TOWSON UNIVERSITY

OFFICE OF GRADUATE STUDIES

"THE EFFECT OF ROAD SALT ON THE METAL BINDING ABILITY OF ADSORPTIVE MEDIA"

by

Ashley C. Whiting

A thesis

Presented to the faculty of

Towson University

in partial fulfillment

of the requirements for the degree

Master of Science

Department of Environmental Science

Towson University

Towson, Maryland 21252

August 2012

TOWSON UNIVERSITY

OFFICE OF GRADUATE STUDIES

THESIS APPROVAL PAGE

This is to certify that the thesis prepared by Ashley C. Whiting

entitled "The effect of road salt on the metal binding ability of adsorptive media"

has been approved by the thesis committee as satisfactorily completing the thesis requirements for the degree Master of Science.

Chair, Thesis Committee	Date 8/7/12
Committee Member	Date 7/30/12
Committee Member	Date 8-3-12
Janet V DeLany, Dean of Graduate Studies	Date 8-14-12

ACKNOWLEDGMENTS

Thank you to Imbrium Systems Inc. and Contech Construction Products Inc. for providing the adsorptive media used in this project. Scott Perry and Joel Garbon from Imbrium Systems Inc. provided advice and support regarding their media and the column study. Thank you to Dr. Joel Snodgrass for his help with statistical analyses. I owe many thanks to Mark Monk of Towson University for technical help with instrumentation.

ABSTRACT

"The Effect of Road Salt on the Metal Binding Ability of Adsorptive Media"

Ashley C. Whiting

The first part of this study included stormwater sampling from highway bridges. The second part of the project evaluated media to remove metals in the presence of salt. Media tested included eleven adsorptive materials. Batch tests were conducted with three levels of salt (none, 2.5, 5 g/L NaCl) mixed with a standard combination of metals (Cu, Zn, Pb, Ni, Cr) based on the values found in highway bridge runoff sampled. The third part was a column study designed to represent field conditions. Three media were tested with the same stormwater treatments. Effluent was compared based on salt levels and media type to identify the media with the best ability to absorb metals in the presence of salt. It was determined that Imbrium 10, a mixture of aluminum and iron oxides and fine sand, had the highest absorption capacity for zinc and copper in the presence of salt.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

Introduction

1.1 Background

The Chesapeake Bay has the highest watershed land area per volume of water of any estuary in the United States (Shuyler et al. 1995). Therefore, changes to land cover and land use in the Chesapeake Bay watershed have a large impact on the water quality of the bay. The increase of impervious surfaces through urbanization is drastically altering the hydrology of urban streams and rivers (Hatt et al. 2007). Impervious surfaces prevent ground water recharge and increase surface runoff to receiving waters, including streams and rivers (Dunne and Leopold 1978). Stormwater runoff is a leading cause of water quality degradation in urban areas around the world (Shuyler et al. 1995; Hatt et al. 2007). Highway runoff is a major non-point source of pollution to aquatic habitats (Gardner and Carey 2004). Numerous studies have found that stormwater runoff from highways often contains elevated concentrations of metals, dissolved ions, and suspended solids (Davis et al. 2001; Gardner and Carey 2004; Sansalone and Ying 2008; Camponelli et al. 2010). Automobiles are a major source of metals in highway runoff, including zinc and cadmium from tires, copper, lead, chromium, and manganese from brakes, and aluminum, copper, nickel, and chromium from engines (Sansalone et al. 1996). Metals are persistent pollutants because they do not degrade once they are released into the environment (Sansalone 1999; Davis et al. 2001). They are also potentially toxic to plants, animals, and humans (Sansalone 1999).

1.2 Road De-icing Salt

The Maryland State Highway Administration (MD SHA) has used an average of 255,022 tons of rock salt annually over the last twelve years (MD SHA 2011). Sodium chloride is the most commonly used road de-icing method due to its availability and affordability (MD SHA 2011, Bäckström et al. 2004, Pugh et al. 1996). Road de-icing salts are a major contributor to elevated concentrations of dissolved ions (Na^+ and Cl^-) in runoff during winter and spring months, and may contribute all year if groundwater infiltration occurs (Howard et al. 1993). Pitt et al. (1999) reported elevated chloride and sodium concentrations downgradient of stormwater infiltration devices in Maryland year-round, despite the fact that road salt application only occurred three to eight times a year. Further, it was noted that salt infiltration of groundwater may shift the major ion chemistry of the groundwater to a chloride-dominated system (Pitt et al. 1999). Pugh et al. (1996) found that road salt can contaminate soils up to 30 meters away from the roadside. Road salts are known to mobilize soil bound metals through ion exchange (Bäckström et al. 2004). Many studies have found positive correlations between electrical conductivity of soil pore water and concentrations of Zn, Cu, and Cd in groundwater (Bäckström et al. 2004).

1.3 Stormwater Treatment Methods

Currently, methods of stormwater treatment include retention/detention, infiltration, and constructed wetlands (Sansalone 1999). Pitt et al. (1999) reported many kinds of contaminants, including nutrients, pesticides, pathogens, heavy metals, and salts, may infiltrate the groundwater underneath stormwater infiltration devices. Pitcher et al. (2004) found that detention ponds are useful for filtering out suspended solids and particulate-bound pollutants, but not for removing dissolved metals and ions from stormwater runoff. Pitcher et al. (2004) determined that an ion exchange media is needed to remove dissolved metals from stormwater runoff. Infiltration systems and constructed wetlands are also documented best management practices (BMP) for stormwater treatment (Pitcher et al. 2004; Hatt et al. 2007). Most stormwater BMPs are designed to control water flow and reduce flooding by collecting stormwater runoff and allowing it to slowly infiltrate the ground (Genç-Fuhrman et al. 2007). These types of BMPs are effective at removing particulate pollutants, but not dissolved pollutants.

Adsorptive media is currently being utilized as a stormwater treatment method for dissolved pollutants. Sansalone (1999) describes an infiltration device that used iron oxide coated sand (OCS) as a filter for dissolved metals in stormwater runoff. Imbrium Systems Incorporated is a company that specializes in manufacturing adsorptive media for stormwater treatment and installing commercial stormwater management devices. Imbrium Systems Inc. is currently using their adsorptive media in unison with stormwater BMPs such as bioretention cells, or rain gardens, where a layer of adsorptive media is installed below the soil in a garden designed to infiltrate stormwater runoff. Another

BMP that Imbrium uses is stormwater filters that are installed underground near parking lots that contain adsorptive media. The stormwater runoff from the nearby impervious surfaces is channeled into the filter and is treated by the adsorptive media before reaching the environment.

1.4 Ion Exchange

The concept behind ion exchange media is that ions in solution are adsorbed onto the surface of the media. Adsorption is the accumulation of matter at the surface of a solid. This mechanism is different from absorption, in which matter permeates a solid, but does not attach to the surface. Adsorption is an efficient and economical method of wastewater treatment (Wu and Zhou 2009). Ion exchange is the replacement of an ion on a solid with an ion from a solution. The affinity of ions to the surfaces of the media regulates their residual concentrations (An et al. 2001). The ion exchange mechanism is often measured by the ion exchange capacity, which is defined as “the number of moles of adsorbed ion charge that can be desorbed from unit mass of soil, under given conditions of temperature, pressure, soil solution composition, and soil-solution mass ratio” (Sposito 1989). Ion exchange capacity is variable for each ion and adsorptive media, and is pH dependent. The ion exchange process is influenced by the concentration and nature of the ions, pH of the solution, the media to solution ratio, and the crystal structure of the media (McLean and Owen 1969; Castaldi et al. 2008; Mohamed et al. 2009).

1.5 Adsorptive Media

Scientists have researched many different types of materials to find a functional adsorptive media to filter out dissolved stormwater contaminants. Multiple studies have investigated the use of zeolites as stormwater filters. Zeolites are naturally occurring aluminosilicate minerals with a three-dimensional network of SiO_4 and AlO_4 tetrahedra linked together by oxygen atoms (Castaldi et al. 2008; Ćurković et al. 1997; Mohamed et al. 2009; Pitcher et al. 2004). The three-dimensional structure of zeolites forms channels and cavities which can act as molecular sieves and holding spaces where water molecules and exchangeable cations are absorbed (Ghobarkar et al. 1999; Wu and Zhou 2009; Ursini et al. 2006). Zeolites have been used for absorption of many household pollutants, including formaldehyde and ammonia (Ghobarkar et al. 1999). Other commercial uses of zeolites include adsorption for treatment of acid mine drainage and industrial and municipal wastewater (Ćurković et al. 1997; Mohamed et al. 2009).

The isomorphous replacement of Si^{4+} for Al^{3+} results in a net negative charge which attracts metallic cations of similar size but lesser charge to the surface of the media, where they are adsorbed. (MacEwan and Wilson 1980; Pitcher et al. 2004; Castaldi et al. 2008; Mohamed et al. 2009). The amount of exchangeable cations on the surface of a media, (expressed as milliequivalents per 100 g of dry media) is called the cation exchange capacity (CEC). The higher the CEC of a soil or adsorptive media, more cations will be adsorbed to its surface (Pitt et al. 1999). The zeolite structure provides a large surface area to volume ratio, which leads to a high CEC (Moore and Reynolds 1989; Pitcher et al. 2004). The potential of a metal ion to bind to a ligand is dependent upon its charge to radius ratio (Brady and Tobin 1995). An et al. (2001) found that the order of metal removal by adsorptive media was correlated to the ionic radius and covalent index of the metal ions.

A study by Pitcher et al. (2004) used a synthetic zeolite as an ion exchange media. It was found to be effective at removing dissolved metal ions (Pb, Cu, Zn, and Cd) from stormwater. However, it released cations such as Ca^{2+}, Mg^{+}, and Na^{+} into the effluent (Pitcher et al. 2004). Genç-Fuhrman et al. (2007) evaluated 11 different sorbents for metal removal from stormwater (alumina, activated bauxol-coated sand, bark, bauxol-coated sand, fly ash, granulated activated carbon, granulated ferric hydroxide, iron oxide-coated sand, natural zeolite, sand, and spinel). Alumina and bauxol-coated sand were found to have the highest overall removal efficiency for Cd, Cr, Cu, Ni, and Zn, while sand and bark had the lowest (Genç-Fuhrman et al. 2007). The natural zeolites used in this study ranked among the least effective media tested, and released sodium, calcium, and potassium ions (Genç-Fuhrman et al. 2007). Road salt was not considered in either of these studies.

Aluminum and iron oxides are very common minerals, and therefore are readily available and affordable. Iron and aluminum oxides are useful for ion exchange because they have high affinities for metal ions (Benjamin et al. 1996). Iron oxides are considered a very flexible ion exchange media, as they can sorb both anions and cations (Benjamin et al. 1996). Iron and aluminum oxides have a relatively high surface area and surface charge (Lai and Chen, 2000).

Hatt et al. (2007) tested gravel and sand or soil filters in a laboratory experiment to test the longevity and effectiveness of stormwater infiltration systems. They found that gravel filters are very effective at removing suspended sediments and pollutants associated with them (Hatt et al. 2007). This study did not consider road salt in their evaluation of gravel filter media.

Another media that has been suggested as a stormwater runoff filtration device is iron oxide coated sand (OCS) (Benjamin et al. 1996; Sansalone 1999). OCS is effective at removing particles from wastewater and displays enhanced sorption capacity for metal elements (Zn, Cd, Pb, and Cu) compared to regular sand (Benjamin et al. 1996; Sansalone 1999). Lai and Chen (2000) found that OCS was effective at removing copper and lead ions and humic acid from water.

Many types of organic material have been tested as adsorption media for dissolved metals. A study by Brown et al. (2000) tested the ion exchange capacity of peanut hulls and peanut hull pellets. They found that peanut hulls have low adsorptive capacity for the metal ions Pb, Zn, Cu, and Cd. Genç-Fuhrman et al. (2007) tested tree bark as an adsorptive media and found that it has a low metal removal efficiency as well.

One of the main problems associated with stormwater runoff filters would be the potential for the filters to clog. This would depend on the amount of TSS and debris the filter was subjected to. Sansalone (1999) suggests water injection followed by vacuuming as a solution to clogging. Another potential problem is the possibility for ion exchange sites to become saturated, in which case some dissolved contaminants would pass through the filter unimpeded (Pitcher et al. 2004).

Many studies have evaluated the metal sorption capabilities of different types of media, but few have considered the impact of road salt on those media. Bäckström et al. (2004) state that NaCl has been shown to release metals bound to organic matter and particles, including Cr, Pb, Ni, Fe, and Cu. The release of soil-bound metals occurs when sodium reaches high levels in the pore water (Bäckström et al. 2004). More research is needed to determine the effect of road salt on metal sorption to stormwater filtration media.

1.6 Research objectives

The objective of this study was to determine the effects of road salt on the metal binding capacity of various adsorptive media. Specifically, this study addressed the following questions: Does road salt have an effect on the metal binding ability of the adsorptive media tested, and: Which media has the highest metal binding efficiency in the presence of salt?

CHAPTER TWO

Stormwater collection

2.1 Stormwater methods

Stormwater runoff was collected from two bridges during storm events in March 2011 in Baltimore County, Maryland, USA (Figure 1). The highway site was the I-95 bridge over I-195, which was sampled on 3 March 2011. Two grab samples were collected from PVC scuppers on the northbound bridge and one grab sample was collected from a metal scupper on the southbound bridge (Figure 2). The other site was the Stevenson Road bridge over I-695. Grab samples were taken from two PVC scuppers on the outer loop of I-695 on 8 March 2011 (Figure 3).

