PHOSPHORUS REMOVAL FROM STORMWATER
USING ZERO-VALENT IRON

by

Lauren S. Lechner

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Applied Sciences

Summer 2016

© 2016 Lauren S. Lechner
All Rights Reserved
PHOSPHORUS REMOVAL FROM STORMWATER

USING ZERO-VALENT IRON

by

Lauren S. Lechner

Approved: ________________________________
Pei C. Chiu, Ph.D.
Professor in charge of thesis on behalf of the Advisory Committee

Approved: ________________________________
Harry W. Shenton III, Ph.D.
Chair of the Department of Civil and Environmental Engineering

Approved: ________________________________
Babatunde A. Ogunnaike, Ph.D.
Dean of the College of Engineering

Approved: ________________________________
Ann L. Ardis, Ph.D.
Senior Vice Provost for Graduate and Professional Education
ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. Pei Chiu, for his guidance and aid throughout this research project. I would like to recognize my colleagues in the Chiu research group for their assistance in the lab. I would also like to acknowledge the UD Department of Civil & Environmental Engineering.

I want to extend another thank you to my family, friends, and former professors for their constant support.

Finally, I want to thank my funding agency, the Delaware Water Resources Center, and the additional funding agencies Delaware Department of Transportation and Mid-Atlantic Transportation Sustainability Center for the opportunity to pursue this research and my degree.
# TABLE OF CONTENTS

LIST OF TABLES .................................................................................................................. vi
LIST OF FIGURES .................................................................................................................. vii
ABSTRACT ............................................................................................................................... ix

Chapter

1 INTRODUCTION .................................................................................................................. 1

1.1 Problem Statement ......................................................................................................... 1

2 LITERATURE REVIEW ...................................................................................................... 4

2.1 Nutrient Pollution Problem ............................................................................................ 4
2.2 Phosphorus Speciation .................................................................................................... 5
2.3 Nutrient Pollution Effects ............................................................................................... 7

2.3.1 Human Health ............................................................................................................. 7
2.3.2 Environment/Ecosystems ........................................................................................... 8
2.3.3 Economy ..................................................................................................................... 9

2.4 Zero-Valent Iron Structure and Properties ................................................................. 10
2.5 Zero-Valent Iron Treatment Potential .......................................................................... 12
2.6 Field Application .......................................................................................................... 14
2.7 Research Objectives ...................................................................................................... 16

3 EXPERIMENTAL METHODS ........................................................................................... 17

3.1 Sand and ZVI ................................................................................................................. 17
3.2 Solution Preparation ...................................................................................................... 18

3.2.1 Deionized Water ...................................................................................................... 18
3.2.2 Synthetic Stormwater ............................................................................................... 19

3.3 Column Setup ................................................................................................................. 20
3.4 Phosphate Pulse Tests in Deionized Water .................................................................. 23
3.5 Phosphate Pulse Tests in Synthetic Stormwater ............................................................. 24
3.6 Phosphorus Extractions ................................................................................................. 25
3.7 Data Analysis and Modeling ......................................................................................... 27
4 RESULTS AND DISCUSSION

4.1 Control Column (Sand Only) – Deionized Water ........................................................................... 31
4.2 Experimental Column (ZVI + Sand) – Deionized Water .......................................................... 32
4.3 Control Column (Sand Only) – Synthetic Stormwater ......................................................... 37
4.4 Experimental Column (ZVI + Sand) – Synthetic Stormwater ........................................ 38
4.5 Extractions ..................................................................................................................................... 40

5 CONCLUSIONS AND FUTURE RESEARCH .................................................................................. 45

REFERENCES ........................................................................................................................................ 47

Appendix

A RESIDUAL PLOTS .......................................................................................................................... 52
B MEASURED TOTAL IRON CONCENTRATIONS IN EFFLUENT ........................................ 61
LIST OF TABLES

Table 3.1 Composition of synthetic stormwater .............................................. 20

Table 3.2 Column setup characteristics ................................................................. 22

Table 4.1 Deionized water results. (a) Summary of fitted model parameters for control column, at different influent concentrations of PO$_4$-P; (b) Summary of fitted model parameters for experimental (ZVI) column, at different influent concentrations of PO$_4$-P. Note: No parameters are included for the lowest PO$_4$-P concentration in the ZVI column because no breakthrough curve was observed. *Manual integration performed to estimate percent removal ................................................. 37

