REMOVAL OF DISSOLVED METALS FROM STORMWATER RUNOFF

USING PERVIOUS CONCRETE

By

JERIN WILLIAM TILSON

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of JERIN WILLIAM TILSON find it satisfactory and recommend that it be accepted.

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Liv M. Haselbach, Ph.D., Co-Chair

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Cara J. Poor, Ph.D., Co-Chair

_____

Marc Beutel, Ph.D.

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Abstract

by Jerin William Tilson, M.S.
Washington State University
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Co-Chair: Liv Haselbach and Cara Poor

   Due to increased development in recent years and subsequent impervious areas, an

increase in peak stormwater runoff (flooding) and non-point source pollution to aquatic systems

has occurred. Pervious concrete is a low impact development (LID) technique that has been

shown to protect against flooding by allowing stormwater runoff to infiltrate through the

concrete and into the soil. In addition, pervious concrete may be capable of providing water

quality control. An investigation was conducted to test the efficacy of dissolved zinc and copper

removal in stormwater runoff with pervious concrete. Short term tests were performed to

determine the ability of the concrete to remove zinc and copper during first flush conditions. An

equivalent of 12 mm (0.5 inches) of stormwater was applied to three pervious concrete cylinders

for approximately ten minutes with hotspot zinc and copper concentrations of 500 µg/L and 100

µg/L, respectively. These concentrations are found in areas that are exposed to prolonged sitting

and running vehicles. Minimum removal rates of zinc and copper were 96% and 90%,

respectively. Another test was conducted on three concrete cylinders to simulate removal of

typical zinc and copper concentrations (100 µg/L and 20 µg/L, respectively) deposited on

roadways. The pervious concrete cylinders removed zinc and copper from the stormwater at a

minimum of 89% and 87%, respectively. Four other cylinders were subjected to additional typical concentration tests after the columns experienced long term exposure of a theoretical 15 years. Zinc and copper was removed at a minimum of 87% and 83%, respectively, after 15 events (approximately 7 years) of long term exposure, and a minimum of 86% of both copper and zinc after 24 events (approximately 12 years). To determine the long term efficacy of the pervious concrete, twelve cylinders were loaded with 30 events at concentrations forty times typical concentrations for a projected 15 years of exposure. Zinc and copper were removed at a minimum of 59% and 56%, respectively. This study indicates that pervious concrete is a viable best management practice for treatment of zinc and copper in stormwater, particularly in areas with limited space.

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1. Introduction

Low Impact Development (LID) techniques minimize the impact of development at a site on the hydrologic cycle (Ahiablame, 2012). LID techniques address water quality issues as well, mitigating and treating flow close to the source of the stormwater runoff. Various LID techniques include, but are not limited to, biorentention, infiltration wells/trenches, constructed wetlands, permeable pavements, green roofs, vegetated buffer strips, preservation of natural site features, and native vegetation utilization. The use of LID techniques minimizes the need for curbing, stormwater drains, piping, and other conventional stormwater practices (Ahiablame, 2012). However, the capabilities of some techniques are not fully known. Pervious concrete is one such LID technique in which the potential for stormwater treatment is unknown. Pervious concrete is concrete with large pore spaces, allowing water to infiltrate through it. Copper and zinc are common roadway contaminants, accumulating on roadway and parking lot surfaces from brake pads (copper) and the galvanized surfaces (zinc). Stormwater typically carries metals from impervious surfaces to local bodies of water. Parking lots and other locations where cars idle are considered "hot spots" for metal pollutants. Concentrations of zinc and copper in water samples taken from an oil grit separator at a gas station were 554 μg/L and 112.6 μg/L, respectively (Schueler and Holland, 2002). .

Elevated concentrations of dissolved metals are an environmental concern because they do not biodegrade, transport easily in aquatic habitats, and are available for absorption in plants and animals (Sansalone et al. 1997). Zinc causes damage to fish gills (Eisler, 1993) and affects reproduction (EPA, 2011). Acute and chronic concentrations are both 120 μg/L for freshwater. For saltwater, acute and chronic concentration levels are 90 μg/L and 81 μg/L, respectively

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(EPA, 2013). Copper causes death in fish and amphibians at acute concentrations. At chronic concentration levels, the ability of fish to survive and reproduce is reduced (EPA, 2012). Acute and chronic concentration levels for Chinook salmon are 25.02 µg/L and 5.92 µg/L for freshwater, respectively (EPA, 2007). For saltwater, acute and chronic concentration levels are 4.8 µg/L and 3.1 µg/L, respectively (EPA, 2007). By allowing surface runoff to infiltrate concrete, it may be possible to eliminate or minimize these effects of zinc and copper.

This study focuses on determining the efficiency of removing dissolved metals, zinc and copper, from stormwater runoff as the runoff infiltrates through the pervious concrete. Research using pervious concrete in this specific way is limited, but there are closely related studies. One study compares metal removal from stormwater using impervious asphalt and pervious asphalt (Berbee et al., 1999). Metal concentrations were ten times lower in pervious asphalt samples compared to impervious. The study supports that pervious surfaces reduce metal concentrations, but they only investigate metals in particulate phase. Another study showed porous pavement materials composed of various plastic lattices, vegetation, aggregate, sand, and soil to reduce dissolved metal loadings (Brattebo and Booth, 2003). Subbase material was tested for metal removal for another study. At an initial concentration of 660 µg/L, gravel, basalt, and limestone material removed 97%, 98%, and 88% of zinc, respectively. At an initial concentration of 470 µg/L, 96%, 96%, and 94% of copper was removed using the same materials, respectively (Dierkes et al., 2007).

Many studies have been conducted to investigate the behavior of metals in soils. This data is an indication of the fate of contaminants as they pass through pervious concrete since reaction conditions and characteristics in soil are similar. Effective treatment of metals within soil is dependent on certain properties, such as pH. An increase in metal uptake has been shown

with increasing pH (Yong, 1993). This study suggests that retention of metals in soil is dependent on pH because complexation with hydroxides, sulfates, and chlorates species occurs around a neutral pH. The results show that almost 100% of metal contaminants, added individually, are absorbed in the soil at pH greater than 5, 5.5, 7, and 7.5 for lead, copper, zinc, and cadmium, respectively (Yong, 1993). Carbonate is a main source of metal retention in soil, and has been shown to limit precipitation for pH above 4. Metal adsorption in concrete most likely will not behave exactly the same in soil, but it provides some basis of comparison. The pH levels of the soil compared to the pervious concrete are similar, and carbonate appears to have an effect on the ability of the soil to retain metals. These soil studies provide some insight into how metals may be retained in pervious concrete. Both the pH and carbonate content of the concrete will likely favor adsorption of metals in stormwater.

The characteristics of pervious concrete, including pH, porosity, and its chemical composition, indicate that it has potential for removing metals from stormwater. Initially after curing, pervious concrete has a pH of approximately 11.4. However, pH decreases due to carbonation, where calcium hydroxide is replaced with calcium carbonate from the adsorption of carbon dioxide from the air (Thomle, 2010). The equation below shows the reaction that occurs when pervious concrete adsorbs carbon dioxide (Haselbach and Ma, 2008).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
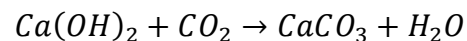
The pH of the concrete is important in the process of removing metals from water because it determines if the metals will bind with concrete, stay in soluble form, or precipitate. From the metal retention studies discussed previously, one can conclude that metals can be retained in pervious concrete in a similar fashion. Further investigation needs to be performed if the pH of the pervious concrete is high enough to adsorb the contaminants.

Porosity is another important characteristic of pervious concrete that may control the degree of sorption of the metals to concrete. Contact time, also known as residence time, of the metal reacting with the surface of the concrete is a function of porosity. A study on metal sorption in soils showed that contact time affects the amount of metals sorbed (Plassard et al., 1999). If the metal ions do not have adequate time to react in the soil, the reaction may not completely equilibrate. Similarly, if the pervious concrete is too porous, the contaminated water may not have adequate contact time with the concrete. If the concrete is not porous enough, the concrete may not have adequate infiltration for the surface runoff in the area or it might become clogged (Haselbach and Freeman, 2006). Further research is needed to better understand the correlation between metal adsorption and porosity.

The chemistry of pervious concrete is also important in understanding how heavy metals can be filtered. Concrete contains calcium hydroxide, and as it carbonates, it is replaced with calcium carbonate. Soil studies have shown that metals have an affinity to complex with hydroxides and carbonate. Free metals ions become strongly bonded to these ligands forming complexes (Gnecco et al., 2008). The metals are no longer dissolved in the stormwater, but are bonded to surfaces of solids and removed from solution. A similar reaction may occur with surface sites on aggregate in the pervious concrete. The metals may adhere with the surface by bonding with calcium carbonate, however, more studies need to be conducted to fully understand how the metal ions will interact with the surface of the concrete. A hydraulic model with predictive chemical speciation capabilities can simulate the hydraulic and chemical functions of the pervious concrete with dissolved metal loaded stormwater flowing through it, and aid in understanding how the metal ions interact with the ligands on the concrete surface.

The potential for pervious concrete to remove metal contamination from stormwater could improve water quality. Contamination of surface water has declined with increasing development and construction of new impervious surfaces, which inhibits stormwater from infiltrating into the soil. Instead, stormwater runs off of impervious surfaces, carrying contaminants with it, and enters directly into aquatic systems. As a result, increased peak flows, a larger volume of water, and higher mass loading of contaminants negatively impact receiving water bodies. Related studies using porous surfaces to remove metals from stormwater have been done, but research on pervious concrete removing dissolved metals is needed. Studies conducted in soil and about specific pervious concrete parameters indicate that pervious concrete may effectively remove metals from stormwater. This study was performed in a controlled lab environment in which pH, porosity, and residence time was controlled to determine the efficacy of metals removal in pervious concrete. The percentage of removal and the long-term efficacy of the concrete were also determined.

The goal of this research is to determine the efficacy of zinc and copper removal in pervious concrete from stormwater. Two types of pervious concrete were used for this test; a concrete mix with 100% ordinary portland cement (OPC) (WB cylinders) and a mix with 25% low calcium fly ash and 75% OPC (WD cylinders). Specifically, the objectives are to:

1: Test effluent concentrations of simulated stormwater with hot spot concentrations of dissolved zinc and copper with no fly ash added to pervious concrete cylinders.

2: Test effluent concentrations of simulated stormwater with typical concentrations of dissolved zinc and copper before and after long term exposure without a fly ash additive in the mixture.

3: Test effluent concentrations of simulated stormwater with accelerated concentrations of zinc and copper for cylinders with fly ash and without fly ash simulating long-term exposure to the metals.

4: Create a model in Hydrus-2D and PHREEQC that simulates hydraulic and chemical behavior of dissolved zinc and copper passing through pervious concrete.

Chapter 1 contains an introduction to the pervious concrete research and why it was conducted. Chapter 2 includes a paper on the results addressing Objective 1. The paper discusses the concrete cylinders loaded with zinc and copper at the hotspot concentration. Chapter 3 is a paper that covers Objective 2. The paper discusses the typical and accelerated loading tests. Chapter 4 covers Objectives 3. The chapter compares the results for the two types of pervious concrete cylinders. Chapter 5 contains the method and results of Hydrus-2D modeling and covers Objective 4. Chapter 6 includes a summary and conclusions.

Summary of Methods

Synthetic rainwater was prepared in the laboratory using rainwater data collected from Southeast Washington. The synthetic rainwater contains five components: sodium chloride, calcium carbonate, potassium nitrate, sodium bicarbonate, and potassium bicarbonate at concentrations of 2.47 mg/L, 0.30 mg/L, 3.92 mg/L, 0.34 mg/L, and 0.30 mg/L, respectively (Flury, unpublished data).

Zinc and copper is added to the synthetic rainwater in the form of zinc chloride and cupric chloride dihydrate. Each metal was added to the synthetic rainwater at three different concentrations for four different tests. The different concentrations are the hot spot

concentration, the typical concentration, and the accelerated concentration. The specific methods of these experiments are described in greater detail in their respective chapters

The tested pervious concrete cylinders were created in December 2008 using ordinary Portland cement (OPC), aggregate, fly ash, and water in the proportions described in Table 1.2 for each type of cylinder. One group of cylinders, designated WB, was made with 100% OPC and another group of cylinders, WD, was made with 25% low calcium fly ash and 75% OPC.

Table 1.1: Materials Used to Make Pervious Concrete Cylinders

	WB	WD
Prepared on	12/18/2008	12/24/2008
Cement (lbs.)	30	22.5
Aggregate (lbs.)	120	120
Aggregate Size	#8	#8
Water (lbs.)	8	8
Fly Ash (lbs.)	0	7.5

The pervious concrete cylinders were exposed to the atmosphere in the laboratory. Thus, the channel surfaces were assumed to have undergone carbonization. The cylinders were also used in pH tests in which the cylinders were tested with deionized water. All cylinders used in metal adsorption tests had porosities that were determined by a porosity test using a modified ASTM C1754 (ASTM 2012). The results from the porosity test are listed in Table 1.3.

Table 1.2: Pervious Concrete Materials

Test	Specimen ID	V_T (in.^{3})	Test Date	Porosity (%)
Accelerated	WB01	91.29	Feb. 2012	24.7
	WB07	91.86	Feb. 2012	24.4
	WB10	89.96	Feb. 2012	24.8
	WB11	91.77	Feb. 2012	25.4
	WB12	91.61	Feb. 2012	25.4
	WB18	91.58	Feb. 2012	25.5
	WD03	91.12	Feb. 2012	24.3
	WD06	91.07	Feb. 2012	24.2
	WD08	91.11	Feb. 2012	24.0
	WD11	90.67	Feb. 2012	24.4
	WD15	90.28	Feb. 2012	23.8
	WD16	90.00	Feb. 2012	24.0
Typical	WB02	91.77	Jun. 2012	24.7
	WB05	91.23	Jun. 2012	24.4
	WB06	90.85	Jun. 2012	25.0
Hot Spot	WB13	91.87	Jun. 2012	24.8
	WB15	91.53	Jun. 2012	24.7
	WB17	92.16	Jun. 2012	25.0

The annual rainfall for Western Washington is 40 inches per year. During a 2 year storm event, the intensity is equivalent to 3 inches of rain per hour, which equals 0.5 inches of rain applied over a duration of 10 minutes (Thompson, 2011). For the 4-inch diameter concrete cylinders, 0.5 inches of water is equivalent to 100 mL applied to each cylinder. Thus, the stormwater was applied to the cylinders at a rate approximately equal to 10 mL/min. In order to apply the water to the concrete cylinders, a glass buret was suspended over a concrete cylinder to drip the stormwater through the cylinder. A glass beaker was placed under the concrete cylinder to collect the effluent from the cylinder. Effluent was collected approximately 10 minutes after stormwater application. The volume of the effluent collected was recorded and samples were

stored in 30 mL high density polyethylene bottles at 4°C acidified to a pH less than 2 with acidic acid (Eaton et al., 2005). Figure 1.3 shows the experimental set up.
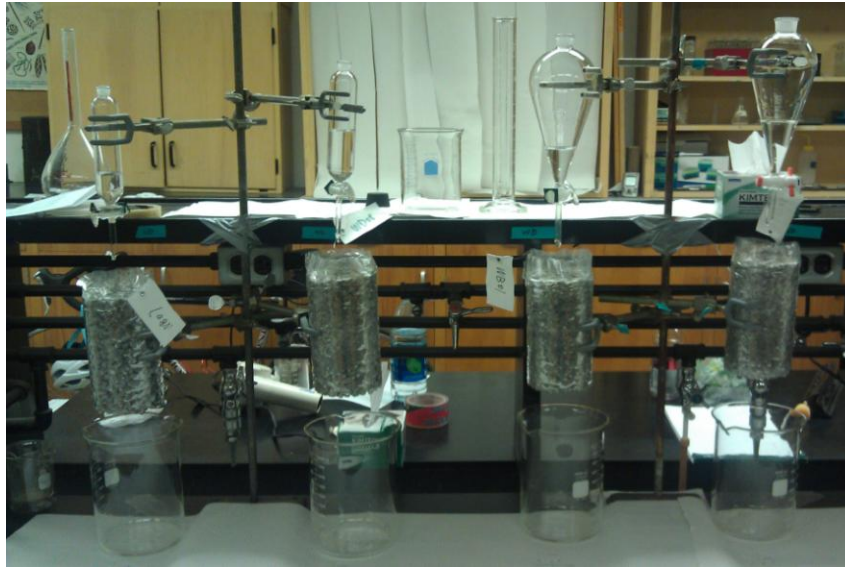
Figure 1.1: Experimental Setup

The mass of the concrete cylinders are measured prior to and after testing. Then the cylinders were placed in an oven for further drying at a temperature no greater than 50°C for a minimum of twelve hours. Influent and effluent samples were sent to the Geoanalytical Laboratory at Washington State University for analysis of total dissolved zinc and copper, where an Agilent Technologies 7700 Series Inductive Coupled Plasma – Mass Spectrometer (ICP-MS) was used.

2. Dissolved Zinc and Copper Retention in Pervious Concrete under Hot Spot Loading Conditions

This chapter covers the hotspot loading tests on the Ordinary Portland Cement (OPC) cylinders, labeled WB, and is in the format of a short proceedings paper. It was distributed at the CASQA conference in San Diego in November 2012.

Abstract

Pervious concrete is a novel pavement material with many environmental benefits such as stormwater management and heat island mitigation. It has been shown that permeable pavements may also reduce stormwater metal pollutant loadings associated with filtered solids. This study evaluated the ability of pervious concrete to retain dissolved metals based on chemistry associated with pH, carbonate species, and hydroxide species in the hydrated cement. Portland cement based pervious concrete cylinders were used. The cylinders had been previously aged under ambient conditions in the laboratory for over three years to represent carbonated field conditions. Hotspot concentrations of dissolved zinc and copper based on typical roadway stormwater levels were applied to the cylinders and the effluent concentrations were analyzed. Removal rates for these elevated conditions initially exceeded 85%. Future long term testing will provide information on the efficiency of pervious concrete systems for hotspot dissolved metal water quality treatment.