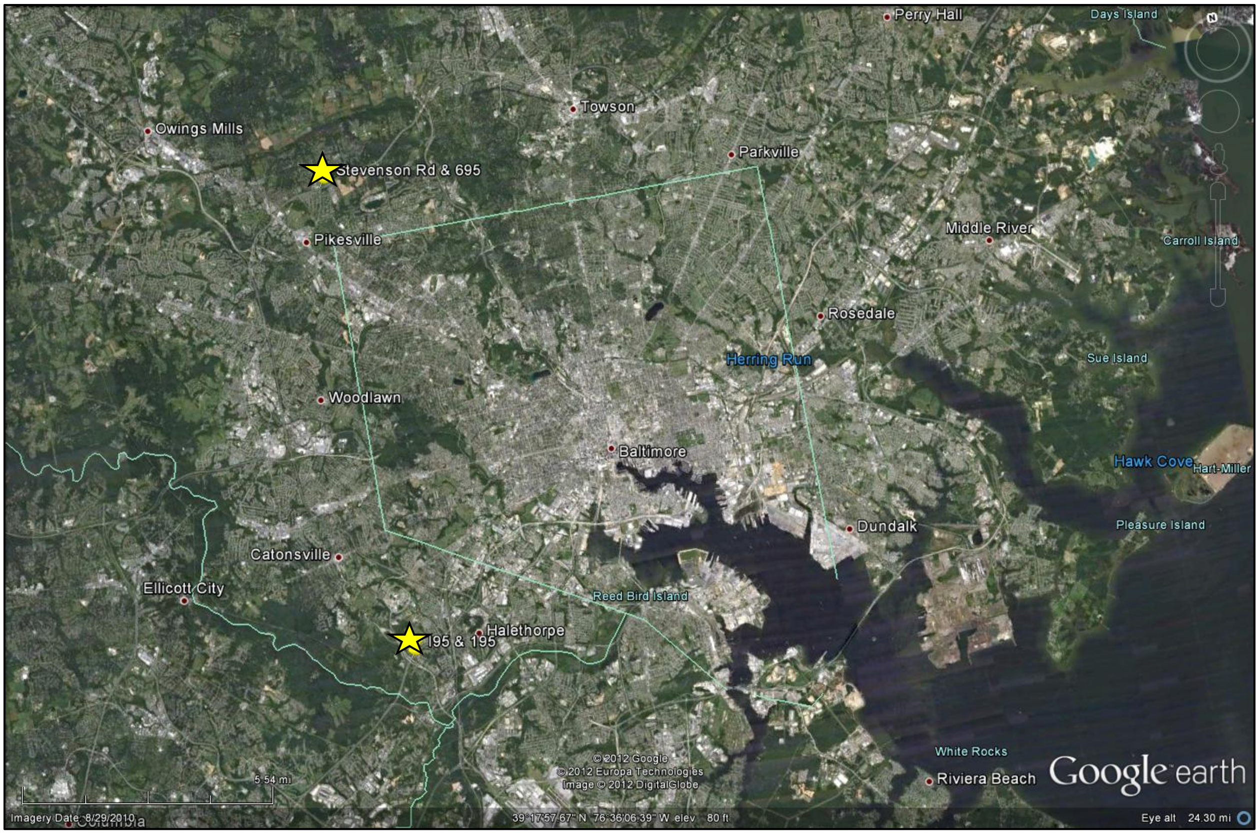

Figure 1. Stormwater sampling locations in Baltimore County, MD, USA (locations labeled with stars). Modified from Google Earth, 2012.

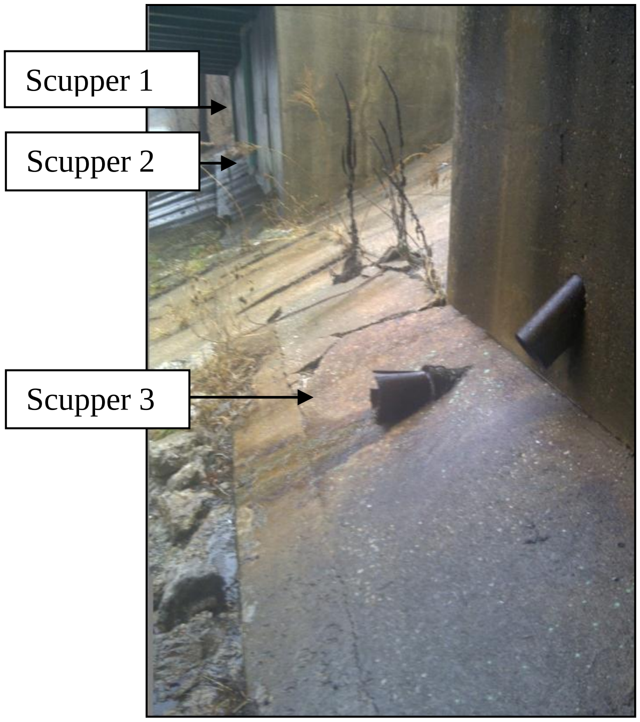

Figure 2. Three scuppers sampled at the Interstate-95 bridge over Interstate-195. Scuppers one and two are PVC pipes that descend vertically from the bridge. Scupper three is a metal scupper built into the bridge which comes out horizontally from the bridge wall.

Figure 3. (A) Scupper 1 on the Stevenson road overpass of 695. (B) Scupper 2 on the Stevenson road overpass of 695. Both scuppers are vertical PVC pipes on the outer loop of 695 in Baltimore County, MD, USA.

All samples were collected using 1L acid-washed bottles. Samples were immediately transported back to the laboratory and frozen until analysis. Collected stormwater samples were analyzed for cation (Ca^{2+}, K^+, Mg^+, and Na^+) and anion (Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) concentrations after 0.45 μm PTFE syringe filtration using a Dionex IC-320 Ion Chromatograph (IC). The IC limit of quantitation (LOQ) were 13 mg/L Cl^-, 4.2 mg/L Na^+, 10.6 mg/L Ca^+, and 1 mg/L SO_4^{2-}. Dissolved metals (Cr, Cu, Ni, Pb, and Zn) were quantified after 0.45 μm PTFE syringe filtration and acidification with 0.2M HNO_3 using a ThermoElementalPQExCell inductively coupled plasma-mass spectrometer (ICP-MS). The ICP-MS LOQ were 0.14µg/L Zn, 0.55µg/L Cu, 1.1µg/L Cr, 3.3µg/L Ni, and 1.9µg/L Pb. NIST Standard reference material 2709 was included in all ICP-MS analyses. Stormwater samples were run in duplicates or triplicates on all IC and ICP-MS analyses. Total suspended sediment (TSS) was analyzed using Environmental Sciences Section method 340.2 (APHA 2005). pH and conductivity were measured using a ThermoScientific Orion 5 Star bench top meter/probe.

2.2 Stormwater results

TSS values ranged from 7.4 to 304.8mg/L in the stormwater samples (Table 1). The pH of collected stormwater ranged from 7.08 to 8.22. In addition to Na^+ and Cl^-, Ca^+ and SO_4^{2-} were detected in the stormwater samples as well (Table 2). Based on the assumption that all sodium and chloride ions in the stormwater came from road salt, those ion concentrations were used to calculate the NaCl concentrations in the samples. The highest NaCl concentration was found in the I-95 southbound metal scupper, at 4.3 g/L

NaCl (Table 2). The lowest was from the I-95 northbound bridge scupper at 0.076g/L NaCl. Analysis of dissolved metals in the stormwater samples showed that commonly the highest concentrated metal was zinc (Table 3). The highest Zn, Cr, and Ni concentrations were found at the Stevenson road site, while the highest Cu and Pb concentrations were found at the I-95 southbound site.

Table 1. Conductivity, pH, and total suspended solids (TSS) of stormwater grab samples.

Sample	**Conductivity (mS/cm)**	**pH**	**TSS (mg/L)**
Stevenson 1	0.617	7.08	38.2
Stevenson 2	1.283	8.01	49.2
I 95-1	2.229	7.71	304.8
I 95-2	0.2723	7.65	176.2
I 95-3	6.41	8.22	7.4

Table 2. Dissolved ion concentrations found in highway bridge stormwater samples. BLOQ indicates a value below the LOQ.

Sample	**Na^+(mg/L)**	**Ca^+ (mg/L)**	**Cl^- (mg/L)**	**SO_4^{2-} (mg/L)**
Stevenson 1	127	11	163	9
Stevenson 2	270	12	373	15
I 95-1	36	BLOQ	46	5
I 95-2	50	BLOQ	68	5
I 95-3	1515	40	2609	59

Table 3. Dissolved metal concentrations found in highway bridge stormwater samples. BLOQ indicates a value below the LOQ.

Sample	**Zn (µg/L)**	**Cu (µg/L)**	**Pb (µg/L)**	**Cr(µg/L)**	**Ni (µg/L)**
Stevenson 1	179	48	38	49	4.4
Stevenson 2	42	39	38	35	BLOQ
I 95-1	32	6	2.0	3.4	BLOQ
I 95-2	16	6	2.1	3.4	BLOQ
I 95-3	108	55	39	40	BLOQ

2.3 Artificial Stormwater Recipe

2.3.1 Origin of values

The artificial stormwater recipe created in this study included ion concentrations that were determined by earlier studies in the Urban Environmental Biogeochemistry Laboratory (UEBL) at Towson University (Table 4). These were similar to the values found in the collected stormwater samples (Table 2).

Table 4. Nominal ion values used in the artificial stormwater recipe created in the UBEL at Towson University.

Species	**mg/L**
Na^{+}	30
K^{+}	1.4
Mg^{2+}	0.7
Ca^{2+}	18
Cl^{-}	62
NO_3^{-}	2
SO_4^{2-}	62

The dissolved metal concentrations used were determined based on the stormwater samples collected in this study and values found in the literature (Tables 3 and 5). The metal concentrations used in the stormwater recipe were 500 μg/L Zn, 100 μg/L Cu, 50 μg/L Pb, 50 μg/L Cr, and 50 μg/L Ni. These concentrations are higher than the concentrations found in the stormwater samples collected (Table 3). However, they are within the values found reported in the literature (Table 5), with the exception of nickel, which is higher than any value from this study or the others reported in Table 5.

Table 5. Values of metals found in stormwater runoff from different sources in the literature.

Source	**Zn (μg/L)**	**Cu (μg/L)**	**Pb (μg/L)**	**Cr(μg/L)**	**Ni (μg/L)**
Camponelli et al. (2010)	87-389	11.3-70.2	---	---	---
Davis et al. (2001)	20-5000	5-200	5-200	---	---
Davis and Birch (2010)	13.5-694.1	3.6-213.3	9.2-306.2	---	---
Gardner and Carey (2004)	83.04	21	0.6216	52	5.11
Sansalone (1999)	106-14,786	12-279	12-44	---	---
Legret and Pagotto (1999)	104-1544	11-146	14-188	---	---

The salt levels for the artificial stormwater treatments used in this study were set at 0, 2.5, and 5 g/L NaCl. These concentrations were based off of the highest and lowest NaCl concentrations calculated from the Na^+ and Cl^- ion values found in the stormwater that was collected. It was assumed that all sodium and chloride ions came from dissolved road salt, and no other source or compound. Therefore, these values may be artificially high.

The pH of the treatments was amended to 7.0-7.2. This pH reflects the pH measured in the stormwater samples collected in this study as well as values reported in the literature (Table 1) (Legret and Pagotto 1999; Camponelli et al. 2010).

2.3.2 Artificial Stormwater Preparation

Artificial stormwater was created by first mixing a 50:1 concentrated ion solution using the values found in Table 6. Metals were first added to e-pure water as their nitrate salts (Table 7) to create single metal solutions. The concentration of each metal ion was calculated, and then an aliquot of each single metal solution was added to a volume of e-pure water to create a multi-elemental 100:1 concentrated metal solution with the following concentrations: 50mg/L Zn, 10mg/L Cu, 5 mg/L Pb, 5 mg/L Cr, and 5 mg/L Ni. After the 50:1 ion solution and 100:1 metal solution had been created, they were diluted together with e-pure water create an artificial stormwater treatment. The treatment was then amended with NaCl (Fisher Scientific Company) to 0, 2.5, or 5 g/L NaCl. The pH of the artificial stormwater treatment was amended to 7.0-7.2 using KOH solution (KOH from VWR added to e-pure water).

Table 6. Mass and manufacturer of compounds added to 2L of e-pure water to create a 50:1 concentrated ion solution.

Compound	**Mass (g)**	**Manufacturer**
$CaCl_2$	2.4789	Fisher Scientific Company
$NaSO_4$	9.1288	J. T. Baker Chemical Company
$NaNO_3$	0.2841	J. T. Baker Chemical Company
KCl	0.2607	Fisher Scientific Company
$MgCl_2$	0.2675	Fisher Scientific Company

Table 7. Chemical formulas and manufacturers of the metal nitrate salts used in this study.