Table 4.2 Synthetic stormwater results. Summary of fitted model parameters [using equations (14) and (15)] for control (sand only) column, at influent concentration of 1.6 ppm PO$_4$-P. Also including fitted model parameters [using equations (12) and (13)] for experimental (7.33% ZVI/92.7% sand, by volume) column, at different influent concentrations of PO$_4$-P. Note: There are no parameters included for the two lowest concentrations of phosphorus in the experimental column because no breakthrough curve was observed. *Manual integration performed to estimate percent removals ................................................. 43

Table 4.3 Side-by-side comparison of all ZVI column fitted model parameters. (S.S. = synthetic stormwater) ................................................................. 44
LIST OF FIGURES

Figure 2.1. Speciation of phosphate versus pH. The species of interest, in this study, is HPO$_4^{2-}$, which is present in the highest fraction around pH 9, which is why this pH was chosen for the solutions. ................................. 6

Figure 2.2. Schematic of a potential bioretention filter design for nutrient removal; areas highlighting ZVI addition and phosphorus removal are circled in orange. ........................................................................ 16

Figure 3.2. Experimental (ZVI) column set up; control (sand only) column setup is the same. .................................................................................................................... 22

Figure 3.3. Column dissection schematic illustrating different layers. .................. 26

Figure 4.1. All data from control (sand only) column for 4 different concentrations: (a) 1.6 ppm PO$_4$-P, (b) 3.3 ppm PO$_4$-P, (c) 8 ppm PO$_4$-P, and (d) 16 ppm PO$_4$-P. ................................................................. 35

Figure 4.2. All data from experimental (5% ZVI by volume/95% sand) column for 4 different concentrations: (a) 1.6 ppm PO$_4$-P, (b) 3.3 ppm PO$_4$-P, (c) 8 ppm PO$_4$-P, and (d) 16 ppm PO$_4$-P. ................................................................. 36

Figure 4.3. All data from both control and experimental columns using synthetic stormwater. ..................................................................................................................... 42

Figure 4.4. Summary of phosphorus extractions. .................................................... 44

Figure A1. Residual plots for DI water pulse with 1.6 ppm PO$_4$-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ........................................................................ 52

Figure A2. Residual plots for DI water pulse with 3.2 ppm PO$_4$-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ........................................................................ 53

Figure A3. Residual plots for DI water pulse with 8 ppm PO$_4$-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ........................................................................ 54
Figure A4. Residual plots for DI water pulse with 16 ppm PO$_4$-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ................................................................. 55

Figure A5. Residual plots for DI water pulse with 3.2 ppm PO$_4$-P in the experimental column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ................................................................. 56

Figure A6. Residual plots for DI water pulse with 8 ppm PO$_4$-P in the experimental column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ................................................................. 57

Figure A7. Residual plots for DI water pulse with 16 ppm PO$_4$-P in the experimental column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ................................................................. 58

Figure A8. Residual plots for synthetic stormwater pulse with 1.6 ppm PO$_4$-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ................................................................. 59

Figure A9. Residual plots for synthetic stormwater pulse with 16 ppm PO$_4$-P in the experimental column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume. ................................................................. 60

Figure B1. Total iron concentrations in effluent over time in ZVI + sand columns; a. deionized water and; b. in synthetic stormwater. In deionized water, total iron measurements were limited due to some samples having undetectable iron levels (detection limit = 0.03 mg/L total Fe). ............ 61
ABSTRACT

Nutrient removal from water sources is becoming increasingly important, as nutrient pollution is emerging as a challenging and critical environmental issue. Nutrient pollution (excess nitrogen and phosphorus) can cause algal blooms, human health issues, and ecological and economic losses. Stormwater runoff can aggravate this issue, because it easily carries pollutants from surfaces into storm sewer systems and is discharged, untreated, to water sources. More recently, transportation agencies have become interested in treating stormwater runoff, particularly which comes off of road surfaces. There have been efforts by these agencies, along with the U.S. EPA to efficiently treat runoff.