Introduction

Certain dissolved metals species in stormwater runoff may be of concern if high concentrations enter bodies of water in which the biota are sensitive to these metals. It has been shown that many permeable pavement systems are effective in removing many metals from stormwater. In a study evaluating the performance of concrete media to filter pollutants from stormwater runoff, different types of porous pavement systems were tested in the field to determine the effectiveness of the removal of contaminants (Brattebo and Booth, 2003). The minimum detection limits were 1.0 µg/L and 5.0 µg/L for copper and zinc, respectively. Results varied due to the different types of paver systems tested. 97% of influent samples contained metal concentrations that were considered toxic. After treatment, however, 31 of 36 samples tested for metals were below toxic levels. Furthermore, most of these samples were below the detectable limits. In another study by Dierkes et al. (2007), effluent collected from stormwater runoff containing zinc and copper infiltrated permeable pavers with a subbase containing limestone. The infiltrated stormwater through the limestone paver system experienced 88% and 94% removal for zinc and copper, respectively. In a field study in Pennsylvania, metals were removed from stormwater by infiltrating through a pervious concrete system (Barbis, 2009). Stormwater runoff containing 7.1 µg/L of copper infiltrated through a pervious concrete system. The effluent was collected and copper was measured below 2.8 µg/L. The influent concentration for zinc was 90.4 µg/L and it experienced significant removal flowing through the pervious concrete system.

However, much of the aforementioned removal effectiveness might be from filtering of metal laden particulates in the stormwater. In addition, there might be absorption or adsorption to other components in the systems such as retained sediments, or soils and other materials in the

underlying aggregate storage beds or soils. The hypothesis of this research is that the pervious concrete itself can be used to remove various dissolved metal species from stormwater runoff. The focus of this study is focused on removing dissolved copper and zinc. The mechanisms of removal are due to the unique carbonate/hydroxide chemistry of concrete with a fairly high pH. This combination of characteristics may promote copper and zinc complexation along the flow channels and then diffusion into the porous structure of the cement paste in the concrete itself.

The objective of this study is to test the effectiveness of pervious concrete removing dissolved zinc and copper. This is achieved by dripping a known concentration of dissolved metals through the concrete cylinders and testing the effluent concentrations. The volume of water applied and flow rates used are based on typical larger storms such as 6 month to 5 year events, with the concentrations representative of first flush conditions in areas expected to receive higher levels of metal pollutants.

Experimental Methodology

Three similar pervious concrete cylinders, labeled WB, were used in this experiment. They were made with 100% OPC. The metal concentrations used in this experiment are based on reported results from several field investigations found in the literature. The hot spot concentrations were taken from the oil grit separator study (Schueler and Holland, 2002). Other studies include stormwater samples collected from surface runoff from a highway in Texas showed concentrations of 222 µg/L for zinc and 37 µg/L for copper (Barrett et al., 1998). Another study tested influent runoff containing zinc and copper concentrations of 90.4 µg/L and 7.1 µg/L, respectively (Barbis, 2009). To coincide with these ranges, typical concentrations assumed for this experiment were 100 µg/L and 20 µg/L for zinc and copper, respectively. Five

times the typical concentration, known as the hot spot concentration, equals approximately 500 µg/L for zinc and 100 µg/L for copper. Actual concentrations varied slightly and are given in the results.

Results

Table 2.2 shows the porosities for each cylinder, which were nearly identical. Measured influent and effluent volumes and concentrations for each event are also shown in Table 2.2. Approximately 20-40 mL of the stormwater mixture was retained in the cylinder during each event. Data from event 6 was omitted due to experimental error.

Using a mass balance with mass concentration metric approach, the amount of zinc and copper that was retained in each cylinder during events was determined, which is represented in Figure 2.1. Mass concentration metric approach accounts for the volume of water absorbed by the concrete. The standard deviation bars in Figure 2.1 show little variation in results for 10 events. At least 85% of the copper and 90% of the zinc was retained for all events. Figures 2.2 and 2.3 show influent and effluent concentrations for zinc and copper, respectively. As each cylinder is loaded, retention levels do not appear to change. Effluent concentrations for both zinc and copper stay relatively constant throughout the 10 loading events.

Table 2.1: Results for Specimens Loaded with High Concentrations of Zinc and Copper

Specimen ID	Porosity (%)	Event	Influent Volume (mL)	Effluent Volume (mL)	Influent Concentration (µg/L)		Effluent Concentration (µg/L)	
					Zn	Cu	Zn	Cu
WB13	24.8	1	100	76	579	94	43	12
		2	100	80	562	92	18	9
		3	100	72	601	100	42	15
		4	100	73	556	90	33	10
		5	100	63	575	94	29	10
		6	100	68	Experimental Error			
		7	100	64	573	93	38	8
		8	100	66	560	92	47	10
		9	100	71	575	93	40	11
		10	100	64	626	101	19	9
WB15	24.7	1	100	72	579	94	34	11
		2	100	77	562	92	19	9
		3	100	72	601	100	44	14
		4	100	72	556	90	28	9
		5	100	59	575	94	21	8
		6	100	66	Experimental Error			
		7	100	60	573	93	20	7
		8	100	66	560	92	15	7
		9	100	70	575	93	25	9
		10	100	66	626	101	29	11
WB17	25.0	1	100	74	579	94	27	9
		2	100	74	562	92	22	9
		3	100	72	601	100	25	12
		4	100	74	556	90	21	8
		5	100	62	575	94	26	7
		6	100	72	Experimental Error			
		7	100	69	573	93	44	9
		8	100	70	560	92	21	8
		9	100	72	575	93	33	9
		10	100	70	626	101	29	10
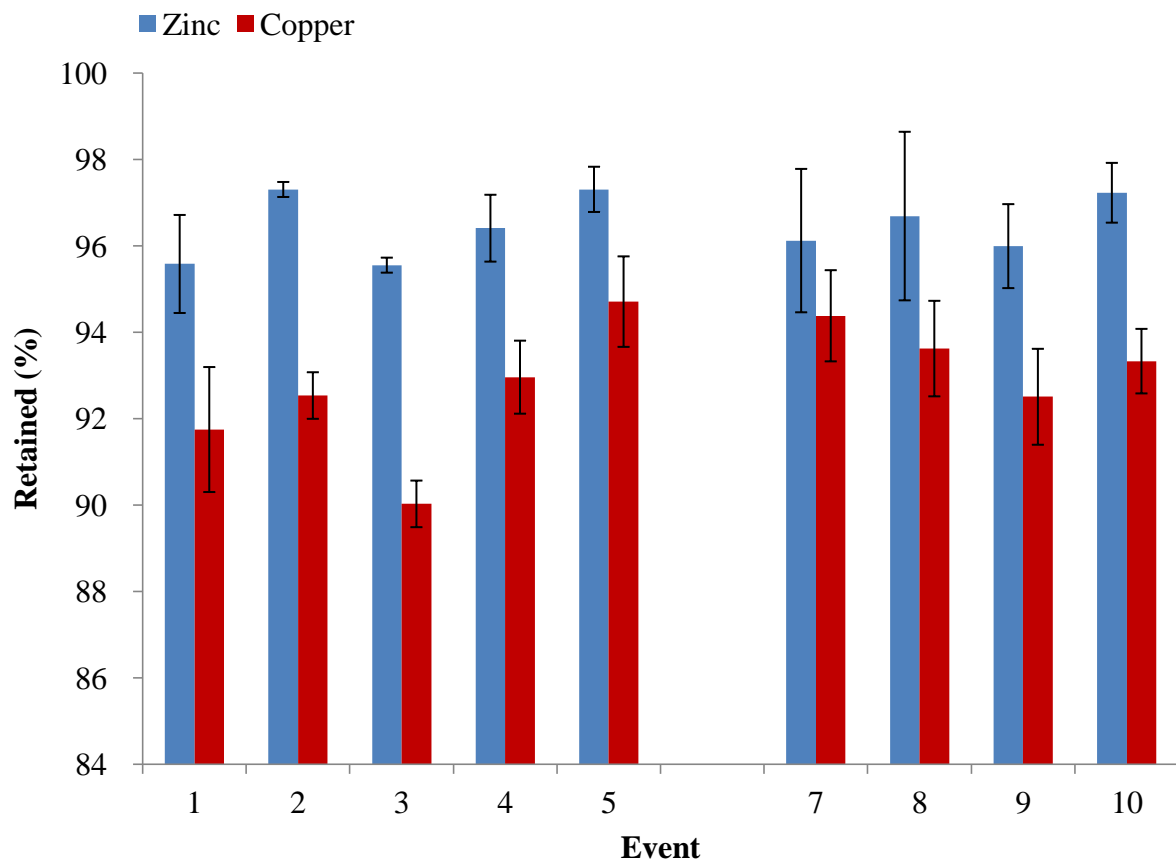
Figure 2.1: Average Percent of Metal Retained at a Hotspot Concentration for Three Cylinders. Bars Represent Standard Deviation.
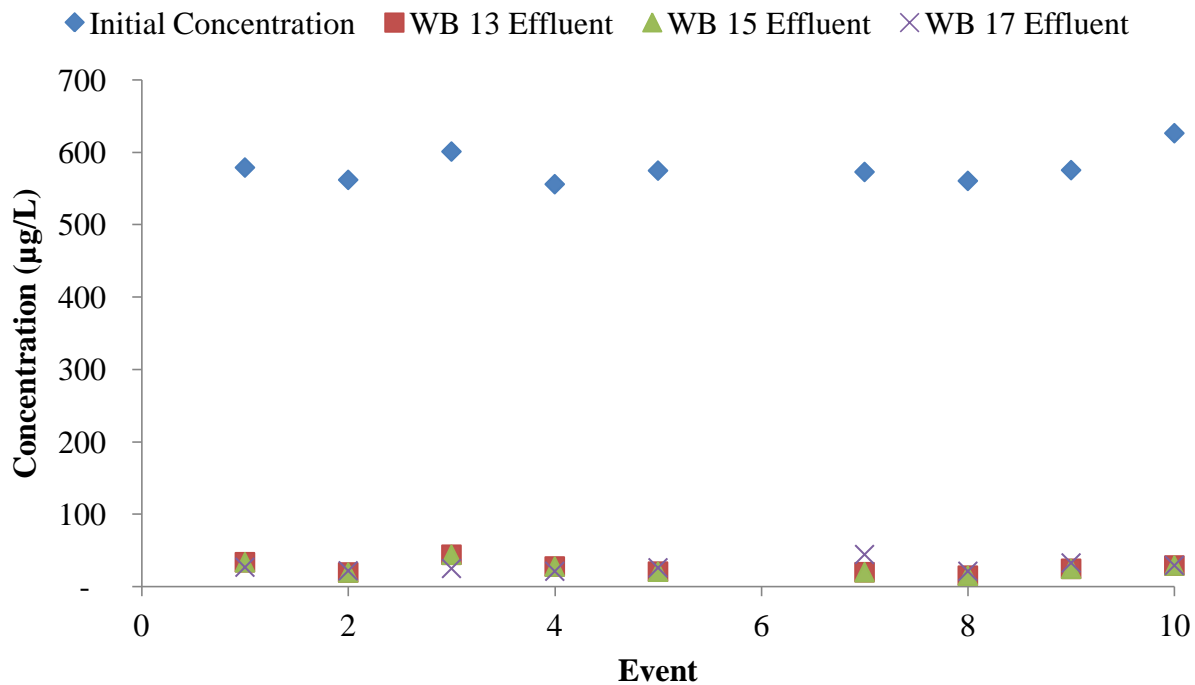
Figure 2.2: Influent and Effluent Concentration of Zinc for each Individual Cylinder
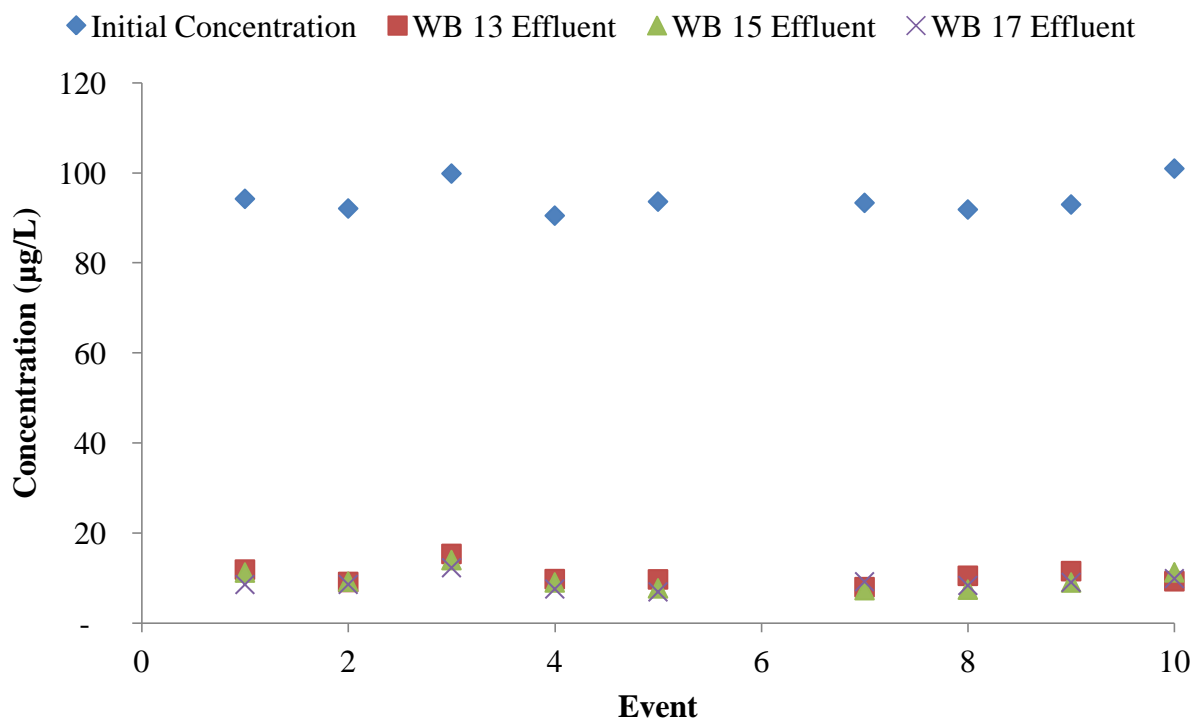
Figure 2.3: Influent and Effluent Concentration of Copper for each Individual Cylinder

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Conclusions

In all cases, at least 85% of the copper and 90% of the zinc were removed from the stormwater mixture and sorbed to the pervious concrete, even after 10 events of consecutive loading. Pervious concrete is made of random, tortuous flow channels, various micropores, and both connected and disconnected macropores. Since the volumetric flow rates were fairly high, there was little chance for equilibrium partitioning to occur between the stormwater mixture and the pervious concrete cylinders. This indicates that pervious concrete has a high affinity for rapid surface sorption of dissolved zinc and copper in its flow channels. The retained metals might then more slowly diffuse into the pervious concrete matrix allowing for longer term retention and additional surface sorption sites in the flow channels. These removal rates achieve levels frequently found in specially designed water treatment media. This experiment indicates that pervious concrete has a high potential for enhanced dissolved zinc and copper removal from stormwater, even at hotspot concentrations and during fairly large storm events.

Future testing for extended times which might mimic decades of metals loading would aid in estimating the life of pervious concrete applications for enhanced metals removal. Other metals and different pervious concrete mix designs should also be tested to determine best practices under various field and material conditions.

Acknowledgements

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3. Dissolved Zinc and Copper Retention in Pervious Concrete from Stormwater Runoff (Ordinary Portland Cement)

This chapter is a manuscript in review at a peer reviewed journal.

Abstract

This research demonstrates that the pervious concrete layer alone in these systems is effective in removing dissolved zinc and copper contaminants from stormwater runoff. Pervious concrete cylinders made with ordinary portland cement were applied in the laboratory with simulated stormwater runoff, and the influent and effluent concentrations and volumes measured. In the short term tests, the stormwater was dispensed onto three cylinders at typical concentrations (100 µg/L Zn and 20 µg/L Cu) simulating ten consecutive storm events of 12 mm (0.5 inches) of rain. Another set of six concrete cylinders were used for accelerated long term exposure over many years and loaded at forty times the typical concentration for 15 to 30 events. The results show that the concrete cylinders remove at least 87% of zinc and copper at the typical concentrations. The cylinders with the accelerated concentrations usually removed greater than 63% of the metals during the accelerated events. Two of these cylinders were removed from the accelerated tests after 15 and 24 accelerated events respectively for further testing to determine performance during subsequent typical storm events, and the removal efficiencies were 83% and higher.

Introduction

This study investigates the ability of pervious concrete alone that the pervious concrete in a permeable pavement system may effectively remove some dissolved metals, especially zinc and copper due to the chemical and physical characteristics of the concrete.

Metals are likely removed from solution due to complexation and solids formation with the hydroxides (OH^-) and carbonates (CO_3^{2-}) that are attached to calcium in the concrete. In aqueous systems, many complexes form between carbonate and hydroxide ligands, and metals such as calcium, zinc and copper. Formation is typically enhanced at higher pH values. These complexes can also form on surface species of the carbonates and hydroxides (Stumm and Morgan; 1996). When ordinary portland cement (OPC) is used to make concrete, the compounds that result include many hydroxide species, including substantial amounts of calcium hydroxide. In the tortuous interconnected flow channels throughout pervious concrete, there are many carbonate species, in addition to the hydroxide species, on the surface due to carbonation from the carbon dioxide in the atmosphere. In fact, XPS analyses have indicated that on cement surfaces there may be up to three carbon atoms for every calcium ion (Haselbach and Ma, 2008). Thus, there is a high affinity for surface complexation of the dissolved zinc and copper ions with both ligands. After complexation during a storm event, there is then the opportunity for diffusion into the microporous structure of the interior pervious concrete matrix. As in any ordinary portland cement concrete specimen exposed to the atmosphere, beyond the highly carbonated surfaces, the concrete will be less carbonated and there will be more hydroxide species remaining (Pade and Guimaraes, 2007). These may also form many complexes with the zinc and copper ions, with the potential for formation of the solid complex species too. The logarithm of the stability constants for the formation of the solid hydroxide species for the three metals are

5.19, 19.3 and 16 for calcium, copper and zinc respectively, indicating a higher affinity for formation of the copper and zinc hydroxide solids than the calcium. The logarithm of the stability constants for the formation of the solid carbonate species for the three metals are 8.2, 9.6, and 10 for calcium, copper and zinc respectively, again indicating a higher affinity for copper and zinc than calcium. In addition to the solid phases, the stability constants for the various complexations generally tend to favor zinc and copper complexation over calcium (Stumm and Morgan, 1996).

Due to the large amounts of surface areas in the channels in pervious concrete, the likely process for pervious concrete sorption of dissolved copper and zinc is rapid surface adsorption forming various complexation species during a storm event, and then diffusion and additional complexation species development in the interior of the concrete matrix. This three step process would then allow for partial renewal of the complexation sites in the channels prior to subsequent storm events.

There are some previous studies which support the hypothesis that OPC concrete may have these sorption capabilities. Fach and Geiger (2005) developed metal adsorption equilibrium curves (isotherms) for the concrete in concrete pavers by pulverizing them and exposing crushed samples to aqueous dissolved metal solutions. Dyer et al. (2009) found that significant amounts of metal hydroxides precipitate on the concrete surface and within the concrete in a study on the impact of soil contaminated with zinc, lead and copper on freshly placed concrete.