Chemical Formula	**Manufacturer**
$Zn(NO_3)_2 \cdot 6H_2O$	Fisher Scientific Company
$Cu(NO_3)_2 \cdot 2\frac{1}{2} H_2O$	Matheson Coleman & Bell Manufacturing Chemists
$Pb(NO_3)_2$	Aldrich
$Cr(NO_3)_3 \cdot 9H_2O$	J. T. Baker Chemical Company
$Ni(NO_3)_2 \cdot 6H_2O$	J. T. Baker Chemical Company

2.4 Stormwater discussion

The pH of collected stormwater at all sites was close to neutral, as expected based on past studies (Blecken et al. 2009; Camponelli et al. 2010). The highest and lowest NaCl concentrations were collected from the same site, indicating a large amount of variation within the site. The highest was from a metal scupper that came out horizontally from the wall, and the lowest was from a PVC scupper that descended vertically from the bridge. It is possible that the horizontal orientation of the metal scupper allowed salt and other contaminants to accumulate over time, thus increasing the concentration in the effluent. The stormwater sample from the metal scupper from I-95 southbound also had the highest pH (8.22) and conductivity (6.41 mS/cm), but the lowest TSS (7.4 mg/L). The highest chloride value detected (2609 mg/L Cl^-) exceeded the EPA's national recommended acute water quality criteria of 860 mg/L Cl^- (US EPA 2012).

Previous studies have identified and quantified the components of stormwater runoff (Sansalone 1999; Davis et al. 2001; Gardner and Carey 2004; Lee et al. 2004; Camponelli et al. 2010). Davis et al. (2001) researched metal concentrations in highway runoff and found that levels followed the general order of Zn (20-5000 µg/L) > Cu = Pb (5-200 µg/L) (Table 5). Dissolved metal concentrations found in the collected stormwater samples fell within the range of concentrations reported in the literature for stormwater runoff.

The stormwater recipe developed in this study included dissolved ions, dissolved metals, a neutral pH, and three different levels of salt. Other contaminants typically found in highway stormwater runoff include suspended sediment, hydrocarbons, nutrients, and dissolved organic carbon (DOC) (Pitt et al. 1999). These contaminants were not included in the stormwater recipe developed in this study because the purpose was to specifically explore the effect of salt on metal adsorption. Past studies have shown that the solubility and mobility of metals is often controlled by complexation with DOC (Murakami et al. 2008). The binding of DOC may change the properties of adsorptive media by increasing its sorption capacity for metal cations, affecting water retention, and increasing stability against acidic dissolution (Kaiser et al. 2001). DOC may complex metals so that they are less available to bind with adsorptive media (Hollis et al. 1996). Khokhotva and Waara (2010) reported that DOC significantly reduced metal removal in wastewater treatment plants. Hollis et al. (1996) found that DOC has a high binding affinity for copper. Blecken et al. (2009) found that adding a carbon source to a stormwater biofilter column enhanced copper adsorption by the column. It was reported that copper has the strongest affinity to both dissolved and solid organic matter, while lead and zinc have much lower affinities for organic matter (Blecken et al. 2009). According to Pitt et al. (1999), lead may be removed from solution by binding with organic matter. Due to the exclusion of DOC from the stormwater treatment used in this study, the results may reflect simplified conditions, and therefore metal adsorption presented here may be different than real stormwater conditions.

CHAPTER THREE

Batch study

3.1 Batch study methods

3.1.1 Adsorptive media

Batch studies were performed as a quick and simple method of determining the metal binding ability of the adsorptive media. Media tested in the batch study included CSF® leaf compost media and zeolite provided by Contech Construction Products Inc., and nine different media provided by Imbrium Systems Inc. (Figure 4). CSF is a granular organic material made from deciduous leaf compost. Zeolite is a naturally occurring aluminosilicate mineral. Imbrium media include a variety of grain sizes consisting of different mixtures of aluminum oxide, iron oxide, clay, sand, limestone, and waste aggregate (Table 8).

Figure 4. Adsorptive media used in the batch studies.

Table 8. Descriptions of adsorptive media provided by Imbrium Systems Inc. for use in this study.

Media Label	**Description**
Imbrium 1	aluminum oxide, 7x14 gradation
Imbrium 2	aluminum oxide and iron oxide, 28x48 gradation
Imbrium 3	aluminum oxide and iron oxide, 14x28 gradation
Imbrium 4	clay, 0.85 – 2.0 mm gradation
Imbrium 5	waste aggregate, 14x28 gradation
Imbrium 6	aluminum oxide, iron oxide, and waste aggregate, 14x28 gradation
Imbrium 7	aluminum oxide, iron oxide, and coarse sand, 14x28 gradation
Imbrium 8	coarse sand, aluminum oxide, and iron oxide, 14x28 gradation
Imbrium 9	aluminum oxide, iron oxide, and crushed limestone, 14x28 gradation

3.1.2 Treatment solutions

Media characterization included extraction with deionized water (DI), an acid extraction using 0.1M HNO_3, and stormwater with no metals or salt added (SW) (Table 9). Experimental stormwater treatments included stormwater with metals and no salt (SWM), stormwater with metals and 2.5 g/L NaCl (SWM+2.5NaCl), and stormwater with metals and 5 g/L NaCl (SWM+5NaCl).

Table 9. Descriptions and abbreviations of all treatments used in the batch tests.

Abbreviation	**Description**
DI	Deionized water
Acid	0.1M HNO_3
SW	Artificial stormwater (no metals or salt added)
SWM	Artificial stormwater with metals (no salt added)
SWM+2.5NaCl	Artificial stormwater with metals and 2.5g/L NaCl
SWM+5NaCl	Artificial stormwater with metals and 5g/L NaCl

3.1.3 Batch test methods

Four different masses of media (1.00, 2.00, 3.50, and 5.00 g) were evaluated in the conducted batch tests. All batch tests used 20 mL of treatment solution. Samples were shaken for five minutes at high speed (300 rpm) on an Orbital Shaker manufactured by VWR Science Products and immediately filtered with a 0.45 μm syringe filter (Millipore Corporation). Filtering was done to effectively end the adsorption reaction, and to limit the contact time to as close to five minutes as possible. A short shaking time was chosen to reflect the duration that stormwater runoff would be in contact with adsorptive media in a real situation. Samples were analyzed for dissolved metals using ICP-MS. The ICP-MS LOQ for zinc was an average of 3.9±2.7 μg/L with a range of 0.8-9.7 μg/L, and the LOQ for copper was 1.3±1.2 μg/L with a range of 0.08-5.8 μg/L. A standard reference material (NIST SRM 2709) was analyzed concurrently with all samples. SRM concentrations were within 85-105% of the certified values, except for chromium and nickel, which on average were within 65% and 81% of the certified values. Stormwater treatment was run in duplicate or triplicate concurrently with samples on all IC and ICP-MS analyses.

3.2 Batch study data analysis

3.2.1 Data Normalization

Batch study data was normalized to the mass of media and volume of treatment for each sample using the following equation:

$$\frac{\left[\left(Treatment\ concentration\ \left(\frac{mol}{L}\right) * volume\ of\ treatment\ (L)\right) - \left(Sample\ concentration\ \left(\frac{mol}{L}\right) * volume\ of\ treatment\ (L)\right)\right]}{mass\ of\ media\ (g)}$$

$$= \Delta \frac{mol}{g\ media}$$

This equation gives the change in mol per gram of media for a given element. A negative change indicates that the media is releasing the element, while a positive change indicates the element is adsorbing onto the media. Batch test data is presented as the change in mol per gram of media to account for the variation in mass and volume of each individual sample. Data presented here are an average (± Standard Error) of all replicates for each sample.

3.2.2 Statistical Analysis

Statistical analyses were completed using SigmaPlot. One way and two way analysis of variance (ANOVA) tests were run on the batch study data. Tukey’s (pair wise multiple comparison) test was performed to analyze the difference between levels of salt treatment. Dunnett’s (multiple comparisons versus control group) method was performed to analyze the difference between mass of media, using 1.00g as the control.

3.3 Batch study results

3.3.1 No metals test

The performance of the media in the absence of metals was evaluated with three treatments: SW, DI, and acid treatments. The purpose of these treatments was to test the media for loosely exchangeable metal ions. It was found that CSF releases a large amount of zinc into the effluent when treated with acid (Figure 5). Additionally, CSF released the most copper into the effluent among the three treatments (Figure 6). Imbrium 5 and 6 also released zinc and copper into the effluent when treated with acid. CSF and Imbrium 2 and 4 released zinc when treated with DI. The only media that release large amounts of copper and zinc when treated with SW was CSF. However, the amount of zinc and copper released from the media when treated with these treatments is insignificant when compared to the amounts of zinc and copper used in the stormwater recipe in this study.

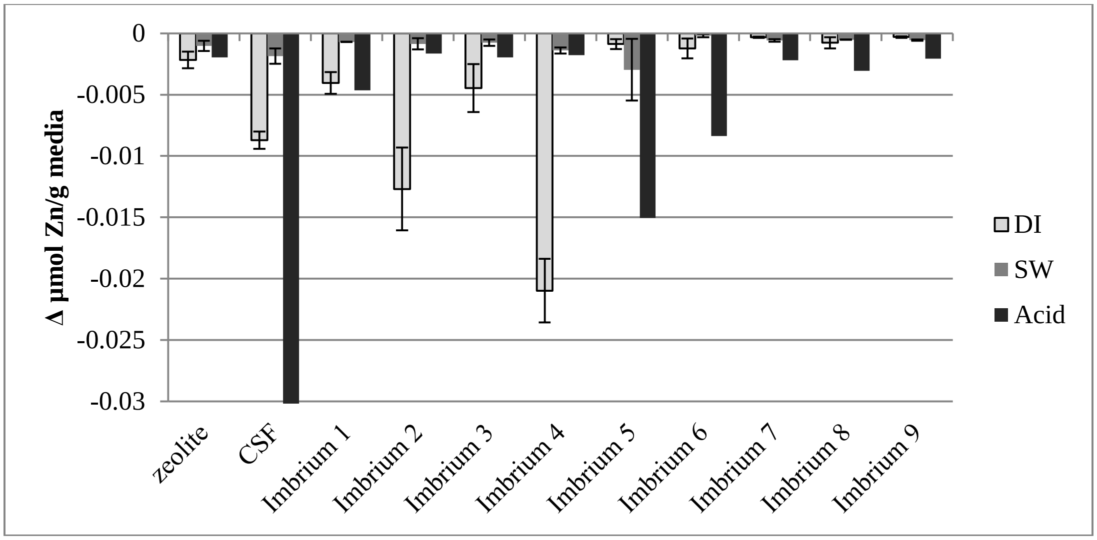

Figure 5. Zinc released from all media. CSF acid treatment result exceeds the axis on this chart (-0.79 µmol Zn/g media). DI and SW values are average of n=2 ±1SE.

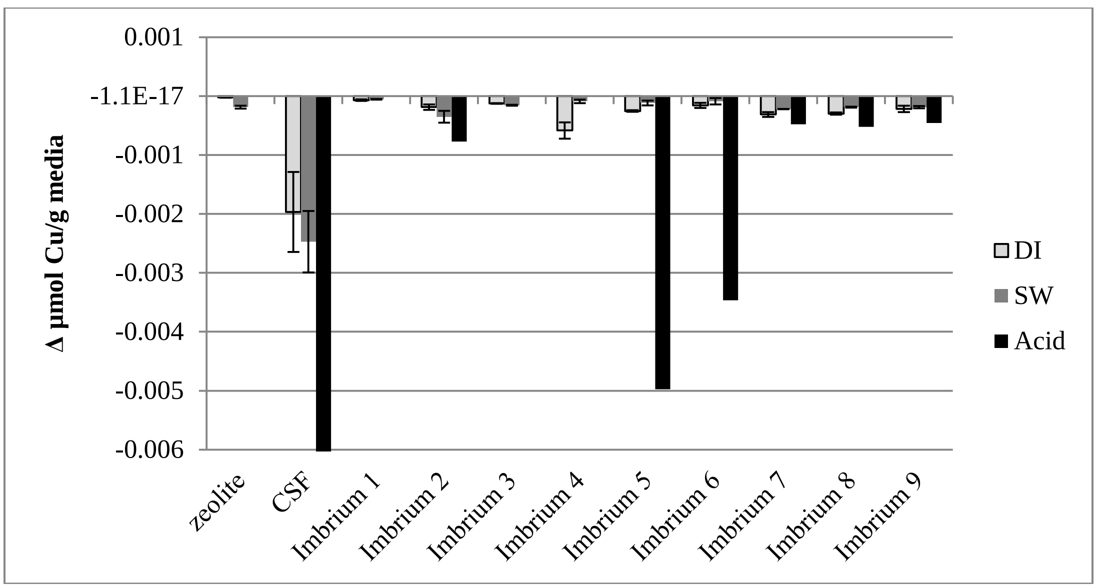

Figure 6. Copper released from all media. CSF acid treatment result exceeds the axis on this chart (-0.0089 µmol Cu/g media). DI and SW values are average of n=2 ±1SE.

3.3.2 No salt test

All 11 media were used in a batch test with the SWM treatment. This test included 1.00g and 2.00g of media with five replicates of each combination. The zinc results of this test are shown in Figure 7. Imbrium 4 was the only media to leach zinc rather than adsorb it. The copper results of this test are shown in Figure 8. Imbrium 4 and 5 both leached copper into the effluent. All other metal results were not consistent. It was discovered that filtering the samples with a 0.45 μm syringe filter has a large impact on Cr concentrations (Table 10). Filtering the effluent is necessary to end the ion exchange reaction in a timely manner and to limit the contact time. It was also found that SRM concentrations were low on average (within only 65% of the certified values for chromium and 81% for nickel). Therefore, Cr and Ni data is not presented. Tukey's test showed that 1.00g of Imbrium 4 SWM zinc results were significantly ($p<0.05$) different from all other media.