This work focuses on removal of phosphorus using scrap iron, or, zero-valent iron (ZVI). ZVI has numerous applications in removal technologies, and in this case, can be used as an amendment into a bioretention system to treat stormwater. By using several phosphorus pulse tests on flow-through columns, on both columns with and without ZVI, we were able to assess the removal efficiency of phosphorus by ZVI, by using the advection-dispersion-reaction equation to confirm our observational data. It was determined that ZVI can remove up to 98% of influent phosphorus at the lowest concentration of phosphorus (1.6 ppm PO$_4$-P) used. At the highest concentration (16 ppm PO$_4$-P), ZVI was shown to still remove up to 36% of incoming phosphorus. Through several phosphorus extractions, it was also determined that the phosphorus
retained in the column is mostly iron-bound (strongly-bound) phosphorus, accounting for over 50% of the total phosphorus extracted. Iron-bound phosphorus will not be easily leached out of the system, since it is very stable, and only extractable with an acid. This has great promise as an amendment into the field for the treatment of excess phosphorus in stormwater.

For future research, it would be advisable to study the effect that pH and flow rate has on the removal efficiency of phosphate by ZVI, as well as conduct a long-term study to determine the physical changes ZVI undergoes, and to determine potential iron-phosphate mineral formation.
Chapter 1

INTRODUCTION

1.1 Problem Statement

Nutrient pollution is a challenging environmental issue that the U.S. is faced with, especially since this leads to polluted bays, rivers, and groundwater. Nutrient pollution is caused by excess nitrogen and/or phosphorus present in the water. This excess can cause harmful algal blooms, human health concerns, and economic and ecological losses (U.S. EPA, 2015). Specifically, in Delaware, the Chesapeake Bay is in poor condition due to nutrient pollution, which results from urban, suburban and agricultural runoff, wastewater treatment plant effluent, and air pollution (Chesapeake Bay Program, 2012). One of the major contributors to nutrient pollution is stormwater runoff, which results in nutrients being carried, untreated, into surface waters, in turn, causing damage. In 2015, urban runoff was the second highest source of phosphorus into the Chesapeake Bay, contributing 2.69 million pounds of phosphorus, just after the agriculture claiming the highest load (Chesapeake Bay Program, 2015).

Phosphorus is one of the two elements responsible for eutrophication, and can be the primary cause of eutrophication in freshwater lakes (Schindler 1977). Phosphorus can be found in many fertilizers and animal waste, contributing to the phosphorus load entering surface waters via stormwater runoff. Since rain events occur intermittently,
stormwater is not a constant source of phosphorus pollution, and there is a need to be able to treat incoming pulses of phosphorus, which may only have short periods of contact time with a treatment area. In the Chesapeake Bay, the phosphorus loads were as high as 25.62 million pounds in 1985, decreasing to 19.23 million pounds in 2009 and again decreasing to 15.36 million pounds in 2015, with the goal to continue this drop to 14.46 million pounds in 2025 (Chesapeake Bay Program, 2015).

ZVI has been used for many treatment applications, and shown to remove a wide variety of chemical contaminants, including metallic ions (Al, Cu, Pb, etc.), halogenated hydrocarbons, and nitroaromatics (U.S. EPA, 2016), as well as biological contaminants, like viruses (You et al., 2005). Previously, ZVI has been shown to bind phosphate, either through adsorption or precipitation at the iron surface (Saxe et al., 2006). It was also reported that continuous iron-supported phosphate removal could be sustained for at least one year (Erickson et al., 2012), as well as remove large amounts of phosphate (Allred, 2012). Hence, it is likely to be an effective removal technique to treat phosphorus-carrying stormwater runoff, before reaching and further polluting surface waters.