This study was conducted in three parts in the laboratory. The first part examined the initial removal of dissolved zinc and copper species by pervious concrete from simulated stormwater runoff with typical concentrations. The second part examined the removal efficiencies of very concentrated solutions of these two metals in order to simulate longer term

loading. The third part examined the effectiveness of the pervious concrete to remove typical

concentrations of copper and zinc after longer term loading.

Materials and Methods

For the typical loading events, zinc and copper concentrations were 100 µg/L and 20 µg/L,

respectively for simulated stormwater. Individual effluent samples were taken from each cylinder

for each event and separately prepared for analysis. The volume of effluent was also recorded for

mass balance purposes. The effluent samples were preserved and stored following the same

standard method as stated previously. After each event the cylinders were allowed to dry for at

least 12 hours in a warm oven (maximum temperature of 50°C). Three of the cylinders were used

for the initial typical loading tests and they received ten consecutive events at these rates and

concentrations. Two of the accelerated loading cylinders (WB10 and WB11) also received three

consecutive typical loading events after a series of accelerated loading. For the accelerated

loading tests, all of the pervious concrete cylinders were loaded at least 15 times. After 15 events

(approximately 7.5 years), Cylinders WB10 and WD03 were loaded with the typical

concentration. Similarly, after 24 events (approximately 12 years), cylinders WB24 and WD15

were subjected to typical loadings tests. The rest of the cylinders were loaded with 30 events

(approximately 15 years). Twelve other cylinders were also loaded with typical and hotspot

concentrations for 10 events.

For the accelerated loading events, the stock solution of zinc and copper was diluted to 4000

µg/L and 800 µg/L, respectively, with simulated stormwater, and a single influent sample

analyzed for each event. The contaminated stormwater was applied to the concrete cylinders

using the same method as described with the typical loading events and the effluent volumes were measured. In this case, the effluent collected for all the cylinders tested were combined into one effluent sample per event. The effluent samples were preserved and stored following the same standard method as stated previously and the same drying method used in other tests was also done.

Results

The influent and the effluent concentrations were used to determine the percentage of metals removed by the pervious concrete. The percentage removal was determined using a mass concentration metric approach for a mass balance for all results. Figure 3.1 shows the average removal of metal for three cylinders with the associated standard deviations. Retention of metals in the concrete was found to be no less than 89% for zinc and 87% for copper at the typical concentration. Results of the percent removal of each metal are the average of three specimens for each event performed. The standard deviation bars in Figure 3.1 show a negligible amount of variation across 10 events.
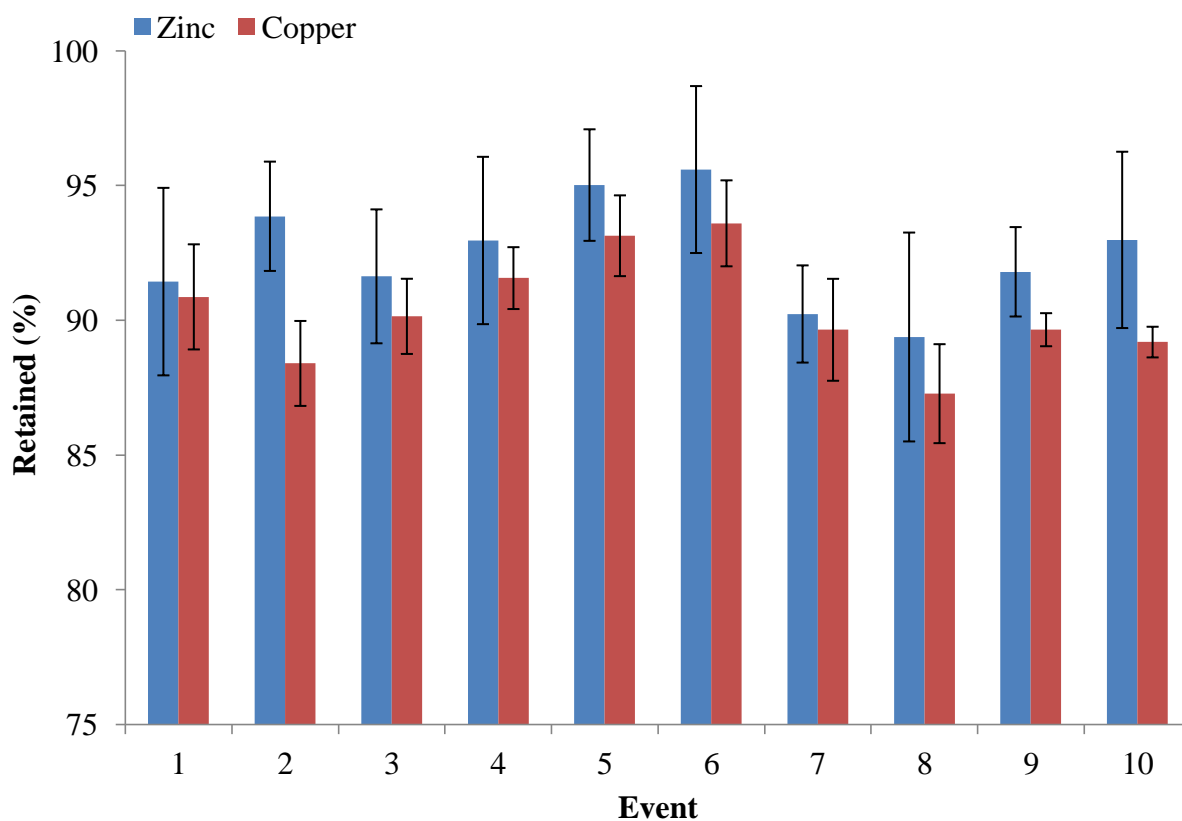
Figure 3.1: Average Zinc and Copper Percent Retained during Typical Concentration Loading Events in Three Pervious Concrete Cylinders. Bars Represent Standard Deviation

The influent concentrations of zinc for the accelerated events fall between 4,285 µg/L and 4,901 µg/L with one that was at a higher concentration of 5,722 µg/L. The removal of zinc for the cylinders was consistent across the 30 events. Figure 3.2 shows that the effluent was concentrated around 2,200 µg/L.
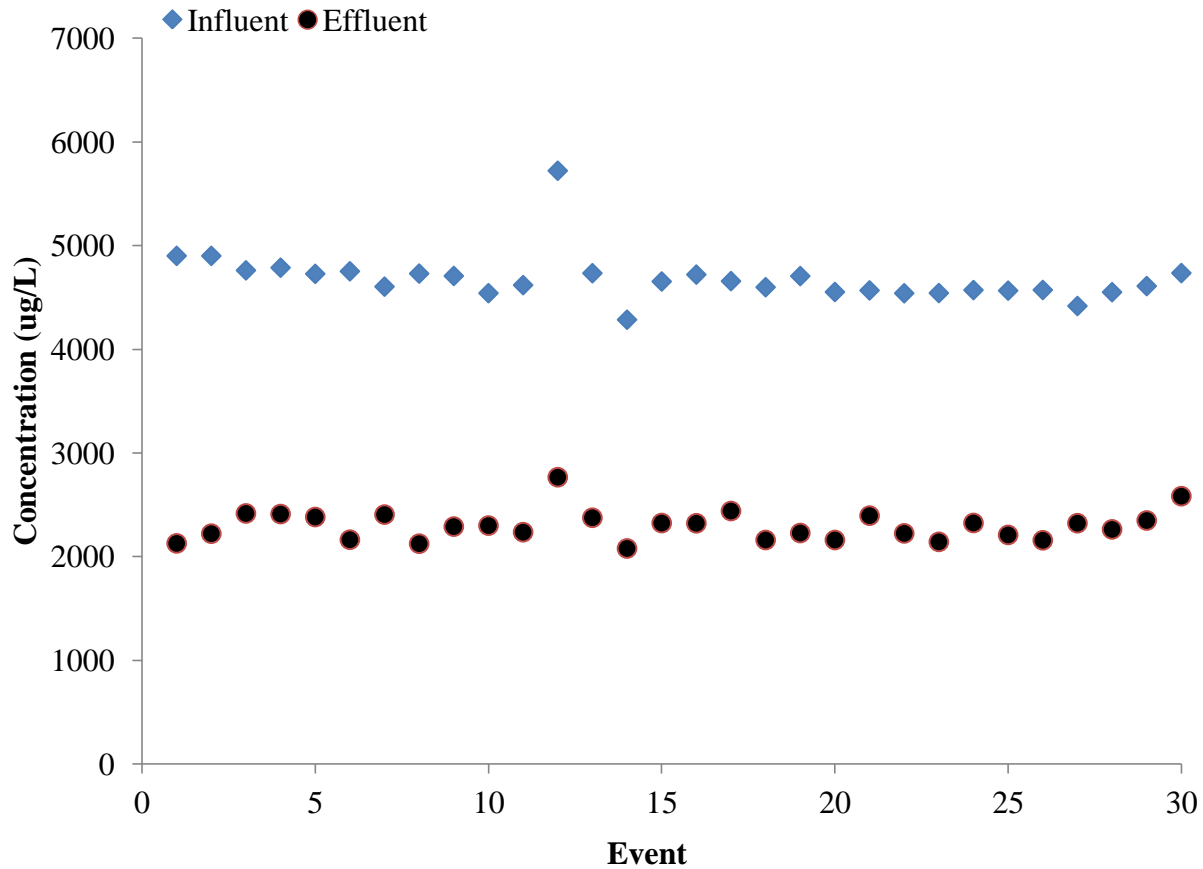
Figure 3.2: Average Measured Concentrations of Zinc in Stormwater for Accelerated Events

In the same accelerated events, Figure 3.3 shows the copper influent concentrations ranged from 745 µg/L to 814 µg/L with one highly concentrated influent sample of 937 µg/L and one low concentrated sample of 715 µg/L. The copper effluent concentration decreased gradually as the cylinders experienced additional events while the influent concentration remained consistent.
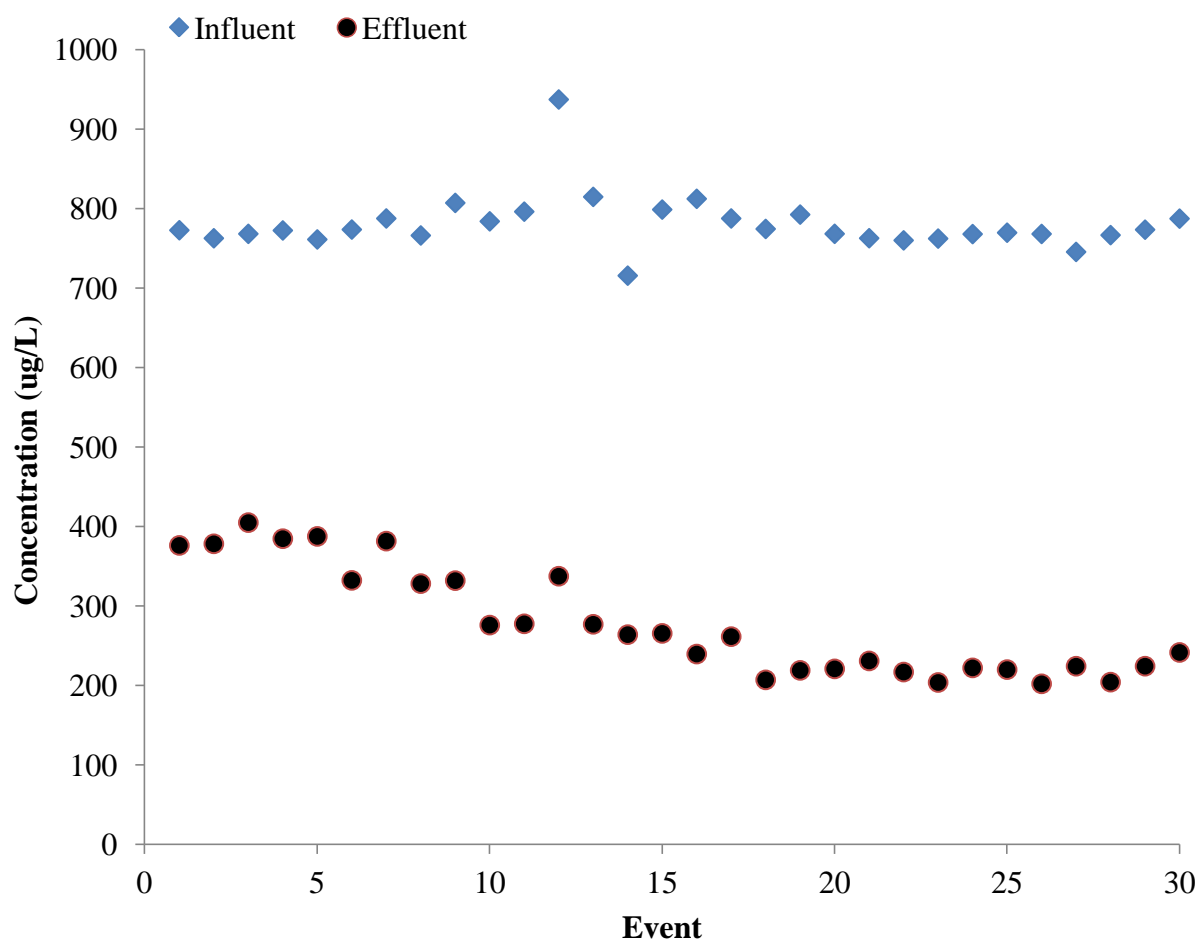
Figure 3.3: Average Measured Concentrations of Copper in Stormwater for Accelerated Events

The cylinders, stock solutions, and simulated rainwater were in a conditioned laboratory during this period, so the temperature difference is expected to be negligible. Thus, the increase in temperature experienced during the March-August 2012 experimental period was not attributed to decrease in concentrations of copper in the effluent.

Based on the individual event influent and effluent composite concentrations and volumes, the percent removal for copper and for zinc were calculated for each accelerated event. The averaged effluent volumes for the accelerated events are presented in Figure 3.4. Note that the effluent volume recorded for Event 30 is an outlier and is assumed to be experimental error

due to misreading of a graduated cylinder which had faint volume markings. This outlier is not included in any of the summaries.
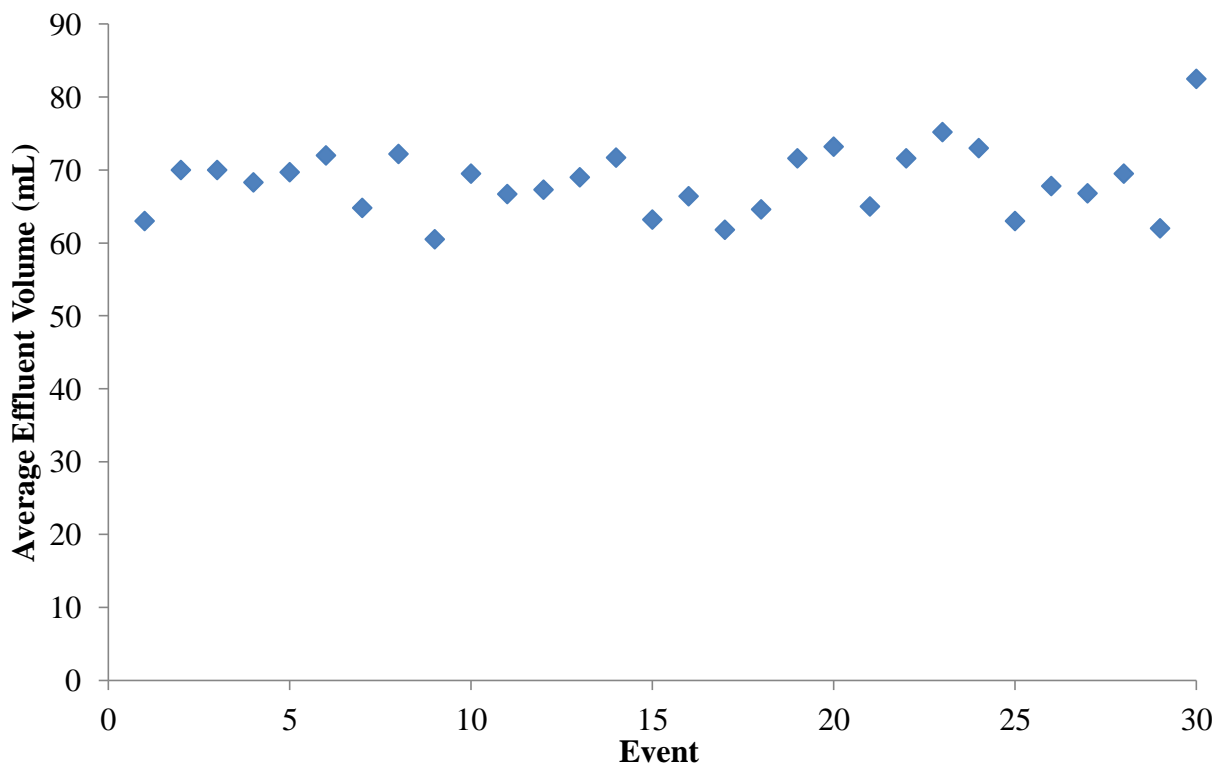
Figure 3.4: Average Effluent Volumes for Each Accelerated Event

The mass balances calculations representing the composite percentage of metals removed for each accelerated event are presented in Figure 3.5. The zinc percent removal was never less than 64%, with the exception of last event. The copper retained in the concrete increased with storm events. Copper removal was 63% at first, slowly increasing to about 80%, except for the final event.
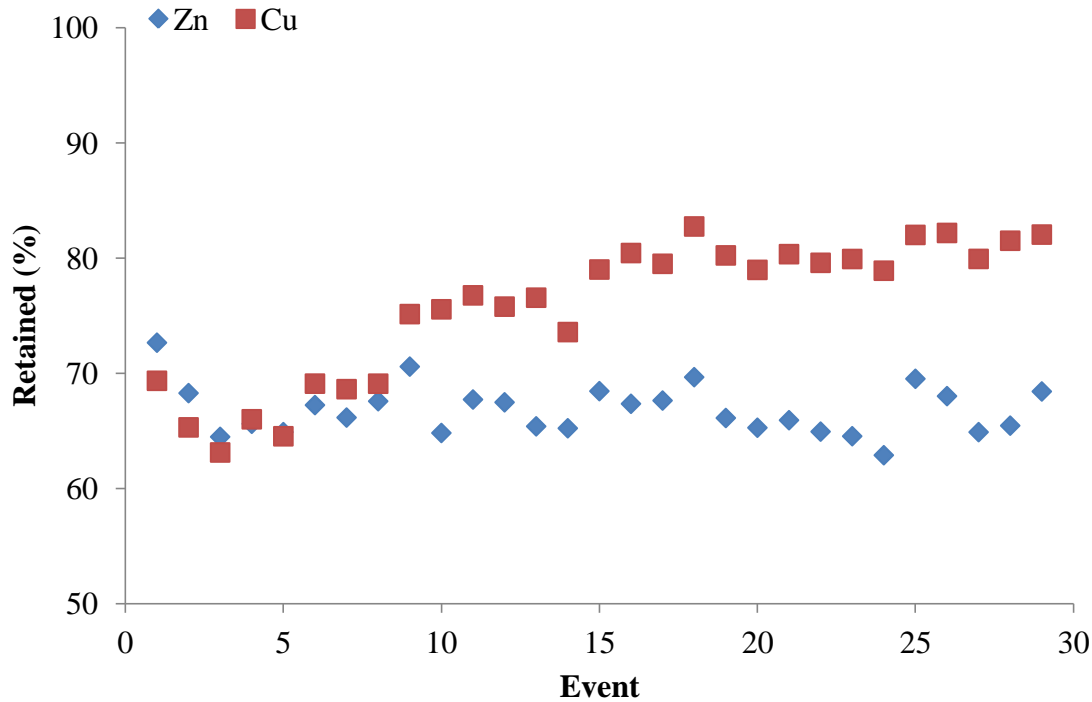
Figure 3.5: Percent of Zinc and Copper Retained in Cylinders during Accelerated Loading Events

As previously mentioned, one of the cylinders (WB10) was removed from the accelerated loading cycles after 15 events and received three consecutive typical loading events. The zinc and copper removal percentages for these three post-accelerated loading consecutive typical loading events were found to range from 92% to 95%, and 87% to 93% respectively, with all values given in Table 1. Another cylinder (WB11) was removed from the accelerated loading cycles after 24 events and received three consecutive typical loading events. Table 1 indicates that the removal percentages ranged from 86% to 93% and 83% to 89% for zinc and copper respectively for WB11 after the 24 accelerated loading events.

