal Batch Experiments								
ZINC - PERLITE					ZINC-Earthlite™ **			
Sample ID	C _{EQ} (mg L ⁻¹)		S (µg g ⁻¹)	% ΔConc.	C _{EQ} (mg L ⁻¹)		S (µg g ⁻¹)	% ΔConc.
	mean	std error			mean	std error		
1	0.030	0.0059	5.5	95	0.024	0.0016	7.5	96.9
10	3.9	0.84	46	54	0.11	0.0045	104	99.0
25	17	0.40	52	23	0.42	0.031	260	98.4
50	38	0.31	50	12	1.3	0.10	490	97.4
75	70	0.55	47	6.3	2.9	0.26	710	96.1
100	99.9	0.20	36	3.5	7.5	0.89	950	92.7
Competitive (Multiple Metal) Batch Experiments								
ZINC-PERLITE					ZINC-Earthlite™ **			
Sample ID	C _{EQ} (mg L ⁻¹)		S (µg g ⁻¹)	% ΔConc.	C _{EQ} (mg L ⁻¹)		S (µg g ⁻¹)	% ΔConc.
	mean	std error			mean	std error		
Cu / Zn								
10 / 25	21	0.22	21.2	9.17	21	0.22	23	10
25 / 62.5	60	0.46	30.5	4.80	60	0.46	22	3.5
50 / 125	119	1.3	33.5	2.72	119	1.3	76	6.0
**Equilibrium concentrations based on free metal ions.								

To find the isotherm model that best fit the experimental data, comparisons of R^2 values were carried out between the Linear, the Freundlich, and the Langmuir isotherm models (see Table 9). Both Cu and Zn in perlite, in addition to Zn in Earthlite™, fit both the Freundlich and Langmuir models well, but were fit best by a Langmuir model for single metal batch experiments as determined by the coefficient of determination ($R^2 = 0.9594$; 0.9538 ; 0.9811 , respectively). The Cu-Earthlite™ system was best fit by the linear model, $R^2 = 0.9893$. Measured sorption versus equilibrium concentrations (sorption isotherms) along with the best fit models are shown in Figures 2 – 7. Both models fit data for the Zn-Earthlite™ system (Figure 7) well. The Freundlich model overestimates sorption at high concentrations for the Zn-Perlite system as seen in Figure 3. The Langmuir model overestimates sorption at low concentrations for the Cu Earthlite™ batch (Figure 4). Both perlite and Earthlite™ have a higher sorption capacity for Cu as compared to Zn, as can be seen in Figures 6 and 7. A plot of sorption versus equilibrium concentration with experimental data for all single metal batch experiments (Figure 8) further illustrates the difference in sorption behavior in perlite compared to Earthlite™, where maximum sorption values are less than $100 \mu\text{g g}^{-1}$ in perlite and greater than $900 \mu\text{g g}^{-1}$ in Earthlite™.

Table 9. Sorption coefficients, isotherm constants, and R^2 values for single-metal and competitive batch experiments in Perlite and Earthlite™ filter media.

Batch Exp.	Batch ID	Linear		Freundlich			Langmuir		
		K_d (L kg ⁻¹)	R^2	K_f (μg ⁽¹⁻ⁿ⁾ ml ⁽ⁿ⁾) g ⁻¹	n	R^2	K_L (L mg ⁻¹)	M (μg g ⁻¹)	R^2
Single-metal	CU_P	0.5333	0.8279	64.8819	0.0625	0.9270	0.6609	85.2954	0.9594
	ZN_P	0.3071	0.8098	22.5949	0.3244	0.7839	2.4093	49.1777	0.9538
	CU_E**	5880.3633	0.9893	12435.9536	1.4044	0.9748	0.6105	9584.0145	0.0382
	ZN_E	55.7440	0.9814	385.9897	0.5208	0.9790	0.8155	1064.6291	0.9811
Competitive	CU_P	0.6934	0.9243	20.9192	0.2756	0.8031	0.5694	54.6825	0.9481
	ZN_P	0.0996	0.7000	16.0894	0.1066	0.0230	-2.3361	18.9969	0.5555
	CU_E**	5255.1879	0.9604	13837.3055	1.3885	0.8793	-5.5776	-488.654	0.2909
	ZN_E	0.5519	0.8169	3.1407	0.5795	0.3313	0.0028	190.5515	0.0098