Currently, there are total maximum daily load (TMDL) regulations put in place in order to decrease the amount of nutrients entering surface waters. TMDLs are made up of three parts, a wasteload allocation for point sources, a load allocation for nonpoint sources, and a margin of safety (DNREC, 2016). Since stormwater runoff is a nonpoint source, it is included in the load allocation for nonpoint sources, which could mean up to a 70% reduction in phosphorus loads for watersheds in Delaware
Due to this high demand, an improved bioretention system is needed, with little land usage but high efficiency. In order to treat nutrient pollution, specifically pertaining to phosphorus, we propose a method for using zero-valent iron (ZVI) as a bioretention system amendment to remove phosphorus from multiple water sources, including stormwater runoff.
Chapter 2

LITERATURE REVIEW

2.1 Nutrient Pollution Problem

With the continuing population expansion in the U.S., from 319 million people in 2014 to 417 million in 2060 (Colby & Ortman, 2014), and growing need for water, it is crucial to have access to clean water. However, clean water is becoming harder to come by, with a prediction of 40 out of the 50 U.S. states expected to experience a water shortage in the next ten years (GAO, 2014), and one of the reasons being due to the impact of poor water quality. One of the United States’ largest water quality impairments is nutrient pollution, caused by the overloading of nutrients, such as nitrogen and phosphorus, in water, leading to eutrophication (NOAA, 2008).

Eutrophication is described as nitrogen and phosphorus being present in excessive amounts (NOAA, 2008). This problem arises in many types of water bodies, including streams, rivers, lakes, bays, and other coastal areas (U.S. EPA, 2016).

Nitrogen and phosphorus are considered non-point source pollution, because of the widespread area of origin, and various ways of transport to receiving waters (Carpenter et. al, 1998). Thus, regulating these pollutants can be quite challenging. The main sources of high levels of nutrients include agricultural runoff, wastewater, and stormwater runoff (Carpenter et. al, 1998). As explained by Carpenter et. al,
stormwater runoff can be responsible for most of the nutrient transport to surface waters, since runoff enters and leaves stormwater drainage systems untreated. Runoff itself can also have many sources, including construction sites, fertilizers, animal waste, biosolids, and wastewater disposal (Carpenter et. al, 1998).

Although both elements play a role in nutrient pollution, phosphorus can be the primary cause of eutrophication in lakes (Schindler 1977), as well as in some coastal ecosystems (Carpenter et. al, 1998). Therefore, it is important to be able to treat phosphorus before it enters surface waters and causes eutrophication.

### 2.2 Phosphorus Speciation

Phosphate ions can exist in three forms, as illustrated by equations 1 – 3 (Stumm and Morgan, 1996) and Figure 2.1, and is controlled by the pH of the solution. At the typical environmental pH range of 4 to 6, phosphate will take on the form $H_2PO_4^-$, whereas at higher pH ranges, like seen in cultivated soils, more $HPO_4^{2-}$ can exist (Holtan et. al, 1988).

\[
H_3PO_4 = H_2PO_4^- + H^+ \quad pK_a_1 = 2.1 \quad \text{...................................................... (1)}
\]
\[
H_2PO_4^- = HPO_4^{2-} + H^+ \quad pK_a_2 = 7.2 \quad \text{...................................................... (2)}
\]
\[
HPO_4^{2-} = PO_4^{3-} + H^+ \quad pK_a_3 = 12.3 \quad \text{...................................................... (3)}
\]
Figure 2.1. Speciation of phosphate versus pH. The species of interest, in this study, is HPO$_4^{2-}$, which is present in the highest fraction around pH 9, which is why this pH was chosen for the solutions.

In soil systems, most of the phosphorus is sorbed to soil particles or in soil organic matter (Holtan et al, 1988). In aquatic systems, phosphate takes on the forms, including, particulate, soluble, soluble reactive, and soluble unreactive phosphorus, and most of which in solution is tranformed by either release of soluble phosphorus from solids or uptake of dissolved phosphorus by solids (Holtan et. al, 1988).

Phosphorus sources in stormwater include fertilizers, automobile exhaust, plants, both living and decaying, animal remains, and detergents (Liu & Davis, 2013). Phosphorus can be transported into water in both particulate and dissolved forms, through either agricultural or forest runoff, or from wastewater treatment plant effluent (Holtan et. al, 1988). Additional sources include groundwater discharge and
atmospheric deposition, which all contribute to the phosphorus loading in surface waters, leading to eutrophication and algal blooms (Holtan et. al, 1988).

If phosphorus is deposited in water or sediments, even in low concentrations, it can form a mineral, over which more than 200 phosphate minerals have been found (Holtan et. al, 1988).