Table 3.1: Material Characteristics of Pervious Concrete Cylinders and Representative Summary Results for Typical Loading Events

Cylinder ID	Porosity (%)	# of Accelerated Events	Metal Removal for Typical Loadings (%)					
			Post Accelerated Events					
			Event 1		Event 2		Event 3	
			Zn	Cu	Zn	Cu	Zn	Cu
WB10	24.8	15	92	90	95	93	92	87
WB11	25.4	24	93	89	86	86	92	89
			No Accelerated Events					
			Event 1			Event 10		
			Zn		Cu		Zn	Cu
WB02	24.7	--	88		90		93	89
WB05	24.4	--	94		93		96	90
WB06	25.1	--	92		89		90	89
Avg.	24.7	--	91		91		93	89

Table 3.1 also provides some of the removal percentages for the typically loaded cylinders without the long term accelerated loading. Comparing the results of the initial typically concentrated storm events to the typical storm events after the accelerated loading, the long term loading did not significantly decrease the zinc and copper removal capacity of pervious concrete.

Discussion

The removal of typical stormwater concentrations of dissolved zinc and copper through a layer of pervious concrete prove to be efficient, even after many simulated events. The accelerated testing events included 30 applications of 12 mm (0.5 inches) of rain with 40 times the typical concentrations of dissolved zinc and copper with 15 years of rainfall in a region with 1.02 m (40 inches) annual rainfall. In a similar manner, the two cylinders which were sacrificed

to perform the subsequent typical event trials were sacrificed at 7.5 and 12 years of metal loading for similar rainfall averages.

The removal efficiency of zinc and copper through pervious concrete is remarkable compared to other best management practices with known removal efficiencies for the same metals. Biorention facilities have recorded removal efficiencies of 85% and 98% in the top layers of the cells. Assuming the bioretention cell is new to compare the removal efficiencies to the typical events, zinc was removed 89% to 95%. Copper was removed 87% to 93%. The pervious concrete is as efficient as a bioretention cell. (Hinman, 2005). The efficiency of pervious concrete greatly exceed reported values for best management practices such as, wetlands and wet ponds. Wetland treatment has shown 47% and 42% removal for zinc and copper. Wet ponds have shown 57% and 64% removal for zinc and copper. (Winer, 2007). Extensive testing has also been performed on permeable pavements. The permeable pavements, including porous pavers, plastic lattices, and permeable asphalt, and porous concrete, have been evaluated for their effectiveness for removing metals from runoff. The porous concrete is crushed material with a subbase which is significantly different from the porous concrete tested in the experiments described. The removal efficiencies reported for the media were greater than 85%. The media also showed signs that metals were collecting in the top layer (Ahiablame et al., 2012). This has not been shown with the pervious concrete tested, Based upon the compilation of various studies, removal efficiencies that mimic field conditions using the pervious concrete tested have not been previously presented.

The increase in the affinity for copper sorption in the accelerated experiments modeling longer term exposure is an interesting phenomenon. The values of the logarithm of the stability constants for the copper carbonate and hydroxide solids versus the zinc carbonate and hydroxide

solid species may provide some reason for this. The logarithm of the solid carbonate values for these constants are 9.6 for copper and 10.0 for zinc implying a small preference for the zinc species when the dissolved ion concentrations are the same. With the higher dissolved concentrations of zinc in the simulated runoff, surface sorption of the zinc is expected to occupy more surface sites. However, the logarithm of the stability constants for the solid copper and zinc hydroxide ligands respectively are 19.3 and 16, giving a small preference for the copper species when the dissolved ion concentrations are the same (Stumm and Morgan, 1996). This implies that the copper may have a preference for forming the interior hydroxide species. An alternate consideration is that, if competition between the two metal ions is not considered, the higher dissolved zinc concentrations in the simulated stormwater implies that over time the surface sites might have a larger concentration of zinc. However, if this was the governing process explaining changes in the affinity for the two metal ions, then the affinity for zinc should be decreasing with the number of storm events. After 30 events, this has not happened, implying that the affinity for sorption in the channels has not yet reached saturation.

Continued testing well beyond the 30 event accelerated methodology would be useful in determining life expectancies, as would batch testing for absorption in equilibrium with allowable effluent levels. It is also recommended that similar experiments are performed using variable ratios of the two metals, and/or other metals to explore competition for adsorption sites. Factors such as, temperature, pH of the rainwater, and the introduction of solvents in the stormwater, are subject to further investigation to gain a better understanding of the ability of concrete to retain metals.

Additional tests are required to fully understand the capabilities of treatment. To enhance the results of this study, more than six pervious concrete cylinders should be tested at the

accelerated event concentration until the effluent concentration significantly increases. This would yield a more accurate representation of the removal of metals over a long period of time in the concrete. More than six cylinders would be desirable so that more than one cylinder could be sacrificed at a time for intermediate long term testing. This would help account for variability of effluent concentrations for various cylinders. Also, the accelerated event samples should not be combined into composite samples in order for statistical analysis to be performed. The method of applying the stormwater solution over the concrete could be modified. The problem with using one buret and dripping it over one spot on the concrete surface is that the entire concrete cylinder is not being wetted. Figure 6.1 shows a general depiction of how the water prefers to move through the concrete cylinder.
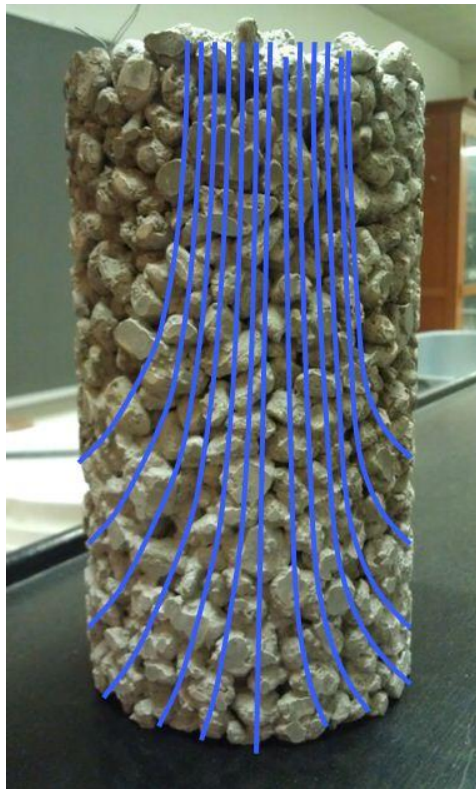
Figure 3.6: Water Flow Path through Pervious Concrete

An apparatus that is capable of covering the entire surface of the concrete so that the stormwater comes into contact with all of the surface area would be beneficial. Isotherms using concrete with the applicable concentrations would be valuable in determining equilibrium and kinetic constants. These tests will help model the concrete system in HP2/3. Tests to determine the van Genechten-Mualem parameters would be helpful as well. These additional tests will provide more data on the efficacy of metals removal using pervious concrete.

Pervious concrete has many practical applications for metals removal in stormwater. For some sites, directing flow of stormwater offsite is impractical or even impossible. With its potential for treating stormwater, pervious concrete can provide cleaner and safer water for the environment. Pervious concrete would be useful to treat zinc and copper in stormwater runoff from ferry terminals. They are problematic due to the characteristics of the structure. They extend out over bodies of water and there is limited area for placement LID technologies. Pervious concrete could also be used to treat runoff from roads and parking lots.

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4. Dissolved Zinc and Copper Retention in Pervious Concrete from Stormwater Runoff (Ordinary Portland Cement and Supplementary Fly Ash)

This chapter compares the cylinders with WD cylinders (75% OPC and 25% supplementary fly ash) to those with WB cylinders (100% OPC).

Results of OPC Concrete Cylinders with Twenty Five Percent Supplementary Flash Addition

Accelerated loadings were applied to concrete cylinders with 25% supplementary ash. The zinc effluent removal percentage at the first event was approximately 60% removal. For the next 29 events, the effluent removal percentage followed an overall trend of increasing to 79%. Copper removal percentage over the 30 events followed a similar trend from 62% to 89%. Figure 4.1 shows the results for all 30 events.
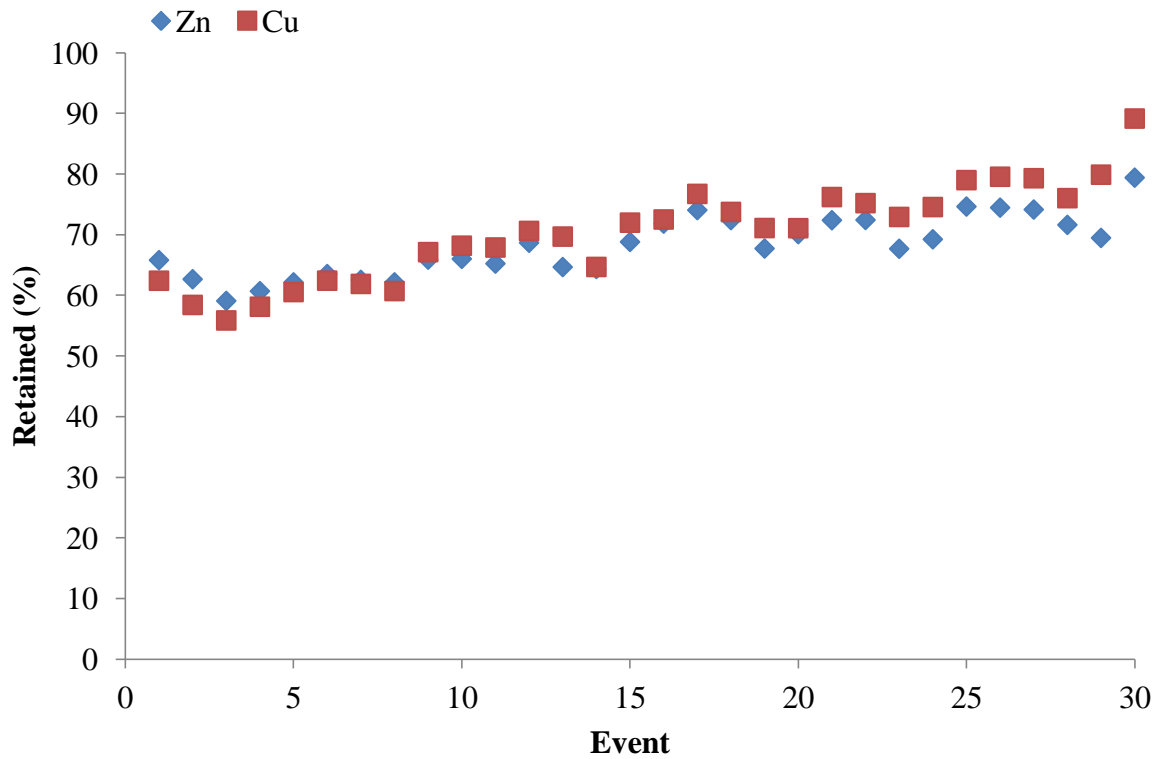
Figure 4.1: Percent of Zinc and Copper Retained in Cylinders with 25% Fly Ash during Accelerated Loading Events

After 15 and 24 accelerated loading events were reached, one cylinder was removed from the experiment and loaded three times at a typical concentration. For the cylinder that only experienced 15 events, percent zinc removal remained 80% and 86%. Percent removal of copper was between 80% and 90%. For the cylinder that experienced 24 events, percent removal of zinc was between 89% and 93%. Percent removal of copper was between 85% and 87%. The post accelerated event data is shown in Table 4.1.

Specimen ID	Porosity (%)	# of Accelerated Events	Metal Removal for Typical Loadings (%)					
			Post Accelerated Event 1		Post Accelerated Event 2		Post Accelerated Event 3	
			Zn	Cu	Zn	Cu	Zn	Cu
WD03	24.3	15	86	82	90	87	80	80
WD15	23.8	24	93	87	89	86	90	85

Comparison of Results from 100% OPC Concrete Cylinders and 25% Supplementary Fly Ash Concrete Cylinders

The results from the two types of pervious concrete cylinders are compared to determine the affect 25% fly ash has on the removal of zinc and copper in the WD cylinders. The absence of fly ash allows more carbonates and hydroxides to be present in the pore spaces of the concrete. A paired t-test is used to determine the significance of certain trends observed in the data. Also, typical loading results after accelerated loadings for both cylinder types are compared.

Figure 4.2 shows results from the OPC cylinder results in comparison with cylinders containing fly ash. Initially, the 100% OPC cylinders (WB) have higher removal efficiencies than the 25% fly ash cylinders (WD). Starting at the tenth event, the percent retained becomes very similar. At the nineteenth event, removal percentages for the WD cylinders exceed those of the WB cylinders. The events were split into three regions based on similar trends. A paired t-test was performed on the data in each region using a confidence level of $P < 0.05$. In region 1, the results show that the data for the two cylinders are significantly different. In region 2, the data for the two cylinders are significantly similar. Finally, the results of region 3 show that the data

points are significantly different again. Based upon the paired t-test, the observed reversal in removal percentages is statistically significant. Fly ash included in the concrete mix may influence percent removal for zinc and copper.
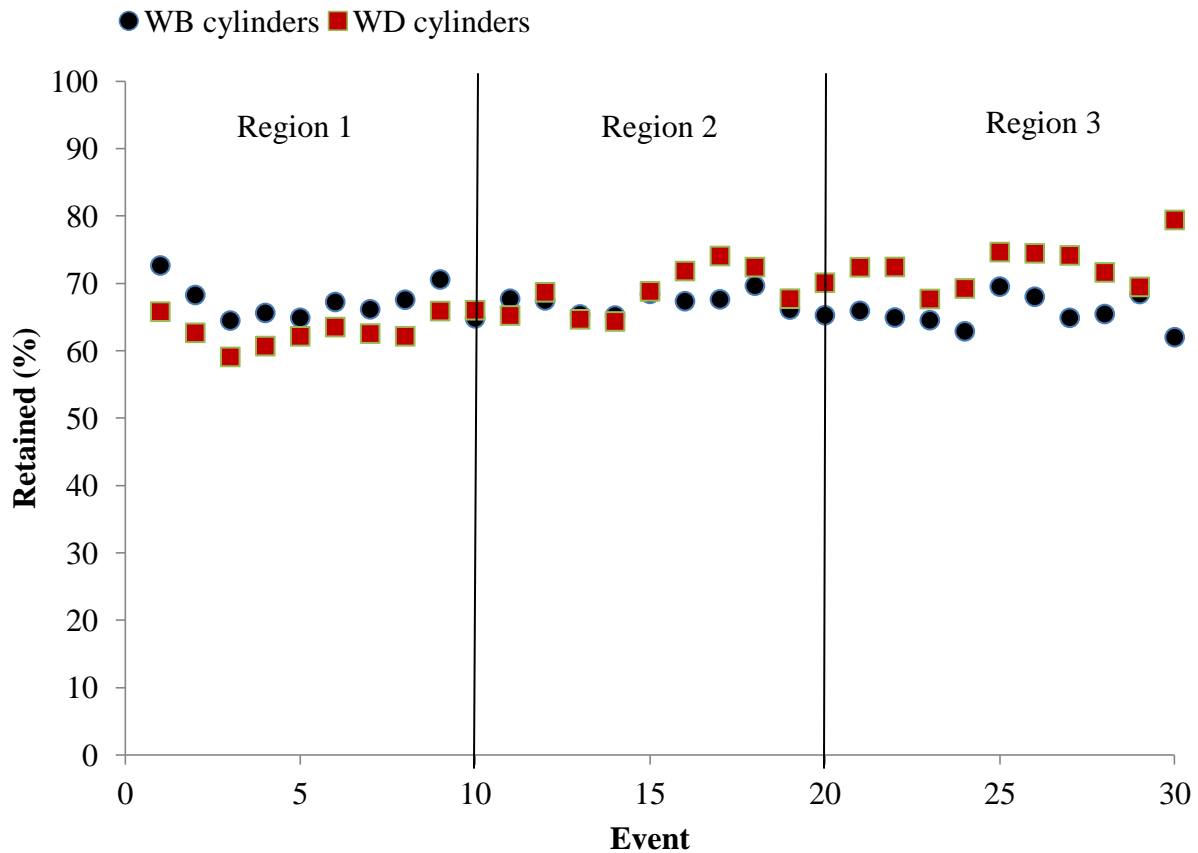
Figure 4.2: Percentage of Zinc Retained in Cylinder with and without Fly Ash