**Equilibrium concentrations based on free metal ions.

Plots of the experimental data with best fit models for the trace metals in competitive batch systems consist of 5 discrete samples at three relative concentrations of copper/zinc in solution (results not shown). These results allow for a comparison of relative magnitudes of sorption which may inform changes in the sorbing potential of each filter media due to competition. For example, in perlite, the maximum sorption value for copper in the presence of zinc is approximately half that measured for copper in single batch experiments (see Figure 9), an indication of the effects of competition. On the other hand, a comparison of the affinity of the sorbent, K_d , for Cu in Earthlite™ under competitive sorption conditions (5880.36 L kg⁻¹) versus non-competitive (5255.18 L kg⁻¹), suggests there is little to no effect for copper uptake to Earthlite™ due to competition (see Figure 11) since magnitudes are consistent and within the same order of magnitude.

Figures 2 – 5. Single metal batch data for Cu and Zn in perlite and EarthliteTM with best fit Freundlich, Langmuir and/or Linear isotherm models.

Figures 6 and 7. Experimental data means and standard error with best fit isotherm models for perlite and Earthlite™ with Cu and Zn (single metal batch experiments).

Figure 8. Perlite and Earthlite™ batch experimental data means and standard error with best fit isotherm models (single metal batch experiments).

Figures 9 and 10. Competitive and Non-Competitive experimental data means and best fit isotherms for perlite with Cu and Zn.

Figures 11 and 12. Competitive and Non-Competitive experimental data means and best fit isotherms for Earthlite™ with Cu and Zn.

DISCUSSION AND CONCLUSIONS

Tested sample concentrations agreed with published median range concentration values (Nason et al., 2012) of Cu, Zn, and TSS in Portland, OR. Tested concentrations ranged from 20 – 30 $\mu\text{g L}^{-1}$ and 180 – 200 $\mu\text{g L}^{-1}$ for Cu and Zn, respectively. To achieve regulatory limits for typical treated stormwater in Oregon, 26 percent removal of Cu and 22 – 30 percent removal of Zn are required for established stormwater effluent concentrations. Data from batch experiments qualifies a 79 percent removal of Cu by perlite in the single metal batch at the target concentration, 1 mg L^{-1} , and 59 percent in the competitive system at the target concentration, 10 mg L^{-1} . Perlite removal of Zn, 95 percent in the single metal batch for target concentration 1 mg L^{-1} , was much lower (9 percent) in the competitive system, at 25 mg L^{-1} .

Given the difference in tested, 25 mg L^{-1} , and expected concentrations, 0.2 mg L^{-1} , perlite removal of Zn is difficult to qualify in the competitive system in terms of those targeted effluent limits. However, it is expected that perlite removal of Zn will meet the necessary removal, 22 – 30 percent removal, to achieve established stormwater effluent concentrations. Earthlite™ removal of Cu was 99.8 percent in both the single metal and competitive batch experiments, whereas removal of Zn decreased from 97 percent in the single metal batch to less than 10 percent in the competitive batch. Competition from other metal ions in solution proved to be important to the sorption capacity for Cu and Zn in perlite, and Zn in Earthlite™. Both perlite and Earthlite™ are expected to meet the necessary removal at established stormwater effluent concentrations per batch results for single metal and competitive batch experiments. Overall, batch results demonstrate Earthlite™ drastically outperformed perlite in terms of sorption capacity.

Much of the sorption behavior observed in this study can be modeled by the application of the Langmuir model, indicative of monolayer sorption and surface homogeneity of the adsorbent, that worked to describe sorption in the Cu-perlite, Zn-perlite and Zn-Earthlite™ batch. Due to statistical reliability, the Langmuir model can be recommended to model sorption behavior of heavy metals in these systems. Behavior in the Cu-Earthlite™ batch, a conservative estimate based on concentrations of free metal ions, was best fit by the Linear model, where affinity of the adsorbent was not dependent on concentration. This behavior was consistent for both single metal and competitive batch systems where sorption likely consists of complexation with surface functional groups on biochar, particularly carboxyl groups for example. Competitive experimental data revealed that both perlite and Earthlite™ preferentially sorbed Cu over Zn. This could be explained by the difference in outer electron shells, where Zn has a full last sub orbital, $4s^2$, as compared to Cu, $4s^1$. For this reason, Cu is more effective at diffuse-layer and specific site binding as discussed by Breault et al. (1996).

The results from this experiment can be applied to estimate the filter lifetime for traditional and advanced stormwater filter systems. Sorption maximums measured and reported in this study can/will inform experimental design in dynamic flow-through experiments using perlite and Earthlite™ filter media. Additional research using complex stormwater matrices to qualify competition between other metals commonly found in stormwater effluent (e.g., aluminum and iron) would contribute to an improved assessment of filter design and implementation in stormwater best management practices.