Table 10. Metal values from filtered and unfiltered stormwater treatments.

	Treatment	**Zn (μg/L)**	**Cu (μg/L)**	**Pb (μg/L)**	**Cr (μg/L)**	**Ni (μg/L)**
Filtered	SWM	1110	11	19	0	29
Filtered	SWM+2.5NaCl	618	18	34	0	28
Filtered	SWM+5NaCl	564	22	34	0	25
Unfiltered	SWM	1186	48	30	8.2	24
Unfiltered	SWM+2.5NaCl	618	36	36	4.4	25
Unfiltered	SWM+5NaCl	572	43	37	9.4	24

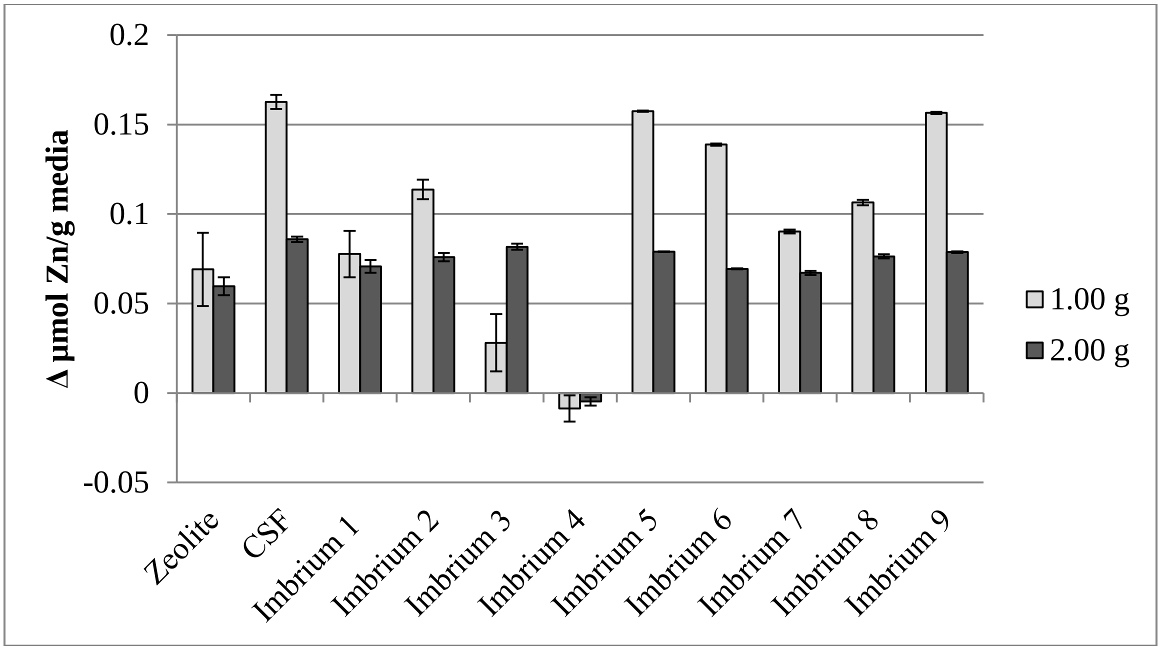

Figure 7. Mean (±SE) zinc adsorbed by two different masses of all media when treated with SWM. (n=5)

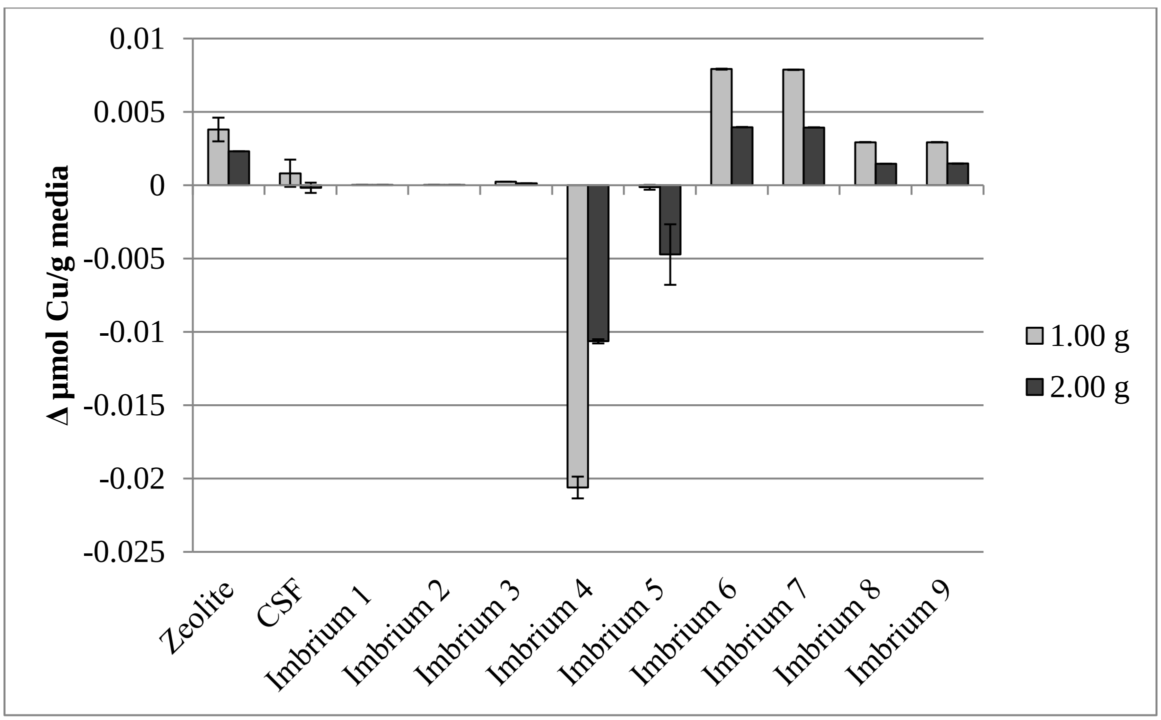

Figure 8. Mean (±SE) copper adsorbed by two different masses of all media when treated with SWM. (n=5)

3.3.3 Adsorption by mass test

A test was run using only Imbrium 3 and the SWM treatment to explore the effect of the fluid to media ratio. Five replicates of each mass of media (1.00, 2.00, 3.50, and 5.00g) were processed with 20mL of treatment. Zinc and copper results are shown in Figures 9 and 10. The total percent of zinc and copper adsorbed by Imbrium 3 in the no salt treatment was calculated to show the difference in adsorption per gram (Figure 11). Zinc adsorption increased with the addition of more media, while copper adsorption reached 100% with 1 g of media. The Imbrium 3 results showed that there is more zinc adsorbed per gram with 1.00g than with 2.00g, as is expected. Dunnett's method of multiple comparisons versus a control group, using 1.00 g data as the control, showed that there is a significant ($p<0.05$) difference between 1.00g and 3.50 g and 5.00 g of media in zinc and copper adsorption, but no significant difference between 1.00g and 2.00 g of media.

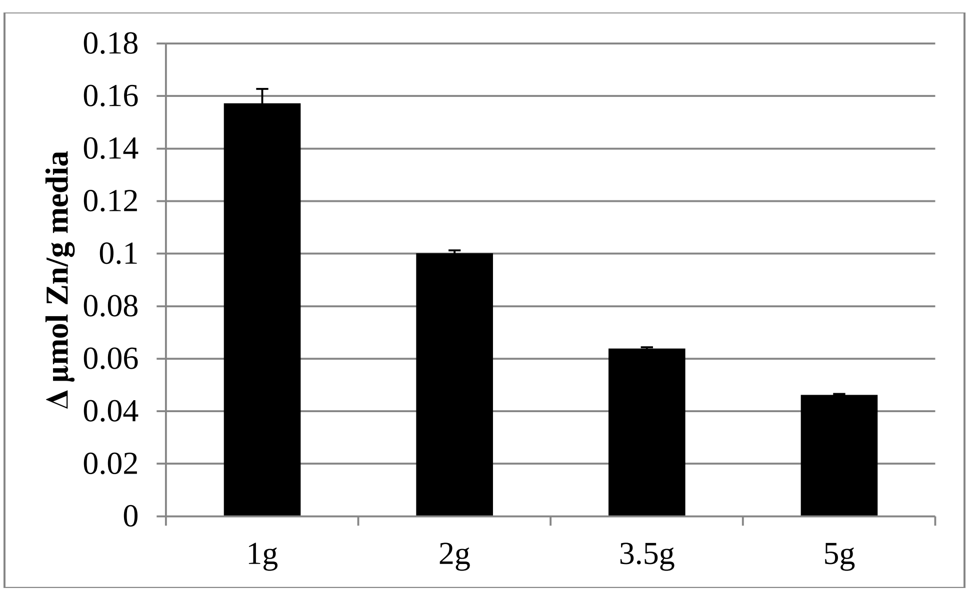

Figure 9. Mean (±SE) Imbrium 3 SWM zinc values by mass. (n=5)

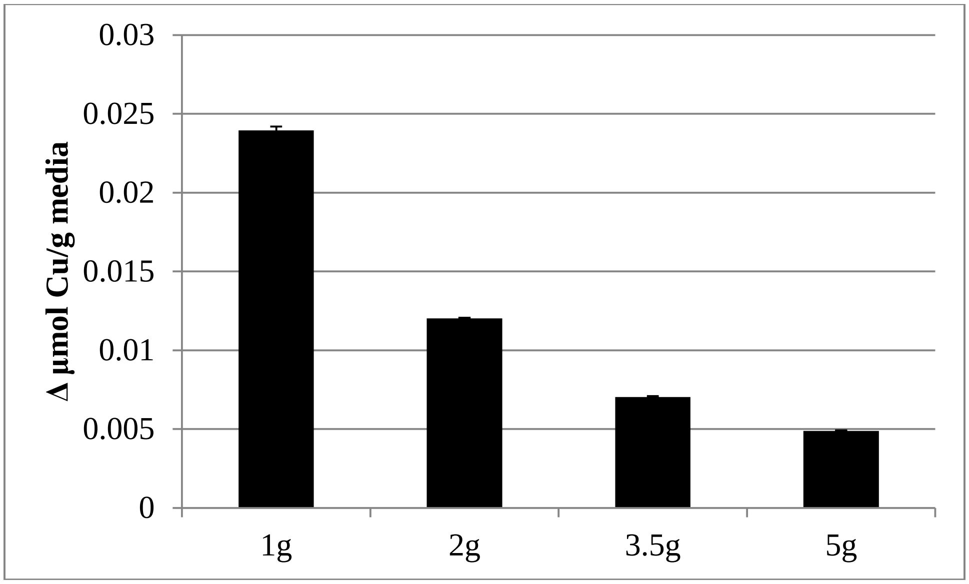

Figure 10. Mean (±SE) Imbrium 3 SWM copper values by mass. (n=5)

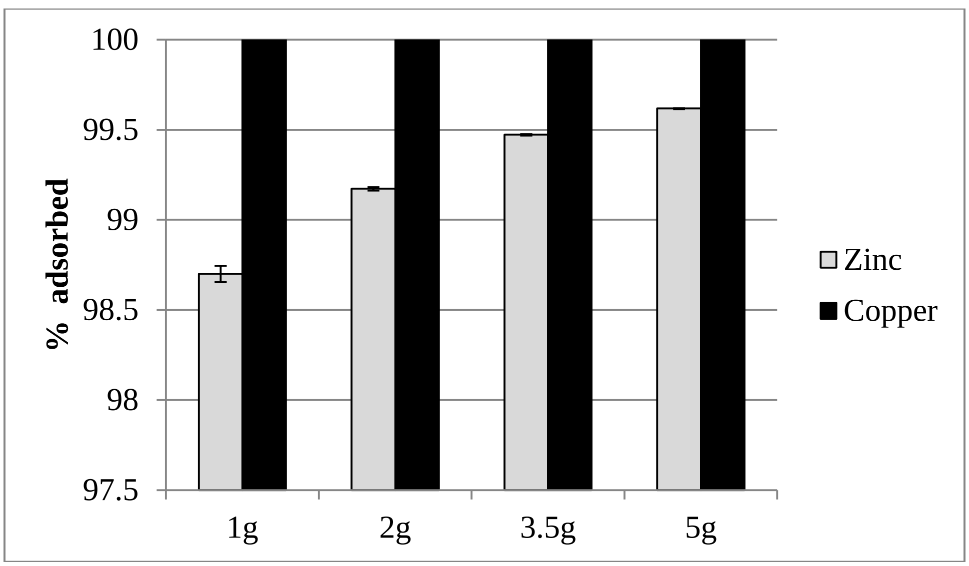

Figure 11. Mean (±SE) percent of total zinc and copper in SWM adsorbed by different masses of Imbrium 3. (n=5)

3.3.4 Effect of salt test

CSF, Imbrium 1-5, and Imbrium 9 were used in a batch test to compare the effects of different amounts of salt on the metal adsorption of those media. 1.00g of each media was used and five replicates of each combination were performed. Zinc results from this test are shown in Figure 12. Copper results are shown in Figure 13. Imbrium 4 was the only media shown to leach zinc and copper into the effluent regardless of the level of salt. Tukey's test was performed after a two way ANOVA to compare the zinc results of the three levels of salt treatments among 1.00g of all the media. The zinc and copper results showed a significant difference between the type of media and the level of salt ($p<0.001$). Overall, there was a significant difference in the metal results between no salt and the two levels of salt, but not between the two levels of salt (2.5g/L NaCl and 5g/L NaCl). There was no significant difference between CSF, Imbrium 5, and Imbrium 9 zinc results. There was no significant difference between Imbrium 1 and Imbrium 2 zinc results.