Percent removal of copper for cylinders with fly ash compared to cylinders without fly ash showed a different trend. Both types of cylinders consistently increased dissolved copper removal during the 30 events. Cylinders with fly ash appear to consistently remove less copper than cylinders without fly ash. The data comparing the two cylinders showing percent removal of copper is presented in Figure 4.3. The last data point for WD may be due to an incorrect reading for the volume of the effluent, thus skewing the concentration of the result.
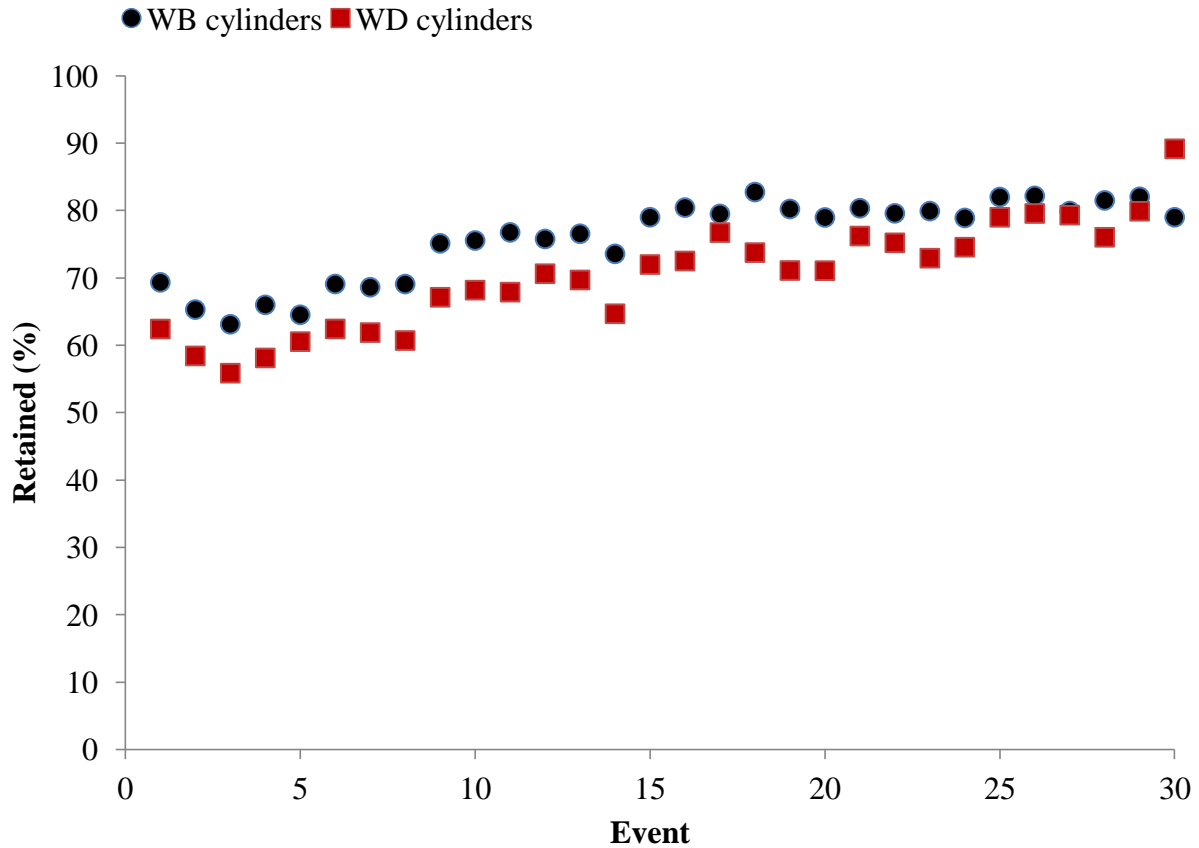
Figure 4.3: Percentage of Copper Retained in Cylinders with and without Fly Ash

Percent removal of zinc and copper in cylinders were compared to cylinders without fly ash at a corresponding number of accelerated events. In all cases, except for two events for zinc, the percent removal for WD cylinders was less than the values for WB cylinders. Table 4.2 shows the comparison of results for both cylinder types.

Table 4.2: Comparison of Percent Removal of Zinc and Copper in Pre-Accelerated Loaded Cylinders with and without Fly Ash

Group	Specimen ID	Porosity (%)	Metal Removal for Typical Loadings (%)					
			# of Accelerated Events	Post Accelerated Event 1		Post Accelerated Event 2		Post Accelerated Event 3	
				Zn	Cu	Zn	Cu	Zn	Cu
Accelerated Loading	WB10	24.8	15	92	90	95	93	92	87
	WD03	24.3	15	86	82	90	87	80	80
	WB11	25.4	24	93	89	86	86	92	89
	WD15	23.8	24	93	87	89	86	90	85

Discussion

The objective of this chapter was to test effluent concentrations of simulated stormwater with accelerated concentrations of zinc and copper for cylinders with no fly ash (WB) and with fly ash (WD). The WB cylinders had higher removal of zinc until the WD cylinders surpassed its metal removal percentages. WB cylinders showed consistently higher removal of copper over WD which supports the original hypothesis. WB shows higher percent removal over WD in most cases for typical loading events after long term exposure, but the WB and WD cylinders for copper removal data from Figure 4.3 appear to converge over time. The convergence of data could be a result of surface sites becoming saturated on the WB concrete cylinder from the bonding of zinc and copper, thus making surface sites less available. The percent removal would decrease and resemble results from the WD cylinders. A similar trend is shown in the data from Table 4.2 where removal data after 15 events shows a 5% to 7% difference in removal between the two cylinders. After 24 events, the difference is closer showing 0% to 3%. This comparison of data also supports the hypothesis in that the high percentages of metal removal in WB cylinders are due higher concentrations of carbonate and hydroxide ligands in the concrete.

Dissolved zinc is loaded at a concentration five times greater than dissolved copper. Zinc removal data for WB and WD experienced the reversal in efficiency. WB cylinders originally removed zinc at a higher percentage compared to WD. As time progressed, WD cylinders removed a higher percentage of zinc. This may be due to the surface sites becoming saturated with the zinc ions, but this was not observed in the copper perhaps because it is loaded five times less. The convergence of the data with copper may be the start of the surface sites becoming saturated similarly just like what happened with zinc.

The time elapsed between events may have an influence of the percentage of the metal the concrete cylinder removes. Table 4.3 shows the correlation between the number of days between subsequent tests and the change in removal percentages that occurred for that event compared to the previous event.

Table 4.3: Time Elapsed Between Performed Tests for Copper Loadings

Event	Date of Experiment	Number of Days Since Previous Test	Difference of Percent Removal from the Previous Test for WB Cylinders with Copper	Difference of Percent Removal from the Previous Test for WD Cylinders with Copper
1	3/26/2012	-	-	-
2	3/28/2012	2	-4.04	-3.99
3	3/31/2012	3	-2.18	-2.56
4	4/2/2012	2	2.88	2.26
5	4/4/2012	2	-1.47	2.42
6	4/6/2012	2	4.57	1.88
7	4/9/2012	3	-0.48	-0.54
8	4/11/2012	2	0.47	-1.18
9	5/5/2012	24	6.05	6.42
10	5/16/2012	11	0.42	1.06
11	5/22/2012	6	1.21	-0.30
12	5/25/2012	3	-0.98	2.74
13	5/29/2012	4	0.78	-0.93
14	5/31/2012	2	-2.99	-5.01
15	6/6/2012	6	5.43	7.31
16	6/13/2012	7	1.43	0.53
17	6/18/2012	5	-0.94	4.22
18	6/20/2012	2	3.24	-2.97
19	6/22/2012	2	-2.51	-2.66
20	6/23/2012	1	-1.26	-0.02
21	7/8/2012	15	1.37	5.13
22	7/18/2012	10	-0.75	-1.01
23	7/20/2012	2	0.33	-2.28
24	7/26/2012	6	-1.02	1.63
25	7/30/2012	4	3.11	4.44
26	8/2/2012	3	0.17	0.56
27	8/6/2012	4	-2.26	-0.24
28	8/8/2012	2	1.58	-3.29
29	8/14/2012	6	0.53	3.87
30	8/16/2012	2	-7.33	9.26

Note: (+) symbolizes increase in removal percentage between two events.

(-) symbolizes decrease in removal percentage between two events.

Event 9 was performed 24 days after the latest test and percent of copper removal increased 6% for WB cylinders and almost 6.5% for WD cylinders. The both cylinders types did not experience a reduction in percent removal for the next five events. Similarly, event 21 was conducted 15 days after the previous event. The difference in percent removal was less than 2% for the WB cylinders while the WD cylinder increased in percent removal by 5.1%. More tests need to be conducted to affirm the correlation because the trend is inconsistent. However, it appears that the greater the time elapsed between tests results in higher removal percentages for the next few events. This may be due to the copper diffusing into the concrete which opens sites for additional bonding.

5. Hydrus-2D and PHREEQC Pervious Concrete Model

The purpose of using a model was to simulate the pervious concrete experiments. The model can aid in understanding the mechanisms of removal and the species formed in the effluent by representing the hydraulic and chemical characteristics of the concrete. Hydrus (2D/3D) was used to construct a model of the pervious concrete. Hydrus (2D/3D) is a flowthrough transport model and is typically used for unsaturated flow and transport of solutes in soil. The program was used to model the pervious concrete by specifying physical concrete characteristics for the soil parameters (Sejna and Simunek, 2011). Hydrus (2D/3D) was coupled with a chemical equilibrium program called PHREEQC to simulate metal solute transport and chemical reactions. PHREEQC incorporates surface reactions, diffusion, and equilibrium reactions. The two coupled programs are referred to as HP2/3 (Hydrus 2D/3D- PHREEQC). The model described is not a completed work, and only represents the physical removal of metals. Chemical reactions were not included. The objective of constructing this model was to create a foundation for further research to be conducted. The pervious concrete model shows the majority of the dissolved metals were removed at the top of the profile. Then, as the concrete becomes saturated, percent removal slowly declined as a function of depth.

Methodology

Flow and Transport Parameters

Pervious concrete was represented as a homogeneous material, and the van Genucten-Mualem hydraulic model was used to simulate infiltration. The values entered for van Genucten-Mualem variables are for gravel and are shown in Table 5.1.

Table 5.1: Material Properties for Water Flow

Mat	Name	Q_r	Q_s	α (1/cm)	n	K_s (cm/min)	I
1	Gravel	0.21	0.63	0.036	3.82	125	0.5

The values of Qr, Qs, α, and n, for gravel were based on a recommendation from an HP2/3 user on the program website (PC-Progress, 2012). The HP2/3 help manual recommends using the default I value (Sejna and Simunek, 2011). The hydraulic conductivity value was calculated by reverse modeling. An arbitrary, initial value was entered in the cell and the rest of the input values were kept constant. Then, the K_s value was determined by trial and error until the effluent exited the concrete model between 3 and 4 minutes, which was the rate observed in the laboratory.

The number of solutes to be transported in the solution was specified as four. Zinc and copper are two of the four components. The other two components are total hydrogen (Total_H) and total oxygen (Total_O). These components are recommended to be included in any solute transport model (Sejna and Simunek, 2011). The PHREEQC database was selected to perform the chemical equilibrium function.

The initial zinc and copper concentrations were specified to be 500 μg/L and 100 μ/L, respectively. The pH of the solution was specified as 6.1. The partial pressure of oxygen value was specified because it is a required part of the solution definitions. It was an automatic input for new solutions.

The bulk density of the pervious concrete was calculated and entered as 1.96 g/cm^3 on the "Soil Specific Parameters" window in Figure 5.2. The 10^{-6} was assumed to be a conversion factor HP2/3 uses for mass units (M) for grams to moles. Since the mass unit (M) was designated as moles and it cannot be changed from Figure 5.1, the bulk density was entered in as 1.96E-06

M/cm^3. A Longitudinal dispersion (Disp. L) coefficient of 5 and transverse dispersion (Disp. T) coefficient of 0.5 were default values and were not changed.

Table 5.2: Soil Specific Parameters

Mat	Bulk D (M/cm^3)	Disp. L (cm)	Disp T. (cm)	Mass Tr. (1/min)	Thlmob
1	1.96E-06	5	0.5	1	0

The "Solute Specific Parameters" window, shown in Table 5.3, had values for molecular diffusion coefficient in free water (Diffus. W.) automatically entered from the PHREEQC database and were not adjusted. Molecular diffusion coefficients for each component in soil air (Diffus. G.) were left at zero.

Table 5.3: Solute Specific Parameters

Name	Diffus. W. (cm^2/min)	Diffus. G. (cm^2/min)
Total H	0.000552	0
Total O	0.000552	0
Zn	0.000552	0
Cu(2)	0.000552	0

Time Variable Boundary Conditions and the associated parameters were in four time increments, shown in Table 5.4, which were specified by the time variable boundary condition records integer. Time variable boundary conditions are 0.001 (essentially zero), 10, 10.001, and 20. The values for hCritA (maximum head value at atmospheric boundary condition) were default values and were not adjusted. Variable Flux 1 (Var. Fl. 1) is 0.0127 which was the application rate of the stormwater on the cylinder. The negative sign denoted that flow traveled in the negative direction across the flux time variable boundary. Concentration value 1

(cValue1) designates the concentration of a specific solution. In this case, 1002 referenced the Solution 1002 that was defined in the "HP2/3 Definitions" window. Var. Fl 1 and cValue1 were zero for the last two records because the application of stormwater stopped at ten minutes.

Table 5.4: Time Variable Boundary Conditions- Parameters

	Time (min)	hCritA (cm)	Var. Fl 1 (cm/min)	cValue1
1	0.001	1000	-0.0127	1002
2	10	1000	-0.0127	1002
3	10.001	1000	0	0
4	20	1000	0	0

After the time variable boundary condition parameters were set, the FE Mesh characteristics were defined. The boundary conditions are shown in Table 5.5. Layer 1, the top of the pervious concrete column, has a code number of -3 (atmospheric boundary condition). The code for layers 2 through 14 is zero (no flux). Water flow was not allowed to move across the side boundaries of the model. The code for layer 15 is -6 (free drainage). The pressure head of the column for all layers was -100 which represented that there is no solution currently in the cylinder.

Results

The results produced include water content, zinc concentration, and copper concentration profiles. Water content results were taken at three different times during the 20 minute experiment: 3.67 minutes, 12 minutes, and 20 minutes, in order to show the trend of the water moving through the column over time. Figure 5.6 shows the results of the water content of the column at 3.67 minutes with the associated water content values.
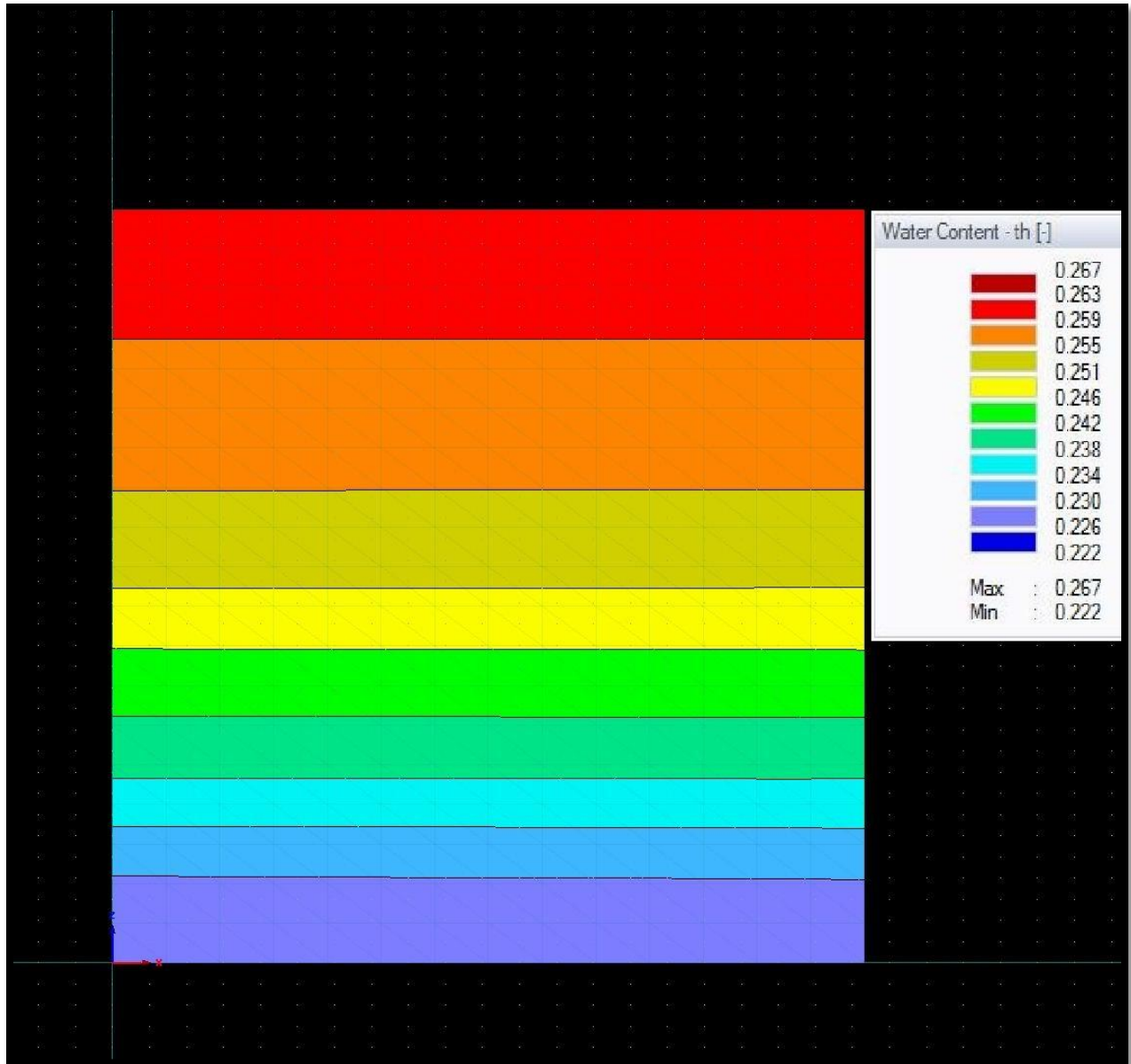
Figure 5.1: Water Content Results at 3.67 Minutes

Water moved down the column and the highest water contents occurred at the top and steadily

moved down the column. The highest water content reached the bottom of the column and the

water content became less as a function of depth. This means that the column started to dry out.

This is shown in Figure 5.7 and it is the expected result based on observations in the laboratory.