2.3 Nutrient Pollution Effects

The U.S. EPA (2016) categorizes nutrient pollution effects into three: human health effects, environmental effects, and economic effects.

2.3.1 Human Health

Although phosphorus itself does not pose an imminent threat to humans, eutrophication of surface waters does. Eutrophication causes an increase in algal growth, with some algae, like blue-green algae (cyanobacteria), producing toxins in freshwater. Specifically, blue-green algae produce hepatotoxins, cytotoxins, and neurotoxins. Hepatotoxins primarily cause liver damage and liver tumors (Falconer 1998). Cytotoxins can cause a variety of organ damage, including liver and kidney damage, with the potential to affect any tissues that rapidly synthesize proteins, and neurotoxins can cause respiratory failure, leading to death (Falconer 1998). Humans are exposed to blue-green algae via recreational activities in lakes and rivers, and exposure illnesses range from gastroenteritis to pneumonia (Falconer 1998, WHO 1998).
In 1998, the World Health Organization (WHO) released a provisional drinking water guideline value for one cyanobactoxin, total microcystin-LR, as 1 ug/L. Additionally, WHO published guidelines for recreational waters in 2003, with low probability of adverse health effects from cyanobacteria of 20,000 cells/mL, and high probability of adverse health effects from cyanobacteria when there is scum formation and/or risk of ingestion (WHO 2003).

In marine and coastal water bodies, red or brown algal tides can form, also known as the Florida Red Tide (*Karenia brevis*). These algae produce neurotoxins, for example, brevetoxin aerosols (Hoagland et. al, 2014), and humans are primarily exposed to them via consumption of shellfish, leading to gastrointestinal disorders. The toxins can also be transported by air bubbles, which humans can inhale, and which cause respiratory problems (Pierce & Henry, 2008). For public health protection, the state of Florida policy enforces a closure of shellfish beds at levels of 5,000 cells *K. brevis*/L (Pierce & Henry, 2008).

### 2.3.2 Environment/Ecosystems

Not only can toxic algae harm humans, but they can harm animals and other organisms, as well. Along with the grown of toxic algae, there is also growth of nontoxic algae, which can interfere with the usage of the water body, for fishing, recreation, or other purposes. When the algae die and are decomposing, the oxygen becomes consumed in the water, creating hypoxic, or dead zones, leading the death of other aquatic organisms (U.S. EPA, 2016). A traditional threshold to confirm hypoxia
is under 2 mg/L of dissolved oxygen (Vaquer-Sunyer & Duarte, 2008). In the Chesapeake Bay Program, the hypoxic volume of the bay was measured at 3,806 million cubic meters, just slightly below the average (Chesapeake Bay Program, 2015). Furthermore, algal blooms can block sunlight and clog fish gills (U.S. EPA, 2016).

The Chesapeake Bay is the largest estuary in the United States, so ecological losses and environmental effects can be tragic. In 1998, there was a ban placed on Atlantic sturgeon fishing, by the Atlantic States Marine Fisheries Commission, as a 40-year ban (Chesapeake Bay Program, 2012). In 2007, Maryland experienced one of its lowest blue-crab harvests since 1942. These losses require immediate attention and restoration in order to keep the ecosystem alive and thriving.

2.3.3 Economy

Economic losses due to nutrient pollution have a wide range of affected areas, including tourism, property value, fishing, water treatment, and control measures. When lakes or coastal areas are closed due to toxic algal blooms, tourism in the area declines, because tourists can partake in water recreational activities. In particular, an algal bloom in an Ohio lake caused a loss of up to $47 million in lost local tourism revenue (U.S. EPA, 2015). The unsightly condition of nutrient overloaded water can affect property value on nearby homes. Waterfront land that was once a commodity could be greatly affected by the unpleasant sight and smell that algal blooms cause. For example, in New England, a 1-meter difference in water clarity is linked to
property value changes up to $61,000 (U.S. EPA, 2015). Commercial fishing experiences losses as well, as exemplified earlier by fishing bans and ecosystem restoration programs. In Maine, an algal bloom required shellfish bed closures, leading to losses of $2.5 million in soft shell clam harvests that season (U.S. EPA, 2015).