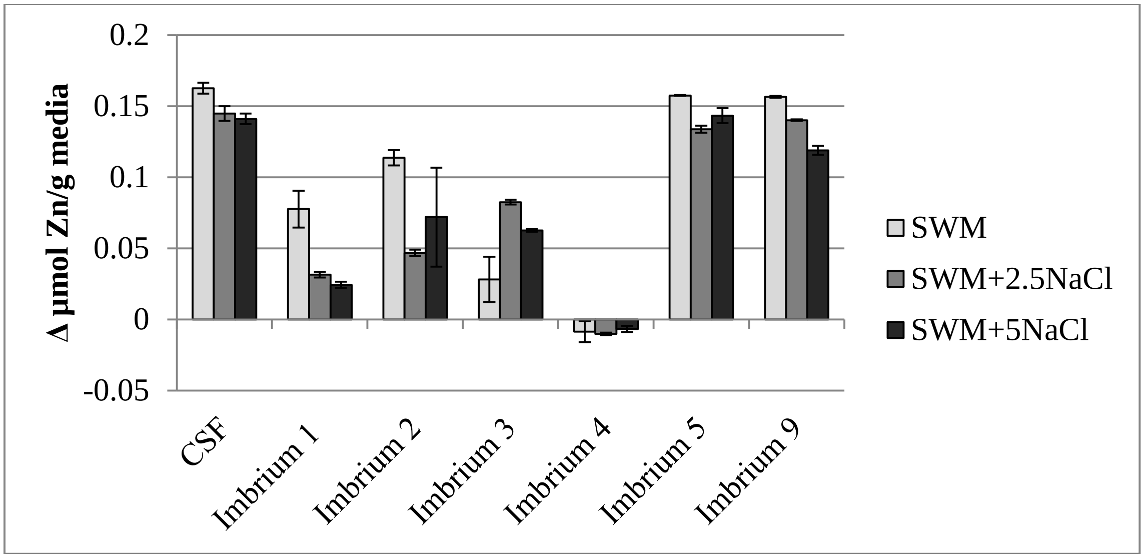

Figure 12. Mean (±SE) zinc adsorbed by 1g of media when treated with three levels of salt treatment. (n=5)

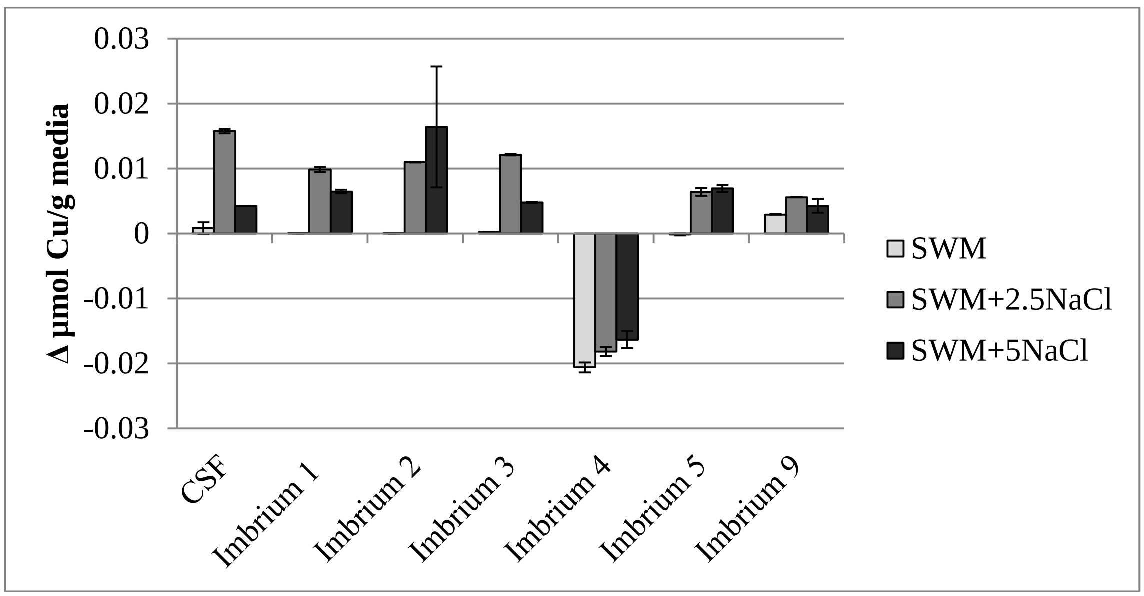

Figure 13. Mean (±SE) copper adsorbed by 1g of media when treated with three levels of salt treatment. (n=5)

3.4 Batch study discussion

CSF (7926 µg/L Zn) and Imbrium 5 (154.8 µg/L Zn) values exceeded EPA's national recommended water quality criteria for acute toxicity in freshwater (120 µg/L Zn) when treated with the acid treatment. CSF (84.69µg/L Cu), Imbrium 5 (47.46 µg/L Cu) and Imbrium 6 (32.74 µg/L Cu) exceeded the EPA's national recommended water quality criteria for acute toxicity in freshwater (13 µg/L Cu) when treated with acid (US EPA 2012). The acid treatment had a pH of 0.92, which is significantly lower than what would be found in a realistic stormwater situation. It was used as an acid extraction to determine the amount of exchangeable ions on each media. Therefore, those values that exceeded the EPA water quality criteria should not be considered normal conditions.

Imbrium 4 is not a suitable media for the purposes of this study, as it was shown to release zinc and copper into the effluent across different masses and levels of salt. Based on the results of these batch tests, CSF, Imbrium 3, 5, and 9 are suggested for use in the column studies. These four media consistently showed the highest capacity to absorb metals across all salt levels (Figures 12 and 13).

CHAPTER FOUR

Column study

4.1 Column Methods

A column study was performed to test the highest performing media from the batch studies in a more realistic filter situation, and to determine the effect of salt on the metal binding ability of the media. Media recommended for use in the columns included CSF, Imbrium 3, Imbrium 5, and Imbrium 9. Due to commercial reasons, Imbrium Systems Inc. decided not to provide Imbrium 5 or 9 for use in the column study. Instead, a new media called Imbrium 10 was provided (Table 11). Therefore, media included in the column study were CSF, Imbrium 3, and Imbrium 10 (Table 11, Figure 14).

Table 11. Descriptions of media used in the column study.

Media Label	Description
CSF	granular organic material made from deciduous leaf compost
Imbrium 3	aluminum oxide and iron oxide, 14x28 gradation
Imbrium 10	aluminum oxide, iron oxide, and medium sand, 28x48 gradation

Figure 14. Three media used in the column study (Left to right: CSF, Imbrium 3, Imbrium 10).

Columns consisted of PVC pipes that measured 15in tall with a 3in internal diameter with PVC caps on the bottom. Pyrex glass wool was placed at the bottom of each column to prevent loss of media. Columns were filled with media to the 9in mark, so each column held approximately 1L of media. Each media had four replicate columns. Columns were sealed around the caps and around the outflow tubing with silicone (GE Silicone II Window & Door, Momentive Performance Materials Inc., Huntersville, NC, USA). The tubing attached to the bottom of each column was goose necked up so that the outflow was at the same elevation as the top of the media bed. This reduced edge effects within the column, ensured an even wetting of media, and an accurate empty bed contact time (EBCT). EBCT is defined as the volume of media divided by the flow rate. The calculated EBCT for this study was 1.2 – 1.4 minutes. The pump used was an Ismatec quick-couple digital drive with a twelve channel mini-cartridge head fitted with 1.85mm ID Tygon tubing.

The column tests used the same artificial stormwater recipe that was used in the batch tests (Table 2). The columns were treated with 5 L of no salt added artificial stormwater (SWM), followed by 5L of SWM+2.5NaCl and 5L of SWM+5NaCl at a flow rate of 105-120 mL/min. This sequence of 15L was repeated twice. The Imbrium 3 and Imbrium 10 columns were treated with the first round of 15L four days before the CSF columns, due to the fact that the necessary amount of CSF was not available until that time. The entire first round of 15L of stormwater treatment was applied to a single column on the same day. The second round of 15L of stormwater treatment was applied to all columns simultaneously over three days. On the first day, all columns were treated with 5L of SWM, the second day they were all treated with 5L of SWM+2.5NaCl, and on the third day, all columns were treated with 5L of SWM+5NaCl. The column study stopped after half of the columns became clogged. A column was considered clogged when hydraulic head measured greater than 7 inches, thus overflowing the top of the column. Effluent was collected in 1L acid-washed bottles. Sample bottles were replaced with empty bottles as they filled. This method created five 1L composite samples for every column and every stormwater treatment. Samples were analyzed for pH (ThermoScientific Orion 5 Star bench top meter/probe), dissolved ions with IC, and dissolved metals with ICP-MS. The IC LOQ were 6 mg/L Na^+, 39 mg/L Cl^-, and 4.3 mg/L SO_4^{2-}. The ICP-MS LOQ for zinc was an average of 5±1.7 µg/L with a range of 2.4-8.0 µg/L, and the LOQ for copper was 1.9±0.9 µg/L with a range of 0.8-3.9 µg/L. A standard reference material (NIST SRM 2709) was analyzed concurrently with all samples. SRM concentrations were within 85-105% of the certified values, except for nickel and lead, which on average were within 79% and 81% of the certified values. Therefore, nickel and lead data are not presented. Stormwater treatment was run in duplicate or triplicate concurrently with samples on all IC and ICP-MS analyses.

4.2 Column Statistical Analysis

Statistical analyses were completed using the "R" project for statistical computing and Microsoft Excel. Statistical analyses included a balanced repeated measures ANOVA test on pH and dissolved metal data to evaluate differences between media and consecutive samples. Separate ANOVA tests were computed for zinc, copper, chromium, lead, and nickel column results to evaluate differences between media and consecutive samples.

4.3 Column Results

CSF column effluent was tan to brown in color due to dissolved organic matter in the compost material. DOC was not quantified in this study. Effluent from Imbrium 3 and 10 columns was clear. All column effluent was free of particulates. The Pyrex glass wool was an acceptable filter for the columns as it retained all particulates within the column but did not adsorb or retain a significant amount of dissolved metals (Ahammed and Meera 2010; Wendling et al. 2012).

No columns clogged on the first round of stormwater treatment (one round of treatment was a total of 15 L, consisting of five liters of each level of salt). The four replicate Imbrium 3 columns never clogged, and were treated to two full rounds of stormwater treatment. One of the four replicate columns of CSF and Imbrium 10 did not clog, and were therefore treated to two full rounds of stormwater treatment. Three of each of the CSF and Imbrium 10 columns clogged during the second round of stormwater treatment. Clogging was most likely caused by fine particulates in the media. The two media that did clog (CSF and Imbrium 10) had small grain sizes and dust particles. It may have been beneficial to rinse the media before the start of the column experiment to wash out the fine particulates that may have caused the columns to clog.

Imbrium 3 decreased the pH of the column effluent (Figure 15). A pattern emerged in the pH of Imbrium 3 column effluent where pH decreased with each additional liter of effluent and with each addition of salt to the stormwater treatment. There was no such pattern observed in the pH results of Imbrium 10. In the two salt treatments, the pH increased over time in the Imbrium 10 column effluent. Imbrium 10 column effluent pH was more varied than the effluent from columns filled with Imbrium 3 or CSF. CSF increased the pH of the effluent in every treatment (Figure 15). There was a significant difference in the pH of column effluent between media ($p < 0.001$), as well as over time, expressed as additional liters of effluent ($p < 0.001$).