While water content was not measured in the lab, it was used as validation that the simulation resembled physical hydraulic behavior water infiltrating pervious concrete.
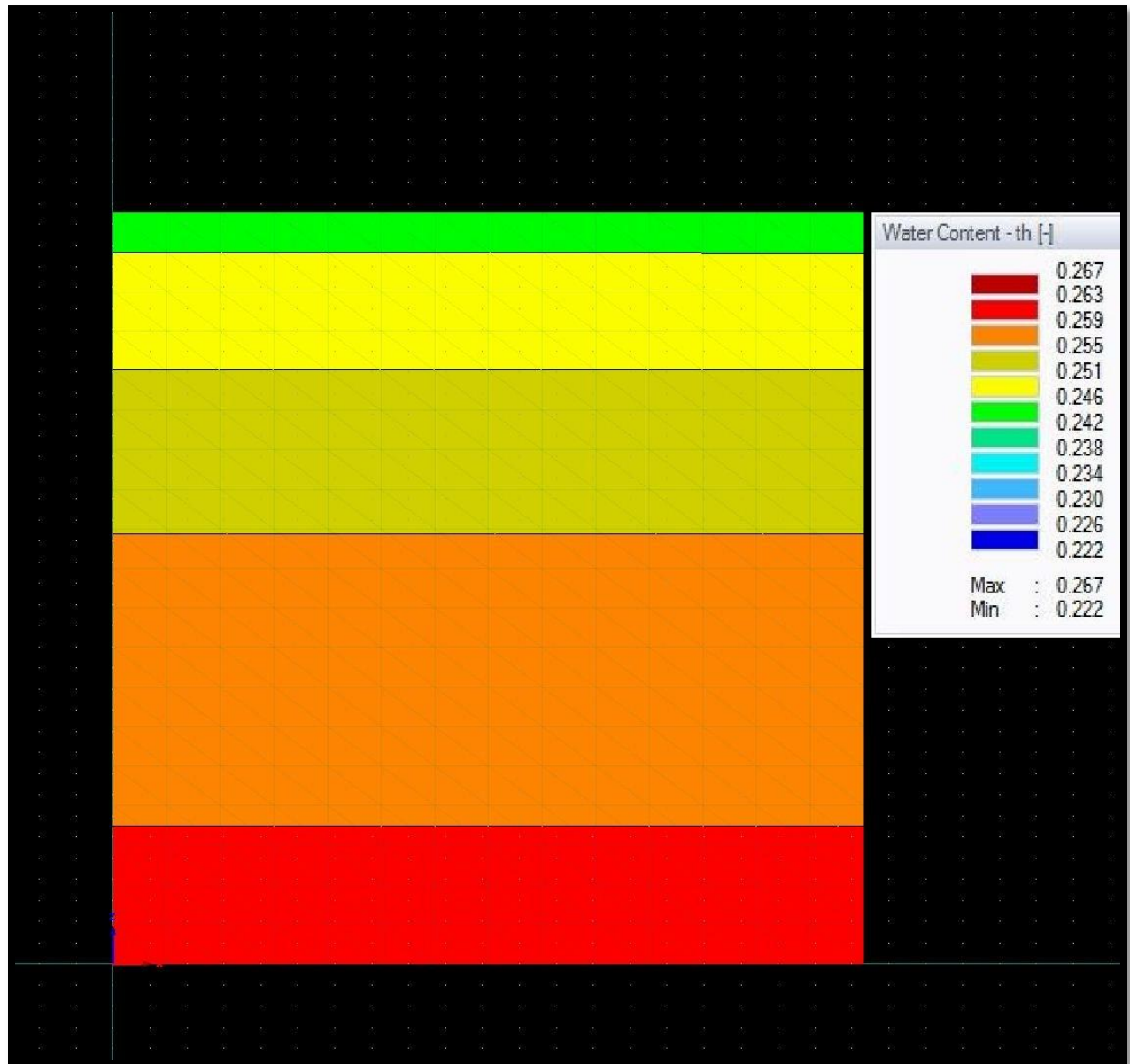
Figure 5.2: Water Content Results at 12 Minutes

After 20 minutes, water was still left in the column, which was observed in the laboratory. Figure 5.8 shows the results of the water content in the column at the end of the 20 minutes.
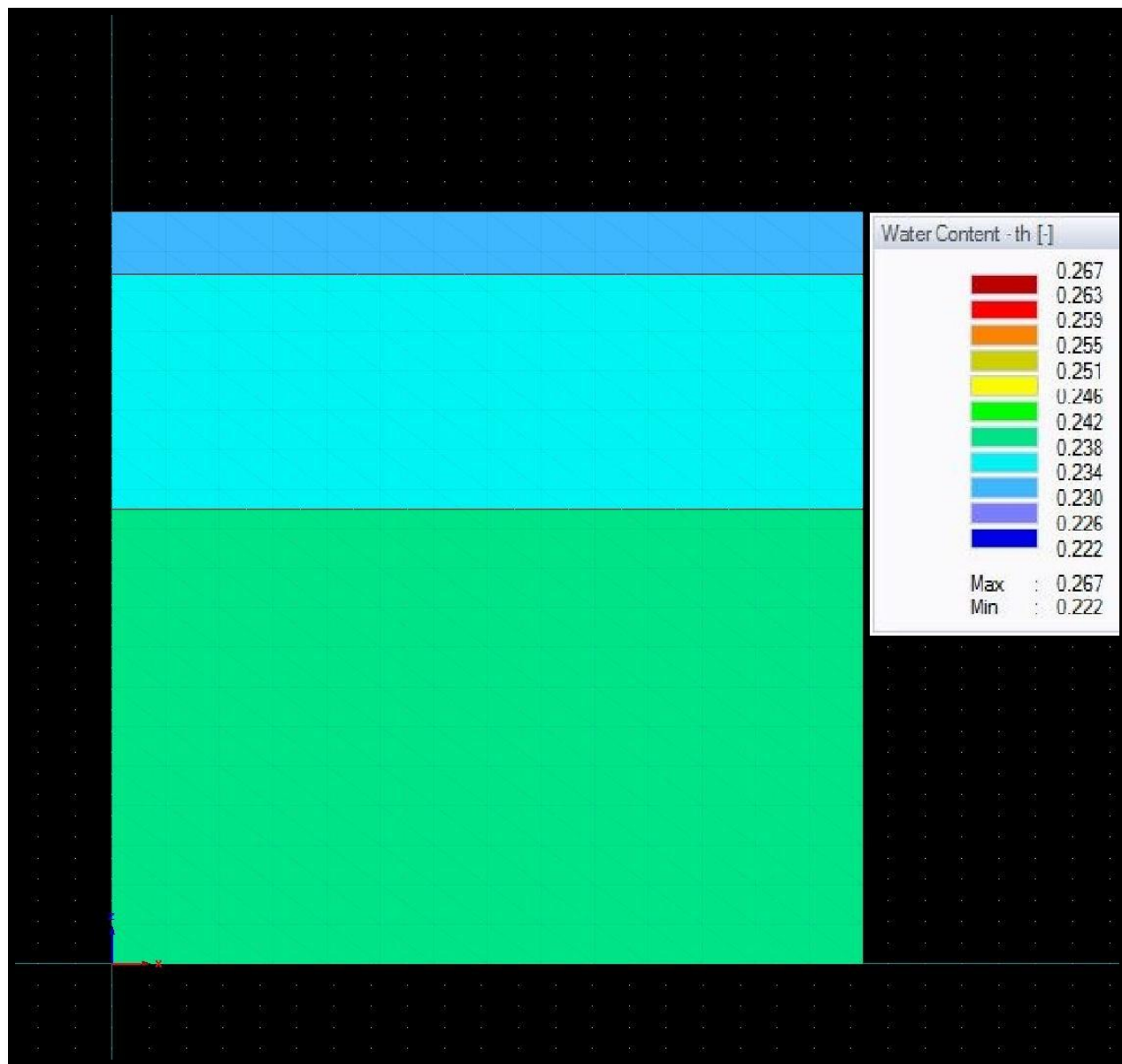
Figure 5.3: Water Content Results at 20 Minutes

Zinc and copper were both transported through the column of pervious concrete and the metals were continuously removed as the water carried them down the column in simulations. A trend that was expected to occur in both zinc and copper is shown in Figure 5.8, in which the

majority of the removal of the metals occurred at the top of the column and removal reduces with depth.
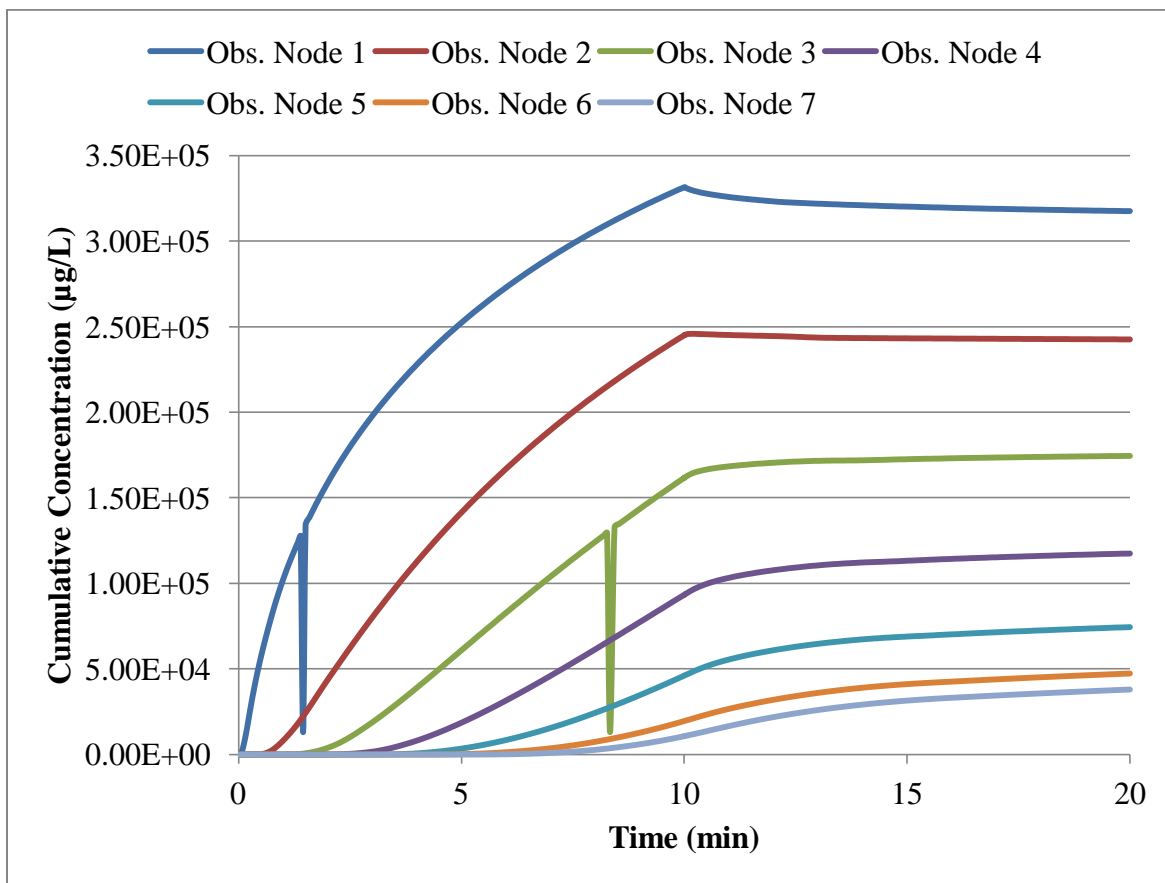
Figure 5.4: Cumulative Concentration of Zinc for Observation Nodes 1 through 7

Observation Nodes 1 through 7 are spaced evenly along the depth of the column producing the result of cumulative concentration that has passed by that specific node. Figure 5.8 shows that the cumulative concentration lines expressing the total concentration that passes by that node with time. The space that separates each concentration line is the concentration of metal removed from solution. The space decreases gradually from observation node 1 to 7 showing that the

concentration of metals removed from solution gradually decreased as a function of depth. The

trend occurred in the copper data as well shown in Figure 5.9.
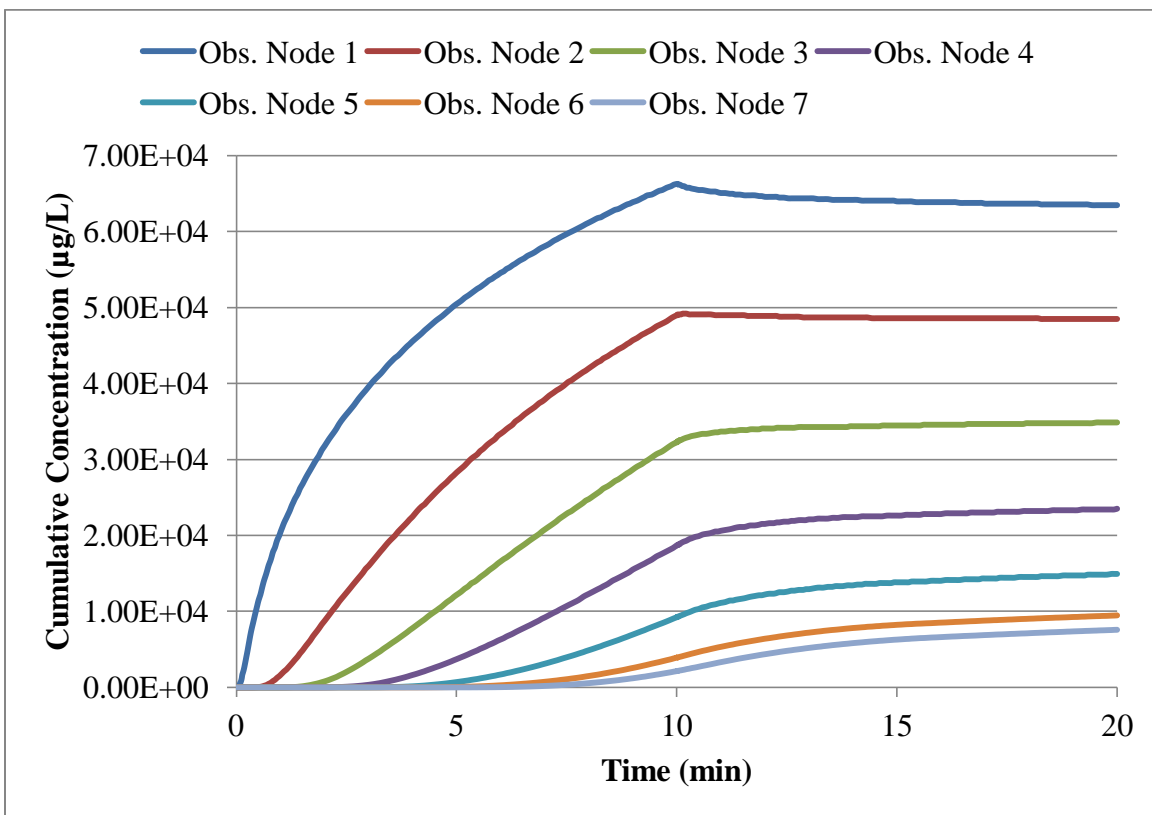
Figure 5.5: Cumulative Concentration of Copper for Observation Nodes 1 through 7

The program predicted the concentration gradient of the zinc along the depth of the

profile with the highest concentration located at the top of the column and decreased in

concentration as depth increased. This trend was expected and is shown in Figure 5.11.
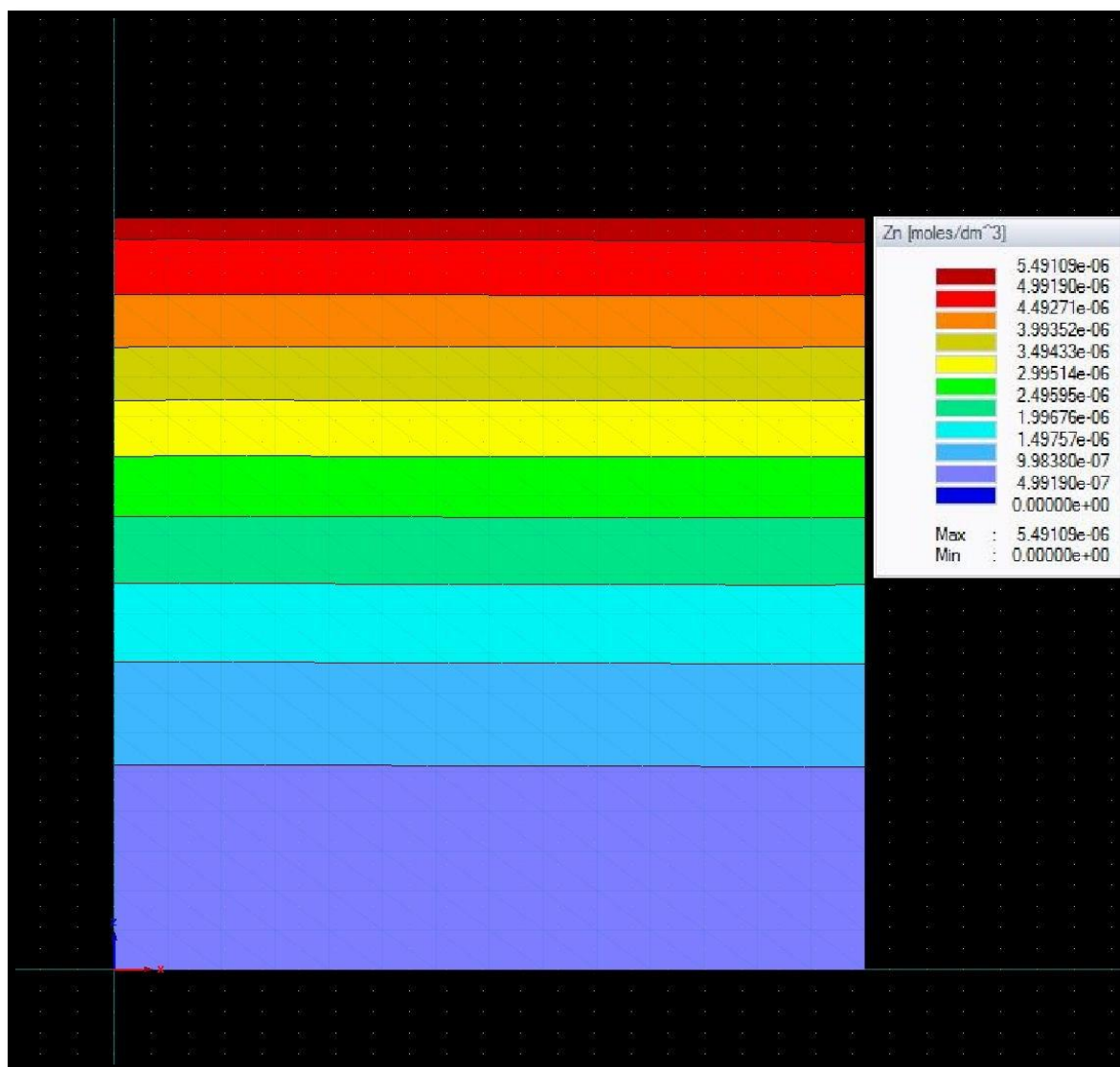
Figure 5.6: Zinc Concentration Simulated at 20 Minutes

The simulation predicted an effluent concentration of 125 µg/L at the end of 20 minutes. Zinc

removal was 75% in the model compared to the first average hotspot zinc removal percentage of

95.5% measured in the laboratory experiments. The difference in removal is likely due to the

absence of surface reactions, diffusion, and other chemical reactions in the model; these

reactions will increase the removal in the model.