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APPENDIX

Table 10. Data for particle distribution analysis of Perlite and Earthlite

Media	Perlite					
Test Duration	5 minutes					
Sieve Number	Mass Total (pan+media) (g)	Mass media (g)	% on Sieve	Cumulative %	Particle Size (mm)	Percent Passing
1/4	347.93	10.95	16.4	16.43	6.3	83.57
4	374.62	26.69	40.1	56.48	4.75	43.52
6	390.36	15.74	23.6	80.1	3.35	19.9
10	399.34	8.98	13.5	93.58	2	6.42
40	399.88	0.54	0.8	94.39	0.42	5.61
200	401.36	1.48	2.2	96.61	0.075	3.39
>200	403.62	2.26	3.4	100	<0.075	0
	Total Mass	66.64				
Weighted Average Particle Size		4.1	mm			
Ideal Column Diameter		207	mm			
		18	cm			
		7.1	inch			
d60 (size at 60% finer)		5.4	mm			
d10 (size at 10% finer)		2.4	mm			
u=d60/d10		2.3				
Media	Earthlite					
Test Duration	8 minutes					
Sieve Number	Mass Total (pan+media) (g)	Mass media (g)	% on Sieve	Cumulative %	Particle Size (mm)	Percent Passing
1/4	375.26	38.28	17.7	17.72	6.3	82.28
4.00	412.67	37.41	17.3	35.05	4.75	64.95
6.00	452.71	40.04	18.5	53.59	3.35	46.41
10.00	493.02	40.31	18.7	72.25	2	27.75
40.00	546.97	53.95	25	97.23	0.42	2.77
200.00	552.95	5.98	2.8	100	0.075	0
>200	552.95	0	0	100	<0.075	0
	Total Mass	215.97				
Weighted Average Particle Size		3	mm			
Ideal Column Diameter		152	mm			
		18	cm			
		7.1	inch			
d60 (size at 60% finer)		4.4	mm			
d10 (size at 10% finer)		0.9	mm			
u=d60/d10		5				

Table 11. Synthetic Stormwater Recipe for samples TA and TB tested for Total Recoverable Metals using EPA 200.8.

Sample ID	TS (mg L ⁻¹)	% Solids (solids sludge ⁻¹)	Sludge L-1 (mg)
A	357	36	996.4
B	128	20	647.2

Table 12. ALS results for metal concentrations of stormwater from TriMet MERLO (A, B, C), PSU 4th and Harrison and sludge from TriMet MERLO (A, B).

Sample ID	units	Cu	Zn
TPL-A5-5	($\mu\text{g g}^{-1}$)	21.1	96.1
TBR-B5-5	($\mu\text{g g}^{-1}$)	8.75	89.7
PSU-RW-4K	($\mu\text{g g}^{-1}$)	20.6	126
PSU-RW-4L	($\mu\text{g g}^{-1}$)	20.1	120
SLG A1-2	(mg Kg^{-1})	51	209
SLG-A2-2	(mg Kg^{-1})	55.4	234
SLG-B1-2	(mg Kg^{-1})	136	1170
SLG-B2-2	(mg Kg^{-1})	130	1100
ASYN 1-2	($\mu\text{g g}^{-1}$)	3.44	9.4
ASYN 2-2	($\mu\text{g g}^{-1}$)	7.75	26.2
BSYN 1-2	($\mu\text{g g}^{-1}$)	14.2	104
BSYN 2-2	($\mu\text{g g}^{-1}$)	14.7	116

Figure 13. Linearized Freundlich isotherm for single metal Cu-Perlite batch.

Figure 14. Linearized Freundlich isotherm for single metal Zn-Perlite batch.

Figure 15. Linearized Freundlich isotherm for single metal Cu-Earthlite™ batch.

Figure 16. Linearized Freundlich isotherm for single metal Zn-Earthlite™ batch.

Figure 17. Linearized Langmuir isotherm for single metal Cu-Perlite batch.

Figure 18. Linearized Langmuir isotherm for single metal Zn-Perlite batch.

Figure 19. Linear isotherm for single metal Cu-Earthlite™ batch.

Figure 20. Linearized Langmuir isotherm for single metal Zn- Earthlite™ batch.

Figures 21 – 24. Competitive batch data for Cu and Zn in perlite and Earthlite™ with best fit Freundlich, Langmuir and/or Linear isotherm models.