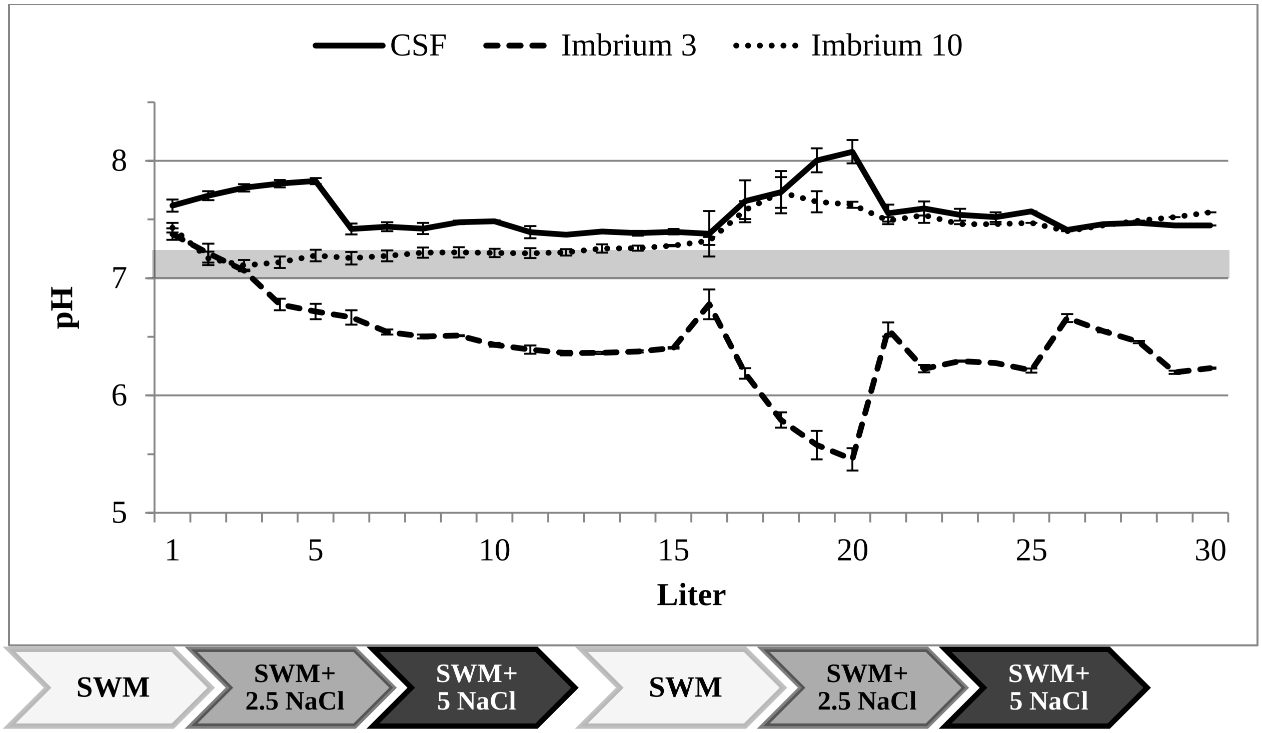

Figure 15. Mean (±SE) pH of effluent from columns. Stormwater treatment pH was 7.0-7.2 (shaded area on chart). Liters of effluent represent each 1L composite sample. Liters 1-5 were SWM, 6-10 were SWM+2.5NaCl, and 11-15 were SWM+5NaCL. Liters 16-20 were SWM, 21-25 were SWM+2.5NaCl, and 26-30 were SWM+5NaCL. (n=4)

Imbrium 3 and 10 released sodium ions into the effluent in the no salt added stormwater treatment (SWM) (Figure 16). Chloride ion values in the effluent closely followed those in the stormwater treatment, indicating that chloride behaved conservatively (Figure 17). There was more chloride in the effluent of all media from the first round of stormwater treatment than the second round of treatment (Figure 17). Imbrium 3 and 10 released sulfate (27g/L and 19g/L respectively) in the first liters of SWM effluent (Figure 18). CSF effluent sulfate ion values ranged from 69.9-83.6 mg/L SO_4^{-2} with a mean of 75.5 mg/L SO_4^{-2} (Figure 18). Imbrium 3 and 10 sulfate ion concentrations were much lower in the second round of stormwater treatment than the first round (Figure 18).

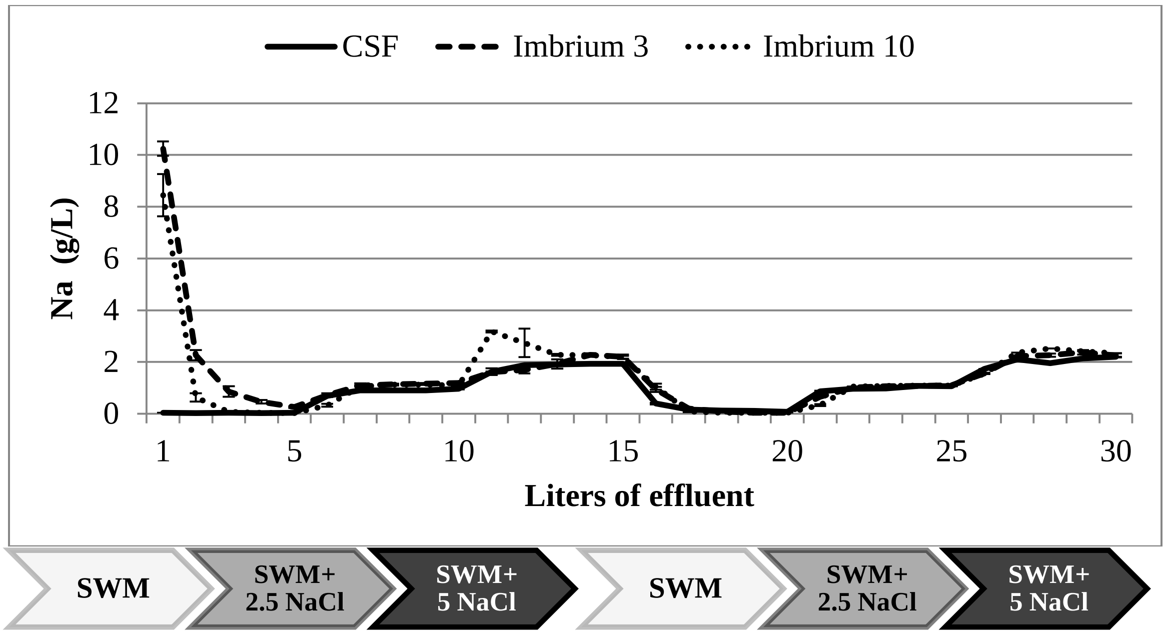

Figure 16. Mean (±SE) sodium ion concentrations of three media. Liters of effluent represent each 1L composite sample. Liters 1-5 were SWM, 6-10 were SWM+2.5NaCl, and 11-15 were SWM+5NaCL. Liters 16-20 were SWM, 21-25 were SWM+2.5NaCl, and 26-30 were SWM+5NaCL. (n=4)

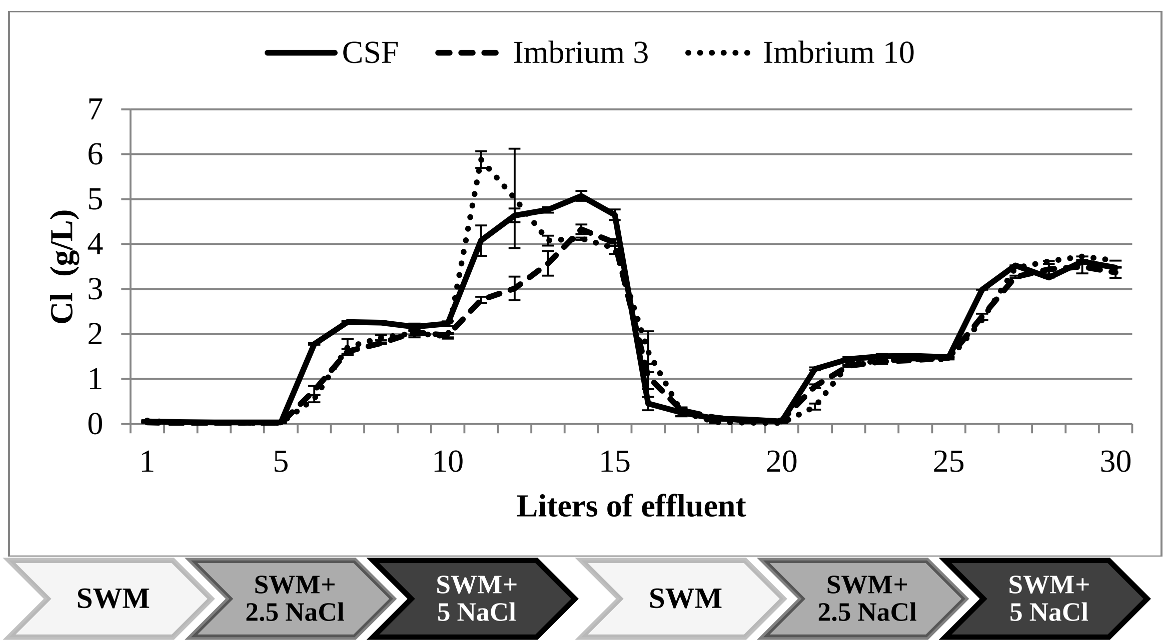

Figure 17. Mean (±SE) chloride ion concentrations of three media. Liters of effluent represent each 1L composite sample. Liters 1-5 were SWM, 6-10 were SWM+2.5NaCl, and 11-15 were SWM+5NaCL. Liters 16-20 were SWM, 21-25 were SWM+2.5NaCl, and 26-30 were SWM+5NaCL. (n=4)

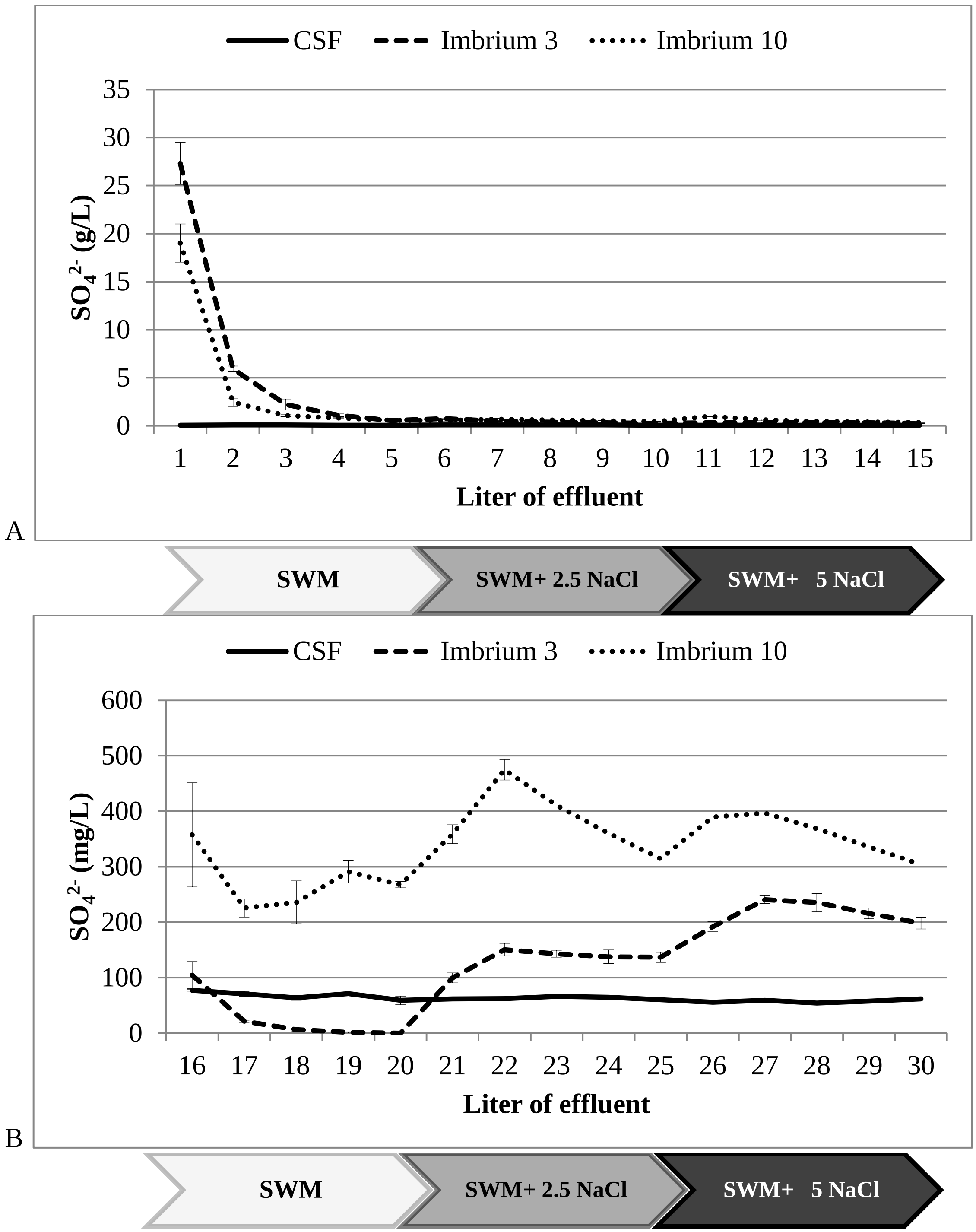

Figure 18. (A) Mean (±SE) sulfate ion concentrations from the first round of column effluent of three media. Liters of effluent represent each 1L composite sample. Liters 1-5 were SWM, 6-10 were SWM+2.5NaCl, and 11-15 were SWM+5NaCL. CSF values ranged from 69.9-83.6mg/L SO_4^{-2} with a mean of 75.5mg/L SO_4^{-2}. (n=4)
(B) Mean (±SE) sulfate ion concentrations from the second round of column effluent of three media. Liters of effluent represent each 1L composite sample. Liters 16-20 were SWM, 21-25 were SWM+2.5NaCl, and 26-30 were SWM+5NaCL. (n=4) The scales for the two charts have different magnitudes.