Similarly to the zinc results, copper concentration gradient decreased with an increase in depth as shown in Figure 5.12.
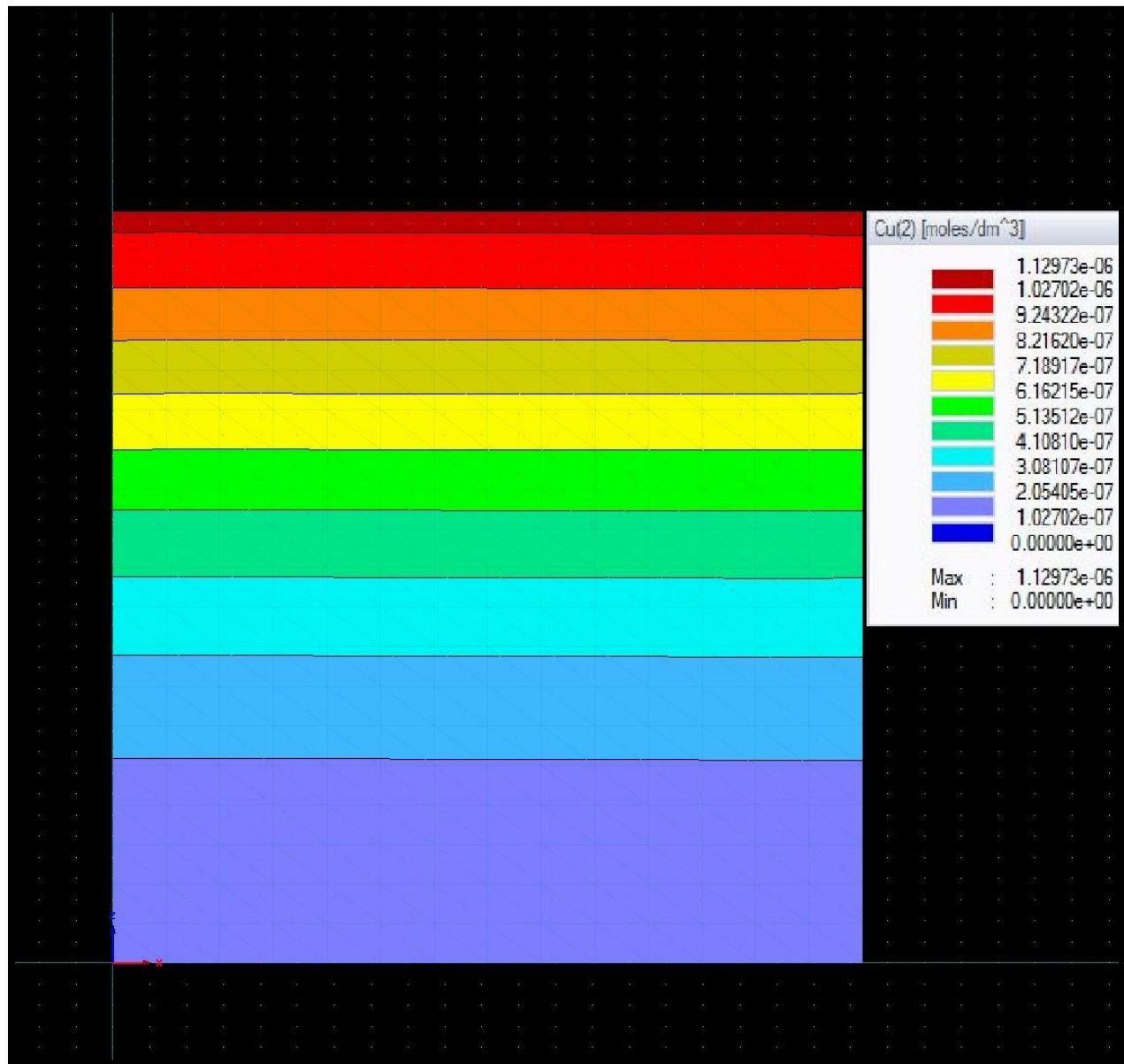
Figure 5.7: Copper Concentration Simulated at 20 Minutes

The predicted effluent concentration of copper was 25 µg/L. From the simulation, copper

removal was 75% compared to the average copper removal percentage of 91.8% from the first

hotspot event in the laboratory experiments. Similar to the zinc model, the difference in removal

is likely due to the absence of surface reactions, diffusion, and other chemical reactions in the

model; these reactions will increase the removal in the model.

Discussion

The objective was to create a model in Hydrus-2D and PHREEQC that simulates hydraulic

and chemical behavior of dissolved zinc and copper passing through pervious concrete. The

model is not complete; however, it will serve as foundation for future modeling of dissolved

metals removal in pervious concrete. The model shows that the majority of metals removal takes

place in the top layer and decreases with depth. This trend is observed in Figures 5.9 and 5.10.

The model appears to mimic the hydraulic behavior of what was observed during the

laboratory tests. The highest saturated part of the concrete starts at the stop and slowly moves

downward until the whole pervious concrete cylinder is saturated. When the application of

stormwater stops, the pervious concrete starts to dry as the remaining water drips down the

cylinder. Although the model appears to mimic what was observed in the laboratory, many of the

variables that describe the pervious concrete are not specifically known, such as the van

Genuchten-Mualem parameters. Tests need to be performed to determine the parameters specific

to the pervious concrete cylinders. Reverse modeling was used to determine the hydraulic

conductivity. Based upon the van Genuchten-Mualem coefficients for gravel, the hydraulic

conductivity was determined by adjusting the value to achieve the volume leaving the cylinder as

observed in the laboratory. The K_s value determined was 125 cm/min. The hydraulic

conductivity of a pervious concrete cylinder with similar porosity of 24.9% was determined to be 14.6 cm/min from a study conducted by Gaither and Haselbach (2007). The hydraulic conductivity from the model is almost an order of magnitude higher than that determined by Gaither and Haselbach (2007). The van Genuchten-Mualem parameters will need to be verified by measuring the actual hydraulic conductivity in the laboratory.

The model achieved the purpose of reproducing the effluent concentrations from the laboratory results. However, adjustments to the chemical portion of model are needed to correctly represent what occurs inside the column. The model does not include chemical components of the concrete. This needs to be specified in the geochemical model. Chemical mechanisms, such as diffuse layer and surface complexation, need to be added to the model. These mechanisms will likely increase removal in the model so it is closer to removal observed in laboratory experiments. Conclusions about the data and the reactions or speciation, however, cannot be affirmed without the chemical component in the model.

6. Conclusion

As a result of this study, we determined that:

1: Metals were removed at minimum of 96% and 90% for zinc and copper, respectively, when pervious concrete cylinders without fly ash (WB) were loaded with hotspot concentrations. The reliability of the concrete to accomplish this task is proven in the consistency to remove the contaminants through 10 consecutive events. Statistically, removal stayed constant as shown by the slight variation in standard deviation.

2: The results from the typical concentration loadings after the accelerated loadings revealed that the long-term exposure had little effect on the removal of copper and zinc. The WB cylinder that was exposed to 15 prior events (approximately 7 years) of the accelerated concentration of stormwater removed a minimum of 92% of zinc and 87% of copper. After 24 events (approximately 24 years), zinc and copper were both removed at a minimum of 86%. Removal did not change significantly with concrete exposed to long-term concentrations of metals, which is evident when comparing these later events to the tenth typical loading event in which removal was a minimum of 90% for zinc and 89% for copper.

3: The removal of zinc was consistently between 60% and 75% for cylinders with fly ash (WD) and without fly ash (WB) for the accelerated loading tests. The data shows that WB cylinders without fly ash remove more zinc until the 9th event. Then, removal efficiency for WD and WB cylinders is very similar from the 10th event through the 19th event. From the 20th event to the 29th event, WD cylinders remove a higher percentage of zinc. Thus, the two types of cylinders switched in efficiency during the test. Copper results show that WB and WD cylinders removed between 60% and 70% for the first eight events. However, it was removed at an increased percentage. Between the 9th and 15th events, copper was removed between 73% and

79%. After event 15, the removal of copper continued to increase and plateau between 78% and 82%. The increase in removal of copper may be due to the diffusion of the copper into the concrete causing more bonding sites to be available on the surface of the concrete. This same trend does not occur with zinc most likely because zinc is applied to the cylinders at a concentration five times that of the copper concentration. Thus, bonding sites could be saturated with zinc ions. Breakthrough was not observed in the data, which would have appeared as a dramatic drop in percent removal. The cylinders were loaded with typical concentrations after the accelerated concentrations were applied. Copper was removed by 80% to 90% for both types of cylinders after 15 events (approximately 7 years). After 24 events (approximately 12 years), 85% to 93% of copper was removed for both types of cylinders. The efficiency switch for the WB and WD cylinders with zinc is most likely due to zinc being loaded at a concentration five times greater than copper. The surface sites were most likely saturated while copper was not loaded at a high enough concentration to cause a switch in efficiency. The convergence was observed in the copper data comparing the two cylinders which may be the beginning of the surface sites filling with copper ions. Copper showed a positive trend of removal as time increased which is most likely due to diffusion of the copper into the pervious concrete.

4: The computer model shows stormwater flowing through the concrete cylinder with a water content gradient that increases from the bottom of the cylinder to the top for the duration of the test. After the stormwater stops dripping, the cylinder dries and the water continues to drip out the bottom of the concrete. This is shown by the areas of high water content moving down the column as a function of time. The trend in the simulation is similar to what is expected to occur in actual concrete. The concentration gradients for zinc and copper were also shown in the column. The simulation showed the concentration gradient of sorbed metals moving downward

where the highest concentration is located at the top of the column. The geochemical model was not included in the simulation. Thus, surface complexation and diffusion are not represented in the model. The physical trapping of metals in the media is the only mechanism of removal considered.

The zinc effluent concentrations for typical concentration tests before accelerated events vary from 2 to 36 µg/L. Copper concentrations vary from 1 to 5 µg/L. The zinc and copper effluent concentrations for typical concentrations after 15 events of accelerated loadings are 10, 18, and 21 µg/L and 4, 5, and 3 µg/L for the three events, respectively. After 24 events, the zinc and copper effluent concentrations are 11, 13, and 21 µg/L and 3, 4, 5 µg/L for the three events, respectively. In fresh water, the concentrations from pre- and post- typical concentration loadings are well below acute concentration limits of 120 µg/L and 25 µg/L for zinc and copper, respectively. The lowest limit for fresh water is the chronic copper concentration of 5.9 µg/L and the effluent concentrations remained below or equal to the limit (EPA, 2007). For salt water, zinc concentrations were below the zinc effluent limits for both acute (90 µg/L) and chronic (81 µg/L) concentrations (EPA, 2013). For copper, acute and chronic concentrations are 4.8 µg/L and 3.1 µg/L, respectively (EPA, 2007). Some of the effluent concentrations exceeded the limits, but not by more than 2 µg/L.

The removal efficiency of zinc and copper through pervious concrete is remarkable compared to other best management practices with known removal efficiencies for the same metals. Bioretention facilities have recorded removal efficiencies of 85% and 98% in the top layers of the cells (Hinman, 2005). When the pervious concrete was loaded with typical concentrations, 89-95% removal of zinc, and 87-93% removal of copper was observed. Removal efficiencies in pervious concrete are similar to bioretention cells. Pervious concrete exceeds

reported values for wetlands and wet ponds, where removal rates of 47% for zinc and 42% for copper and 57% for zinc and 64% for copper were observed, respectively (Winer, 2007).

The removal efficiencies of zinc and copper through pervious concrete are also comparable to studies conducted on using porous pavers with subbase material to remove metals. The limestone subbase, which contains carbonate, removed 87.1% and 93.8% zinc and copper, respectively (Dierkes et al., 2007). The subbase material was loaded with similar concentrations as the pervious concrete, and the concrete produced similar results.

This study indicates that pervious concrete is a viable best management practice for treatment of zinc and copper in stormwater, particularly in areas with limited space.

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8. Appendices

Appendix A: Hotspot Concentration Data

HS-#: Hotspot Influent Concentration

WB#: Sample label corresponding to cylinder

Metal Event 1	7/3/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2837.6	2858.8	76	7
WB15	2870.9	2893.2	72	10
WB17	2862.5	2883	74	10

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
HS-1	579	94
WB13	43	12
WB15	34	11
WB17	27	9

Metal Event 2	7/10/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2835.6	2857.4	80	8.5
WB15	2869.6	2891.1	77	10
WB17	2861.5	2883	74	8.5

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
HS-2	562	92
WB13	18	9
WB15	19	9
WB17	22	9

Metal Event 3	7/12/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2841.4	2826.2	72	7
WB15	2875.8	2896.9	72	6.5
WB17	2867.2	2885.3	72	7

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
HS-3	601	100
WB13	42	15
WB15	44	14
WB17	25	12

Metal Event 4	7/19/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2833.8	2856.5	73	10
WB15	2867.4	2890	72	9.5
WB17	2860.3	2881.6	74	10

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
HS-4	556	90
WB13	33	10
WB15	28	9
WB17	21	8

Metal Event 5	7/24/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2815.4	2847.1	63	9
WB15	2847.6	2882.4	59	7
WB17	2841.7	2872.1	62	7

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
HS-5	575	94
WB13	29	10
WB15	21	8
WB17	26	7

Metal Event 6	7/31/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2827.1	2851.9	68	9.5
WB15	2863.4	2889.9	66	8
WB17	2854.3	2876.2	72	9.5

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
HS-6	622	101
WB13	90	14
WB15	1,465	55
WB17	31	9

Metal Event 7	8/3/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2830.4	2853.7	64	9.5
WB15	2865.7	2891	60	11
WB17	2859.3*	2880.2	69	9.5

*Mass was not recorded before test was performed
Estimated to be 2859.3

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
HS-7	573	93
WB13	38	8
WB15	20	7
WB17	44	9

Metal Event 8	8/7/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2832	2856.1	66	9
WB15	2869	2893.6	66	9.5
WB17	2858.8	2880.2	70	9

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
HS-8	560	92
WB13	47	10
WB15	15	7
WB17	21	8

Metal Event 9	8/9/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2833.9	2855.8	71	12
WB15	2868.8	2893.5	70	11
WB17	2860.7	2882.7	72	11

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
HS-9	575	93
WB13	40	11
WB15	25	9
WB17	33	9

Metal Event 10	7/31/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB13	2829.1	2853.4	64	13
WB15	2864.6	2891.9	66	12
WB17	2857.1	2880.3	70	13

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
HS-10	626	101
WB13	19	9
WB15	29	11
WB17	29	10

Appendix B: Typical Concentration Data

TYP-#: Typical Influent Concentration

Metal Event 1	7/3/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2873.5	2889.5	74	10
WB05	2846	2867.3	70	9.5
WB06	2817.6	2835.3	74	10

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
TYP-1	217	35
WB02	36	5
WB05	16	3
WB06	25	5

Metal Event 2	7/10/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2873.4	2889.9	78	8
WB05	2846.9	2866.5	78	9
WB06	2819.4	2836.9	80	8

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
TYP-2	173	27
WB02	16	4
WB05	8	3
WB06	16	4

Metal Event 3	7/12/2012	Inf. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2879.1	2892.2	82	8
WB05	2854.4	2870.7	78	7.5
WB06	2826.4	2841.9	82	10

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
TYP-3	99	17
WB02	12	2
WB05	7	2
WB06	12	2

Metal Event 4	7/19/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2871.8	2888.2	74	9.5
WB05	2847.1	2869.6	69	10
WB06	2819.4	2837.4	76	9.5

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
TYP-4	115	19
WB02	15	2
WB05	6	2
WB06	12	2

Metal Event 5	7/24/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2849.4	2876.8	60	7
WB05	2827.5	2859.2	56	8
WB06	2796.8	2823.6	62	8

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
TYP-5	111	18
WB02	10	2
WB05	5	2
WB06	12	2

Metal Event 6	7/31/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2860.4	2880.7	73	12
WB05	2842.3	2888.2	66	12
WB06	2808.9	2829.8	74	12

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
TYP-6	118	19
WB02	8	2
WB05	2	1
WB06	11	2

Metal Event 7	8/3/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2863.9	2882.3	70	11
WB05	2846.3	2868.2	68	10.5
WB06	2812.2*	2834.7	76	11

*Mass was not recorded before test was performed.
Estimated to be 2812.2 g

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
TYP-7	126	21
WB02	17	4
WB05	22	3
WB06	14	3

Metal Event 8	8/7/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2867.3	2883.2	76	8.5
WB05	2848.9	2868.4	70	9
WB06	2817	2836.7	64	8.5

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
TYP-8	107	18
WB02	12	3
WB05	9	3
WB06	19	2

Metal Event 9	8/9/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2869.8	2887	73	10
WB05	2851.9	2869	68	10.5
WB06	2820.5	2838	72	10

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
TYP-9	101	16
WB02	13	2
WB05	9	2
WB06	12	2

Metal Event 10	7/31/2012	Infl. Vol = 100 mL		
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB02	2869	2886.7	76	12.5
WB05	2875.7	2869	67	11
WB06	2815.3	2836.2	72	12.5

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
TYP-10	114	18
WB02	11	3
WB05	6	3
WB06	16	3

Appendix C: Accelerated Concentration Data

AL-#: Accelerated Loading Influent Concentration

W(B/D)-ME#: Accelerated Loading Effluent from Specified Column and Event Number

Metal Event 1	3/26/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2841.9	2867.2	66
WD06	2848.6	2876.4	66
WD08	2875.2	2906.4	66
WD11	2822.7	2849.6	68
WD15	2842.8	2875.5	64
WD16	2792.1	2823.8	60
WB01	2837.2	2868.4	62
WB07	2822.7	2849.3	68
WB10	2814.7	2848.2	60
WB11	2821.7	2850.6	68
WB12	2822.7	2854.0	62
WB18	2820.8	2858.2	58

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-1	4,901	773
WD-ME 1	2,579	447
WB-ME 1	2,128	376

Metal Event 2	3/28/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2842.6	2867.9	74
WD06	2851.1	2877.3	78
WD08	2876.3	2905.0	70
WD11	2825.8	2851.8	78
WD15	2845.2	2877.2	71
WD16	2790.3	2823.6	69
WB01	2831.8	2864.8	60
WB07	2825.4	2851.9	74
WB10	2820.5	2851.2	71
WB11	2821.3	2850.5	73
WB12	2829.9	2856.4	70
WB18	2827.8	2859.2	72

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-2	4,901	763
WD-ME 2	2,497	433
WB-ME 2	2,222	378

Metal Event 3	3/31/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2839.1	2863.2	74
WD06	2850.5	2874.8	78
WD08	2877.2	2905.8	70
WD11	2822.7	2850.8	78
WD15	2839.7	2871.8	70
WD16	2788.1	2820.9	68
WB01	2823.6	2861.0	57
WB07	2821.8	2852.8	73
WB10	2814.9	2849.0	70
WB11	2816.5	2847.5	75
WB12	2827.8	2857.2	73
WB18	2824.1	2855.1	72

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-3	4,762	768
WD-ME 3	2,669	464
WB-ME 3	2,417	405

Metal Event 4	4/2/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2844.8	2908.2	72
WD06	2857.9	2880.7	77
WD08	2882.9	2870.6	71
WD11	2831.1	2857.1	75
WD15	2853.0	2891.1	69
WD16	2794.5	2824.6	66
WB01	2838.9	2871.8	70
WB07	2830.5	2871.8	72
WB10	2821.3	2854.9	57
WB11	2830.4	2853.2	73
WB12	2834.1	2855.9	70
WB18	2830.2	2868.7	68

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-4	4,787	772
WD-ME 4	2,625	451
WB-ME 4	2,411	384

Metal Event 5	4/4/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2844.7	2868.8	69
WD06	2855.2	2879.4	71
WD08	2884.7	2912.0	68
WD11	2833.0	2858.9	72
WD15	2854.6	2881.8	68
WD16	2799.4	2825.4	66
WB01	2845.6	2872.4	68
WB07	2836.2	2865.1	72
WB10	2826.4	2854.0	72
WB11	2834.5	2859.9	72
WB12	2832.4	2859.3	66
WB18	2830.1	2859.2	68

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-5	4,728	761
WD-ME 5	2,595	435
WB-ME 5	2,382	387

Metal Event 6	4/6/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2848.9	2872.6	72
WD06	2858.8	2880.4	76
WD08	2885.3	2910.7	70
WD11	2836.4	2860.4	74
WD15	2855.4	2881.2	69
WD16	2799.0	2827.2	68
WB01	2847.2	2873.4	70
WB07	2841.9	2868.9	70
WB10	2827.5	2854.3	73
WB11	2839.6	2863.0	74
WB12	2835.9	2856.5	74
WB18	2831.8	2858.5	71

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
AL-6	4,753	773
WD-ME 6	2,426	407
WB-ME 6	2,163	332

Metal Event 7	4/9/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2848.5	2870.4	70
WD06	2856.4	2877.1	72
WD08	2881.8	2907.6	68
WD11	2833.2	2857.2	72
WD15	2852.6	2875.6	68
WD16	2795.7	2825.7	66
WB01	2839.6	2868.2	60
WB07	2839.0	2867.0	66
WB10	2821.9	2851.4	62
WB11	2839.6	2860.5	68
WB12	2832.7	2856.5	66
WB18	2823.2	2853.8	67

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
AL-7	4,604	787
WD-ME 7	2,489	433
WB-ME 7	2,406	381

Metal Event 8	4/11/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2854.0	2872.8	74
WD06	2860.7	2877.6	80
WD08	2889.4	2912.7	75
WD11	2837.8	2859.2	76
WD15	2858.4	2881.5	73
WD16	2802.6	2829.2	70
WB01	2848.5	2873.4	70
WB07	2847.8	2870.2	76
WB10	2829.0	2856.5	69
WB11	2840.1	2864.7	72
WB12	2839.3	2861.6	74
WB18	2832.2	2858.8	72

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-8	4,730	766
WD-ME 8	2,398	403
WB-ME 8	2,125	328

Metal Event 9	5/5/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2826.6	2860.7	62
WD06	2832.6	2868.3	67
WD08	2855.3	2894.1	64
WD11	2808.4	2838.0	70
WD15	2830.6	2869.2	62
WD16	2773.6	2808.0	66
WB01	2812.7	2857.7	52
WB07	2816.7	2855.3	59
WB10	2797.1	2841.2	54
WB11	2809.2	2843.4	68
WB12	2803.5	2842.1	68
WB18	2811.1	2845.0	62

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-9	4,708	807
WD-ME 9	2,463	407
WB-ME 9	2,290	332

Metal Event 10	5/16/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2838.8	2867.9	68
WD06	2846.0	2874.7	71
WD08	2869.6	2900.2	64
WD11	2816.6	2846.6	68
WD15	2844.8	2871.8	70
WD16	2785.6	2816.3	72
WB01	2832.6	2864.5	64
WB07	2832.5	2854.2	74
WB10	2815.3	2844.8	64
WB11	2821.4	2846.3	72
WB12	2821.6	2845.4	74
WB18	2822.6	2851.3	69

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
AL-10	4,542	784
WD-ME 10	2,244	362
WB-ME 10	2,300	276

Metal Event 11	5/22/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2833.8	2859.6	72
WD06	2841.0	2867.4	70
WD08	2859.9	2891.2	72
WD11	2780.6	2813.3	67
WD15	2810.8	2839.9	69
WD16	2837.3	2867.1	71
WB01	2826.7	2863.4	60
WB07	2822.6	2852.0	70
WB10	2802.1	2836.1	68
WB11	2812.0	2841.5	69
WB12	2812.3	2842.4	68
WB18	2809.4	2845.9	65

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
AL-11	4,619	796
WD-ME 11	2,288	364
WB-ME 11	2,236	277

Metal Event 12	5/25/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2835.2	2864.9	69
WD06	2844.0	2869.5	67
WD08	2868.0	2896.3	62
WD11	2789.0	2815.6	72
WD15	2813.9	2843.1	64
WD16	2840.7	2868.6	65
WB01	2833.6	2863.2	65
WB07	2830.6	2858.5	68
WB10	2807.5	2840.5	68
WB11	2814.8	2841.8	69
WB12	2817.3	2846.0	66
WB18	2820.8	2849.1	68

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
AL-12	5,722	937
WD-ME 12	2,696	414
WB-ME 12	2,766	337

Metal Event 13	5/29/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2833.6	2856.1	73
WD06	2842.6	2869.0	68
WD08	2871.5	2900.7	68
WD11	2815.5	2844.2	72
WD15	2840.9	2869.1	73
WD16	2786.7	2815.2	69
WB01	2830.8	2864.5	64
WB07	2824.9	2846.5	77
WB10	2805.2	2838.7	62
WB11	2812.7	2843.9	68
WB12	2819.5	2846.3	69
WB18	2821.3	2848.1	74

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
AL-13	4,734	815
WD-ME 13	2,373	350
WB-ME 13	2,375	277

Metal Event 14	5/31/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2843.2	2869.1	70
WD06	2854.0	2875.1	78
WD08	2882.0	2906.5	74
WD11	2828.2	2851.7	75
WD15	2851.3	2874.3	72
WD16	2796.2	2821.1	72
WB01	2843.3	2870.2	67
WB07	2830.6	2855.6	77
WB10	2821.1	2848.7	71
WB11*	2824.2	2847.9	-
WB12	2826.3	2851.8	74
WB18	2826.4	2851.9	71

*WB sample does not contain effluent from WB11. WB sample contaminated. Estimated to be 70 mL.

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-14	4,285	715
WD-ME 14	2,079	344
WB-ME 14	2,079	264

Metal Event 15	6/6/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD03	2830.9	2858.7	68
WD06	2839.3	2868.0	68
WD08	2870.1	2898.4	64
WD11	2814.3	2840.7	66
WD15	2840.2	2867.2	70
WD16	2782.1	2812.7	66
WB01	2818.9	2858.9	56
WB07	2817.8	2846.1	70
WB10	2802.5	2840.5	56
WB11	2813.8	2842.0	68
WB12	2815.4	2844.6	65
WB18	2811.3	2844.3	64

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-15	4,654	799
WD-ME 15	2,167	334
WB-ME 15	2,324	265

Metal Event 16	6/13/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2848.8	2876.3	64
WD08	2875.9	2904.5	68
WD11	2820.3	2849.3	68
WD15	2845.2	2871.5	70
WD16	2790.5	2820.2	66
WB01	2831.5	2865.1	56
WB07	2821.3	2858.0	65
WB11	2825.0	2848.0	72
WB12	2822.7	2849.1	71
WB18	2820.2	2846.7	68

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-16	4,721	812
WD-ME 16	1,979	332
WB-ME 16	2,322	239

Metal Event 17	6/18/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2841.4	2867.9	60
WD08	2864.7	2894.8	60
WD11	2810.9	2840.7	63
WD15	2836.7	2864.9	64
WD16	2785.1	2815.6	62
WB01	2819.5	2859.4	52
WB07	2825.4	2847.7	64
WB11	2814.0	2843.5	66
WB12	2815.4	2844.7	64
WB18	2814.1	2845.7	63

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
AL-17	4,658	787
WD-ME 17	1,955	297
WB-ME 17	2,440	261

Metal Event 18	6/20/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2853.8	2879.2	70
WD08	2876.0	2904.8	60
WD11	2822.4	2852.7	60
WD15	2846.9	2874.5	60
WD16	2792.5	2820.0	62
WB01	2840.6	2869.7	64
WB07	2832.4	2856.2	66
WB11	2824.9	2851.1	65
WB12	2827.4	2851.6	62
WB18	2824.7	2852.0	66

Sample ID	Eff. Zn Conc. (μg/L)	Eff. Cu Conc. (μg/L)
AL-18	4,599	774
WD-ME 18	2,033	326
WB-ME 18	2,160	207

Metal Event 19	6/22/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2860.2	2881.8	74
WD08	2882.7	2909.4	68
WD11	2833.9	2858.6	76
WD15	2854.6	2879.5	72
WD16	2797.8	2825.7	72
WB01	2847.1	2874.5	68
WB07	2837.8	2861.2	72
WB11	2832.4	2856.7	74
WB12	2834.8	2858.3	74
WB18	2833.6	2860.1	70

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-19	4,706	792
WD-ME 19	2,098	316
WB-ME 19	2,228	219

Metal Event 20	6/23/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2860.5	2882.1	72
WD08	2885.3	2912.2	69
WD11	2835.3	2858.1	74
WD15	2857.0	2882.4	70
WD16	2799.8	2826.8	72
WB01	2847.4	2874.9	70
WB07	2843.8	2866.2	74
WB11	2838.6	2862.5	76
WB12	2836.8	2861.4	74
WB18	2833.9	2859.6	72

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-20	4,553	768
WD-ME 20	1,907	311
WB-ME 20	2,160	221

Metal Event 21	7/8/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2834.0	2863.4	69
WD08	2857.6	2894.1	60
WD11	2809.3	2840.9	68
WD15	2830.7	2864.5	62
WD16	2781.2	2814.7	64
WB01	2822.1	2860.9	56
WB07	2822.4	2849.0	70
WB11	2812.2	2841.9	65
WB12	2813.8	2845.3	68
WB18	2814.2	2845.3	66

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-21	4,568	763
WD-ME 21	1,953	281
WB-ME 21	2,395	231

Metal Event 22	7/18/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2854.6	2875.0	72
WD08	2880.6	2905.2	68
WD11	2828.7	2853.2	68
WD15	2852.6	2877.8	67
WD16	2799.4	2822.3	68
WB01	2845.8	2868.8	68
WB07	2838.4	2858.0	72
WB11	2830.6	2852.8	72
WB12	2834.0	2854.5	74
WB18	2832.3	2854.7	72

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-22	4,541	760
WD-ME 22	1,825	275
WB-ME 22	2,224	217

Metal Event 23	7/20/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2866.6	2884.0	74
WD08	2894.2	2913.0	77
WD11	2843.0	2863.0	74
WD15	2866.8	2887.4	75
WD16	2810.9	2834.5	72
WB01	2857.1	2876.6	76
WB07	2851.7	2869.0	74
WB11	2844.9	2865.5	74
WB12	2845.5	2863.6	80
WB18	2844.7	2865.0	72

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-23	4,543	762
WD-ME 23	1,973	277
WB-ME 23	2,143	204

Metal Event 24	7/26/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2850.6	2873.6	70
WD08	2878.2	2903.3	68
WD11	2824.4	2851.2	70
WD15	2846.3	2870.8	70
WD16	2792.7	2818.8	69
WB01	2840.2	2866.4	68
WB07	2840.1	2857.7	78
WB11	2831.2	2854.4	75
WB12	2826.9	2851.3	72
WB18	2827.2	2851.2	72

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-24	4,571	768
WD-ME 24	2,026	281
WB-ME 24	2,325	222

Metal Event 25	7/30/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2849.3	2873.5	62
WD08	2873.9	2901.4	58
WD11	2824.4	2850.7	62
WD16	2792.5	2819.9	62
WB01	2836.9	2864.6	60
WB07	2830.7	2855.7	64
WB12	2826.2	2852.7	64
WB18	2820.8	2847.4	64

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-25	4,566	770
WD-ME 25	1,898	265
WB-ME 25	2,209	220

Metal Event 26	8/2/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2852.2	2883.2	61
WD08	2879.3	2905.6	64
WD11	2829.2	2855.6	68
WD16	2795.7	2820.8	66
WB01	2841.0	2867.1	65
WB07	2834.2	2856.1	66
WB12	2832.2	2854.8	72
WB18	2827.4	2852.7	68

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-26	4,572	768
WD-ME 26	1,802	242
WB-ME 26	2,157	202

Metal Event 27	8/6/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2850.3	2873.4	68
WD08	2867.5	2897.0	64
WD11	2819.0	2846.9	64
WD16	2786.4	2816.9	62
WB01	2826.1	2863.8	52
WB07	2827.5	2846.9	72
WB12	2825.7	2849.2	70
WB18	2816.9	2846.4	73

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-27	4,418	745
WD-ME 27	1,770	239
WB-ME 27	2,322	224

Metal Event 28	8/8/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2861.6	2882.1	70
WD08	2884.0	2908.9	62
WD11	2832.1	2858.1	68
WD16	2800.3	2826.5	66
WB01	2848.2	2873.3	64
WB07	2837.7	2855.0	74
WB12	2835.8	2858.4	70
WB18	2832.2	2856.7	70

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-28	4,551	766
WD-ME 28	1,942	276
WB-ME 28	2,263	204

Metal Event 29	8/14/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2842.0	2868.0	62
WD08	2873.0	2902.7	58
WD11	2820.9	2848.9	66
WD16	2785.1	2816.7	62
WB01	2827.4	2863.1	55
WB07	2825.1	2849.7	68
WB12	2823.2	2850.5	64
WB18	2814.7	2845.5	61

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-29	4,610	773
WD-ME 29	2,270	251
WB-ME 29	2,348	224

Metal Event 30	8/16/2012	Infl. Vol = 100 mL	
Specimen ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)
WD06	2854.5	2876.9	66
WD08	2885.3	2911.4	60
WD11	2832.7	2857.4	66
WD16	2800.0	2827.0	66
WB01	2845.1	2870.3	79
WB07	2837.3	2855.1	86
WB12	2834.8	2857.1	84
WB18	2880.3	2854.9	81

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Cu Conc. (µg/L)
AL-30	4,735	787
WD-ME 30	1,512	132
WB-ME 30	2,583	241

Appendix D: Typical Concentration post Accelerated Event Data

S#-E#: Set #- Event # is the influent concentration. The S# variable denotes how many AL events the cylinder experienced prior to typical events and E# variable is the event number for that cylinder

S1: 15 AL events prior to typical loadings

S2: 24 AL events prior to typical loadings

S1-E1	6/26/2012	Infl. Vol = 100 mL		
Sample ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB10E1	2808.7	2840.5	62	13.5
WD03E1	2836.0	2864.7	67	12.5

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Zn Conc. (µg/L)
S1-E1	134	22
WB10E1	18	4
WD03E1	19	4

S1-E2	7/3/2012	Infl. Vol = 100 mL		
Sample ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB10E2	2820.8	2846.6	50	10
WD03E2	2845.1	2865.1	54	10

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Zn Conc. (µg/L)
S1-E2	217	35
WB10E2	21	5
WD03E2	23	5

S1-E3	7/13/2012	Infl. Vol = 100 mL		
Sample ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB10E3		2852.1	74	10
WD03E3		2871.1	72	8.5

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Zn Conc. (µg/L)
S1-E3	99	17
WB10E3	10	3
WD03E3	20	3

S2-E1	7/31/2012	Infl. Vol = 100 mL		
Sample ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB10E1	2830.1	2854	73	9
WD03E1	2846.1	2874.1	66	10

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Zn Conc. (µg/L)
S2-E1	118	19
WB11E1	11	3
WD15E1	11	3

S2-E2	8/7/2012	Infl. Vol = 100 mL		
Sample ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB10E2	2842.8	2855.1	70	10
WD03E2	2848.8	2874.5	70	9

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Zn Conc. (µg/L)
S2-E2	107	18
WB11E2	21	4
WD15E2	17	4

S2-E3	8/10/2012	Infl. Vol = 100 mL		
Sample ID	Pre-Test Mass (g)	Post-Test Mass (g)	Eff. Vol (mL)	Time (min)
WB10E3	2838	2860.7	64	11
WD03E3	2854.7	2879.9	66	10.5

Sample ID	Eff. Zn Conc. (µg/L)	Eff. Zn Conc. (µg/L)
S2-E3	101	16
WB11E3	13	3
WD15E3	16	4

Appendix E: Statistical Analysis of WB and WD Cylinders Comparison

Statistical analysis performed on data from Figure 4.1

Section 1	Events 1 to 10	
	Variable 1	*Variable 2*
Mean	67.22115911	63.04462886
Variance	7.168954622	5.333808101
Observations	10	10
Pearson Correlation	0.610444783	
Hypothesized Mean Difference	0	
df	9	
t Stat	5.934356169	
P(T<=t) one-tail	0.000109769	
t Critical one-tail	1.833112923	
P(T<=t) two-tail	0.000219538	
t Critical two-tail	2.262157158	
Reject Ho	V1≠V2	

Section 2	Events 11 to 20	
	Variable 1	*Variable 2*
Mean	67.02309275	68.78216347
Variance	2.21721567	11.3779371
Observations	10	10
Pearson Correlation	0.545736771	
Hypothesized Mean Difference	0	
df	9	
t Stat	-1.952953142	
P(T<=t) one-tail	0.04128706	
t Critical one-tail	1.833112923	
P(T<=t) two-tail	0.08257412	
t Critical two-tail	2.262157158	
Fail to Reject Ho	V1=V2	

Section 3	Events 21 to 30	
	Variable 1	*Variable 2*
Mean	64.951932	72.54855172
Variance	16.3214796	11.40911981
Observations	10	10
Pearson Correlation	-0.450391998	
Hypothesized Mean Difference	0	
df	9	
t Stat	-3.797232025	
P(T<=t) one-tail	0.002117666	
t Critical one-tail	1.833112923	
P(T<=t) two-tail	0.004235332	
t Critical two-tail	2.262157158	
Reject Ho	V1≠V2	