There was a significant difference in percent zinc adsorbed by the three different media ($p = 0.0148$), as well as over consecutive samples ($p = 0.00623$) in the first round of stormwater treatment (Table 12, Figure 19). It was not possible to run a balanced repeated measures ANOVA on the second round of stormwater treatment data due to the unequal numbers of samples collected because of clogged columns. There was a significant difference in percent copper adsorbed by the three different media ($p <0.001$) (Table 13, Figure 20). CSF column effluent consistently had the lowest percent of copper adsorbed regardless of salt concentration or liter of effluent (Figure 20). There was no copper detected in the Imbrium 10 effluent after the second liter of treatment, therefore the media adsorbed 100% of the copper available (Table 13, Figure 20).

Table 12. Mean percent of zinc in the stormwater treatment adsorbed by each media (n=5).

Liters	Treatment	CSF	Imbrium 3	Imbrium 10
1-5	SWM	96	85	91
6-10	SWM+2.5NaCl	98	99	97
11-15	SWM+5NaCl	97	99	100
16-20	SWM	92	64	100
21-25	SWM+2.5NaCl	83	97	93
26-30	SWM+5NaCl	75	78	100

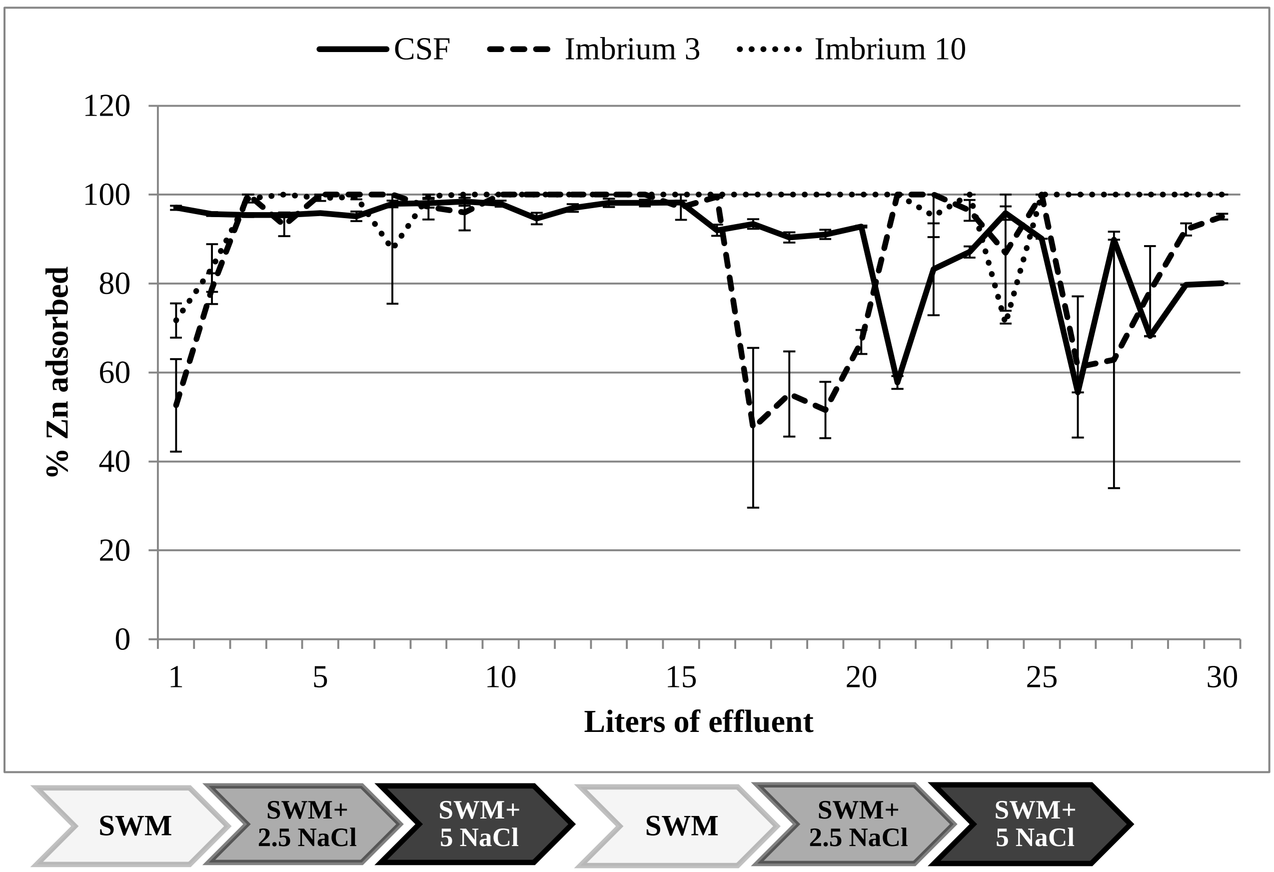

Figure 19. Mean (±SE) percent of zinc in stormwater treatment adsorbed by the media in the columns. Stormwater treatment initial concentration was 500 µg/L Zn. Liters of effluent represent each 1L composite sample. Liters 1-5 were SWM, 6-10 were SWM+2.5NaCl, and 11-15 were SWM+5NaCL. Liters 16-20 were SWM, 21-25 were SWM+2.5NaCl, and 26-30 were SWM+5NaCL. (n=4)

Table 13. Mean percent of copper in the stormwater treatment adsorbed by each media (n=5).

Liters	Treatment	CSF	Imbrium 3	Imbrium 10
1-5	SWM	61	71	78
6-10	SWM+2.5NaCl	93	100	100
11-15	SWM+5NaCl	95	100	100
16-20	SWM	61	87	100
21-25	SWM+2.5NaCl	27	100	100
26-30	SWM+5NaCl	17	99	100

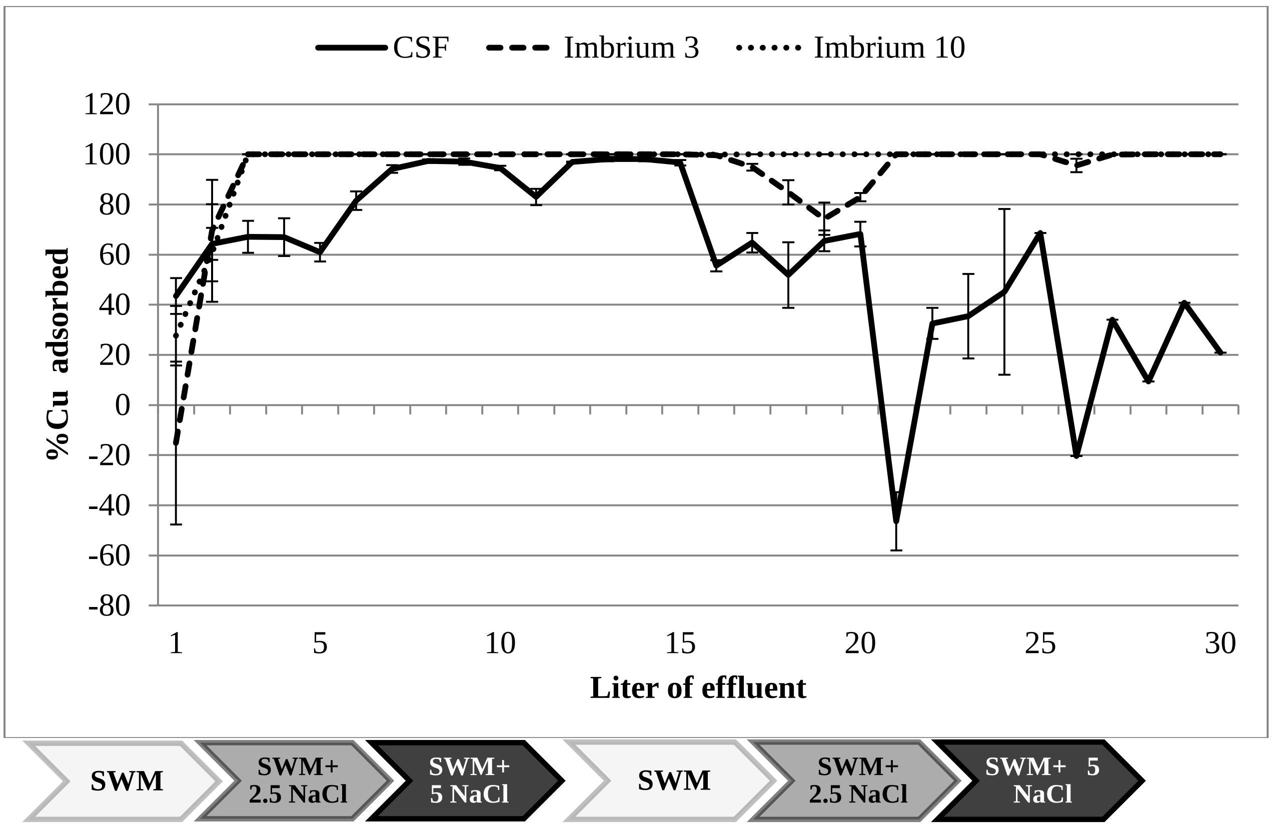

Figure 20. Mean (±SE) percent of copper in stormwater treatment adsorbed by the media in the columns. Stormwater treatment initial concentration was 100 µg/L Cu. Liters of effluent represent each 1L composite sample. Liters 1-5 were SWM, 6-10 were SWM+2.5NaCl, and 11-15 were SWM+5NaCL. Liters 16-20 were SWM, 21-25 were SWM+2.5NaCl, and 26-30 were SWM+5NaCL. (n=4)

4.4 Column Discussion

Past columns studies have used a variety of flow rates and column sizes. The flow rates from other column studies include 0.2mL/min (Wendling et al. 2012), 1.0mL/min (Jordan et al. 1997) and gravity flow (Ahammed and Meera 2010). The flow rate used in this study varied slightly from 105 to 120 mL/min. This study used the fastest flow rate achievable by the pump and tubing combination employed. A fast flow rate was preferred to simulate highway runoff entering a stormwater management installation during a storm event. Runoff rates vary depending on the rainfall rate and the size and gradient of the catchment area. Impervious surfaces such as highways have been shown to significantly increase the runoff rate and pollutant loadings to surface waters (Davis and Birch 2010).

CSF and Imbrium 3 effluent exceeded the EPA's acute water quality criteria for zinc (120μg/L Zn) several times over the course of the column study (US EPA 2012). All three media exceeded the EPA's acute water quality criteria for copper (13µg/L Cu) at least once throughout the column study (US EPA 2002). Chloride values exceeded the EPA acute freshwater national recommended water quality criteria (860mg/L Cl^-) in the effluent of every media tested when treated with the two salt treatments (US EPA 2012). Pitt et al. (1999) state that soil is not effective at removing salts. In a study on Long Island, NY, it was found that metals were significantly reduced during infiltration into the soil, while chloride was not reduced at all (Pitt et al. 1999).

Imbrium 3 significantly decreased the pH of the column effluent, and therefore should not be used in watersheds that are already impacted by acidic deposition. Pitt et al. (1999) stated that iron oxidation may lower the pH of water because the oxidation reaction adds H^+ ions to the water. Imbrium 3 consisted of a mixture of aluminum and iron oxides. CSF would be a better adsorptive media to use in acidified watersheds as it characteristically increased the pH of column effluent, especially when treated with SWM. Sansalone (1999) also found that some adsorptive media has the capacity to increase the pH of the effluent.

There was a dramatic increase in sodium and sulfate ions in the first liter of effluent from the Imbrium materials 3 and 10 columns. Imbrium 3 and 10 consisted of aluminum and iron oxides (Table 11). The manufacturing methods and conditions of the Imbrium materials are unknown to the author due to proprietary rights. It is most likely that the sulfate in the effluent originated from the media itself. Based on the large flush of sulfate and sodium that was released in the first liter of effluent, it is possible that they were absorbed by the media prior to the start of the study, or that they were bound to the surface of the media, and were exchanged for other ions in the stormwater treatment. According to Potter and Yong (1999), natural oxides are likely to contain structural and/or adsorbed sulphate. They also stated that a solution with a $pH > 6$ will cause the release of adsorbed sulfate ions as a result of displacement by hydroxyl ions (Potter and Yong 1999). Imbrium 10 column effluent had the highest pH, which may be the cause of the high sulfate ion concentrations. None of the cations quantified in the column effluent (sodium, calcium, magnesium, and potassium) matched up on a molar basis with the sulfate concentrations found in the effluent from the columns (Table 14).

Table 14. Sums of ion concentrations found in the first 15 L of column effluent of Imbrium 3 and 10.

Media	**Na^+(mol/L)**	**Ca^+ (mol/L)**	**Mg^+ (mol/L)**	**K^+ (mol/L)**	**SO_4^{2-} (mol/L)**
Imbrium 3	1.2640	0.0028	0.0000	0.0014	0.4257
Imbrium 10	1.1554	0.0888	0.0021	0.0037	0.3080

There was also a noted increase in zinc and copper concentrations in the first liter of each salt addition in the first round of stormwater treatment in the effluent of all columns (Figures 20-21). This first initial liter of stormwater creates a high pollutant concentration effluent. To avoid this first liter symptom, it may be beneficial to rinse the media with artificial stormwater with no salt or metals (SW) before installation in the field. This is not to be confused with the first flush phenomenon found in highway stormwater runoff during the first large storm of a season. Lee et al. (2004) found that the first storm of the winter season creates stormwater runoff with higher pollutant loads than storms later in the season (Lee et al. 2004). The existence of the first flush of stormwater phenomenon has been debated and defined over numerous studies.

Imbrium 10 was able to adsorb the most copper and zinc overall (Tables 12-13, Figures 19-20). In fact, except for the first liter, there was little to no zinc or copper detected in the Imbrium 10 effluent. However, there was a high concentration of sulfate ions in Imbrium 10 column effluent compared to the other two media.

CHAPTER FIVE

Conclusions

This study proposed to answer two research questions: Does road salt have an effect on the metal binding ability of the adsorptive media tested, and: Which media has the highest metal binding efficiency in the presence of salt?

Imbrium 10 was shown to have the highest metal binding efficiency in the presence of salt of the media tested in this study. Imbrium 10 had a small grain size (28x48 gradation) and included aluminum oxide, iron oxide, and sand particles. The small gradation and mixed nature of Imbrium 10 are ideal characteristics for ion exchange, as they provide a large surface area and varied binding sites. However, there was still sodium and chloride present in high concentrations in the effluent. Imbrium 10 was the first media to clog the columns in this study and was shown to release sulfate ions in the first liter of stormwater treatment. It may be beneficial to rinse the media with artificial stormwater treatment before installation in the field to avoid the large concentration of pollutants that were released in the first liter of effluent.

The conditions and contaminant concentrations used in this study were designed to mimic real world stormwater runoff. It is apparent that when high concentrations of salt are present in stormwater, there will be acutely toxic amounts of chloride in the effluent from the media tested in this study. There were multiple exceedances of the US EPA's national recommended water quality criteria for chloride, zinc, and copper over the course of this study. It appears that sodium and chloride ions went through the columns without much interference from the adsorptive media. The sodium and chloride effluent concentrations closely followed the concentrations in the stormwater treatment, with the exception of the first flush phenomenon.

This subject needs further research. A field study testing the media where it is installed in a stormwater management system would be ideal. Road salt application is still the most commonly used method of de-icing roads during the winter months in many countries. Even when treated with adsorptive media, toxic levels of chloride and metals can be released into the environment through stormwater runoff.

This study shows that it is very likely that stormwater treated with these media will exceed the US EPA's national recommended water quality criteria. None of the media tested were successful at completely removing all dissolved metals and salt ions from the stormwater treatment. It may not be possible to completely remove all contaminants from stormwater using adsorptive media. Therefore, other methods of stormwater treatment need to be considered in addition to adsorptive media.

REFERENCES

Ahammed, M. Mansoor, and V. Meera. 2010. "Metal oxide/hydroxide-coated dual-media filter for simultaneous removal of bacteria and heavy metals from natural waters". *Journal of Hazardous Materials*. 181;788-793.

An, H. K., B. Y. Park, and D. S. Kim. 2001. "Crab shell for the removal of heavy metals from aqueous solution". *Water Research*. 35(15):3551-3556.

American Public Health Association. 2005. "Standard Methods for the examination of water and wastewater". 21st ed. APHA, AWWA, WEF. 2-58.

Bäckström, Mattias, Stefan Karlsson, Lars Bäckman, Lennart Folkeson, and Bo Lind. 2004. "Mobilisation of heavy metals by deicing salts in a roadside environment". *Water Research*. 38:720-732.

Benjamin, Mark, M., Ronald S. Sletten, Robert P. Bailey, and Thomas Bennett. 1996. "Sorption and filtration of metals using iron-oxide-coated sand". *Water Resources.* 30(11):2609-2620.

Blecken, Godecke-Tobias, Yaron Zinger, Ana Deletić, Tim D. Fletcher, and Maria Viklander. 2009. "Impact of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters". *Ecological Engineering*. 35:769-778.

Brady, Joseph M., and John M. Tobin. 1995. "Binding of hard and soft metal ions to *Rhizopusarrhizus* biomass". *Enzyme and Microbial Technology*. 17:791-796.

Brown, Pauline, I. Atly Jefcoat, Dana Parrish, Sarah Gill, and Elizabeth Graham. 2000. "Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution". *Advances in Environmental Research*. 4:19-29.

Camponelli, K.M., Lev, S.M., Snodgrass, J.W., Landa, E.R., Casey, R.E. 2010. "Chemical fractionation of Cu and Zn in stormwater, roadway dust and stormwater pond sediments".*Environmental Pollution*. 158:2143-2149.

Castaldi, Paola, Santona, Laura, Enzo, Stefano, Melis, Pietro. 2008. "Sorption processes and XRD analysis of a natural zeolite exchanged with Pb^{2+}, Cd^{2+}, and Zn^{2+} cations". *Journal of Hazardous Materials*. 156:428-434.

Ćurković, L., Š. Cerjan-Stefanović, and T. Filipan. 1997. "Metal ion exchange by natural and modified zeolites". *Water Resources*. 31(6):1379-1382.

Davis, Allen P., Mohammad Shokouhian, and Shubei Ni. 2001. "Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources". *Chemosphere*. 44:997-1009.

Davis, Brett, and Gavin Birch. 2010. "Comparison of heavy metal loads in stormwater runoff from major and minor urban roads using pollutant yield rating curves". *Environmental Pollution*. 158:2541-2545.

Dunne, T., and L.B. Leopold. 1978. Water in Environmental Planning. Freeman, New York, NY.818 pp.

Gardner, Christopher B, and Anne E. Carey. 2004. "Trace metal and major ion inputs into the Olentangy River from an urban storm sewer". *Environmental Science Technology.* 38:5319-5326.

Genç-Fuhrman, Hülya, Mikkelsen, Peter S., and Anna Ledin. 2007. "Simultaneous removal of As, Cd, Cr, Cu, Ni, and Zn from stormwater: Experimental comparison of 11 different sorbents". *Water Research*. 41:591-601.

Ghobarkar, H., O. Schäf, and U. Guth. 1999. "Zeolites – from kitchen to space". *Progress in Solid State Chemistry*. 27(2-4):29-73.

Hatt, Belinda E., Fletcher, Tim D., and Ana Deletic. 2007. "Treatment performance of gravel filter media: Implications for design and application of stormwater infiltration systems". *Water Research*. 41:2513-2524.

Hollis, Lydia, Kent Burnison, and Richard C. Playle. 1996. "Does the age of metal-dissolved organic carbon complexes influence binding of metals to fish gills?". *Aquatic Toxicology*. 35:253-264.

Howard, K.W.F., J.I. Boyce, S.J. Livingston, and S. Salvatori.1993. "Road salt impacts on groundwater quality". *GSA Today* **3**:301–321.

Jordan, Ryan N., David R. Yonge, and Wade E. Hathhorn. 1997. "Enhanced mobility of Pb in the presence of dissolved natural organic matter". *Journal of Contaminant Hydrology*. 29:59-80.

Kaiser, Klaus, Martin Kaupenjohann, and Wolfgang Zech. 2001. "Sorption of dissolved organic carbon in soils: effects of soil sample storage, soil-to-solution ratio, and temperature". *Geoderma*. 99:317-328.

Khokhotva, Oleksandr, and Sylvia Waara. 2010. “The influence of dissolved organic carbon on sorption of heavy metals in urea-treated pine bark”. *Journal of Hazardous Materials*. 173:689-696.

Lai, C. H. and C. Y. Chen. 2000. “Removal of metal ions and humic acid from water by iron-coated filter media”. *Chemosphere*. 44:1177-1184.

Lee, Haejin, Sim-Lin Lau, MasoudKayhanian, and Michael K. Stenstrom. 2004. “Seasonal first flush phenomenon of urban stormwater discharges”. *Water Research*. 38(19):4153-4163.

Legret, M. and C. Pagotto. 1999. “Evaluation of pollutant loadings in the runoff waters from a major rural highway”. *The Science of the Total Environment*. 235:143-150.

MacEwan, D. M. M., and Wilson, M. J. 1980. “Interlayer and intercalation complexes of clay minerals”: in Brindley, G. W., and Brown, G. editors, “Crystal structures of clay minerals and their X-ray indentification”: Monograph No. 5, Mineralogical Society, London, p 197-248.

Maryland State Highway Administration. 2011. “Winter operations facts and figures”. Maryland Department of Transportation.http://roads.maryland.gov/oc/winter_operations_facts_and_figures.pdf. 3p.

McLean, E. O., and E. J. Owen. 1969. “Effects of pH on the contributions of organic matter and clay to soil cation exchange capacities”. *Soil Science Society Am. Proc. 33*:855-858.

Mohamed, R. M., Adel A. Ismail, G. Kini, I. A. Ibrahim, and B. Koopman. 2009. “Synthesis of highly ordered cubic zeolite A and its ion-exchange behavior”. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 348:87-92.

Moore, Duane M. and Robert C. Reynolds, Jr. X-ray Diffraction and the Identification and Analysis of Clay Minerals.New York, NY: Oxford University Press, 1989.

Murakami, Michio, Fumiyuki, Nakajima, and Hiroaki Furumai. 2008. “The sorption of heavy metal species by sediments in soakways receiving urban road runoff”. *Chemosphere*. 70:2099-2109.

Pitcher, S. K., R. C. T. Slade, and N. I. Ward. 2004. “Heavy metal removal from motorway stormwater using zeolites”. *The Science of the Total Environment*. 334-335:161-166.

Pitt, Robert, Shirley Clark, and Richard Field. 1999. “Groundwater contamination potential from stormwater infiltration practices”. *Urban Water*. 1:217-236.

Potter, H. A. B. and R. N. Yong. 1999. "Influence of iron/aluminum ratio on the retention of lead and copper by amorphous iron-aluminum oxides". *Applied Clay Science.* 14:1-26.

Pugh, Alexander L., IV, Stephen A. Norton, Molly Schauffler, George L. Jacobson Jr., Jeffrey S. Kahl, Willem F. Brutsaert, Charles F. Mason. 1996. "Interactions between peat and salt-contaminated runoff in Alton Bog, Maine, USA". *Journal of Hydrology*.182:83-104.

Sansalone, John J. 1999. "Adsorptive infiltration of metals in urban drainage – media characteristics". *The Science of the Total Environment*. 235:179-188.

Sansalone, John J., Seven G. Buchberger, and Souhail R. Al-Abed. 1996. "Fractionation of heavy metals in pavement runoff". *The Science of the Total Environment*.189/190:371-378.

Sansalone, J., and G. Ying. 2008. "Partitioning and granulometric distribution of metal leachate from urban traffic dry deposition particulate matter subject to acidic rainfall and runoff retention". *Water Research*. 42(15):4146-4162.

Shuyler, L.R., Linker, L.C., Walters, C.P. 1995. "The Chesapeake Bay story: the science behind the program". *Water Science Technology*. 31(8):133–139.

Sposito, G. The Chemistry of Soils. New York, NY: Oxford University Press, 1989.

United States Environmental Protection Agency. 2002. National Recommended Water Quality Criteria: 2002. http://water.epa.gov/scitech/swguidance/standards/upload/2008_04_29_criteria_wqctable_nrwqc-2002.pdf.

United States Environmental Protection Agency. 2012. National Recommended Water Quality Criteria. http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm.

Ursini, Ornella, Edo Lilla, and Roberto Montanari. 2006. "The investigation on cationic exchange capacity of zeolites: The use as selective ion trappers in the electrokinetic soil technique". *Journal of Hazardous Materials*. B137:1079-1088.

Wendling, Laura A., Grant B. Douglas, Shandel Coleman, and Zheng Yuan. 2012. "Nutrient and dissolved organic carbon removal from water using mining and metallurgical by-products". *Water Research*. 46:2705-2717.

Wu, Peng, and Yu-shan Zhou. 2009. "Simultaneous removal of coexistent heavy metals from simulated urban stormwater using four sorbants: A porous iron sorbent and its mixtures with zeolite and crystal gravel". *Journal of Hazardous Materials*. 168:674-680.

Ashley C. Whiting

805 Westridge drive (302) 690-3153
Hockessin, DE 19707 acwhiting@gmail.com

Education

Towson University (Towson, MD)
Master of Science in Environmental Science, August 2012
Thesis – "The effects of road salt on the metal binding ability of adsorptive media"
Concentration – Water Resource Management **GPA** 3.96/4.0

Dickinson College (Carlisle, PA)
Bachelor of Science in Environmental Science, May 2008
Concentrations – Aquatic Resources and Geology **GPA** 3.3/4.0

Experience

Towson University (Towson, MD)
Research Assistant – January 2010 – June 2012

- Performed water quality monitoring for the effects of road salt and suspended sediment on yellow perch in the Chesapeake Bay
- Performed data analyses using Microsoft Excel, ion chromatography and inductively coupled plasma mass spectrometry
- Maintained field equipment

Delaware Nature Society (Hockessin, DE)
Teacher/Naturalist – July 2008 – August 2009

- Delivered educational programs for children at Ashland Nature Center and Coverdale Farm on various environmental topics including stream ecology, water monitoring, reptiles and amphibians, and farm life

ALLARM (Alliance for Aquatic Resource Monitoring)
Dickinson College Environmental Studies Department (Carlisle, PA)
Laboratory Coordinator - August 2006 – May 2008

- Trained volunteer water quality monitors
- Collected and identified benthic macroinvertebrates
- Performed chemical water quality monitoring tests
- Created material safety data sheet (MSDS) database

Ultrachem Incorporated (New Castle, DE)
Intern - July – August 2006

- Updated material safety data sheets (MSDS)
- Performed Spanish translations over the phone
- Researched alternative lubricant ingredients