Water treatment costs rise, in order to treat the current pollution, and prevent future pollution. Water to be used for drinking requires extra treatment, typically by activated carbon, to remove excess algal blooms and nutrients. This could require installation of additional treatments and monitoring equipment, as well as additional maintenance costs, resulting in millions of dollars spent; current treatment costs for excess phosphorus in lakes have been shown to can exceed $70 million, in total costs (U.S. EPA, 2015). Restoration of contaminated areas can reach up to $28 million, in initial capital (U.S. EPA, 2015).

2.4 Zero-Valent Iron Structure and Properties

ZVI can be used in many forms, from nanoscale to scrap granules. In this study, scrap iron granules were used, due to the high availability and low cost. Although contrary to what the name suggests, under ambient conditions, the surface of ZVI granules will oxidize, and have a coating of iron oxides (Fe$^{2+}$ and Fe$^{3+}$). During the corrosion of iron particles, iron oxide products can include the following: ferric and ferrous hydroxides, in both aerobic and anaerobic conditions (Fu et al., 2014); magnetite, at pH > 9 and $E_h$ measured at approximately -0.3 V (Odziemkowski et al.,
1998); siderite, which can form in carbonate-containing waters, due to the increase in pH from the anaerobic corrosion of iron (Mackenzie et al., 1999); goethite, at a pH > 12, and $E_h$ approximately -0.07 V (Encina et. al, 2015); ferrihydrite, in the presence of silicon, calcium, and chromium, pH 9.5, and $E_h = -0.347$ V (Furukawa et al., 2002); lepidocrocite, akaganeite, mackinawite, and maghemite, in the pH range of 8.8 to 9.8 (Gu et al., 1999). These products can have large sorption capacities for a range of contaminant compounds, from explosives, like 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Oh et al., 2003) to viruses (You et al., 2005).

ZVI can be corroded under both aerobic and anaerobic conditions, with anaerobic corrosion at 25°C, shown in Equation 4a (Filip et. al, 2014), and aerobic corrosion, at pH 7, shown in Equation 4b (Katsoyiannis et. al, 2008).

$$ Fe^0 + 2H_2O \rightarrow H_2 + Fe(OH)_2 \quad \text{-----------------------------} \quad (4a) $$

$$ 4Fe^0 + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3 \quad \text{-----------------------------} \quad (4b) $$

The presence of heat in the anaerobic reaction will accelerate the corrosion of ZVI, by approximately one order of magnitude faster (Filip et. al, 2014). At different pH’s, the corrosion of ZVI can produce different iron-products, including protonated $Fe(OH)_3$ (Katsoyiannis et. al, 2008).

ZVI is versatile and multi-functional; it is a strong reducing agent ($E^o = -0.44$ V) (Fu et al., 2014) and its oxidation products are good sorbents for those contaminants mentioned earlier. Contaminants, in general, can be removed from water directly through physical and chemical processes such as adsorption, oxidation-
reduction reactions, and precipitation, and these have been documented throughout literature (Filip et. al, 2014).

2.5 Zero-Valent Iron Treatment Potential

Through the corrosion of ZVI, we hypothesize that the corrosion products can react with incoming phosphorus, as depicted in Equation 5, to remove the phosphorus before reaching surface waters.

\[ Fe_xO_y + HPO_4^{2-} \rightarrow Fe - PO_4 \text{ surface complexes/precipitates} \]

\[ \downarrow..........................\text{(5)} \]

In 2006, Saxe et al., demonstrated that phosphate can interact so strongly with ZVI, that it can impede the interaction of other compounds with ZVI. It was determined that phosphate concentration varied linearly with contaminant reduction, suggesting that ZVI can bind increasingly higher concentrations of phosphate, up to 5 mM PO$_4^{3-}$ (155 ppm PO$_4$-P), either through adsorption to Fe(III) oxides, precipitation of iron phosphates on the ZVI surface, or both.

It has been demonstrated there can be at least three dominating surface complexes between ZVI and phosphate ions, where phosphate coordinates to Fe(III) ions at the surface of ZVI. The differing surface species are due to differing degrees of protonation of the phosphate ion (Persson et al., 1996). Furthermore, at pH > 7.5, it was shown that the predominant formation was nonprotonated bidentate binuclear species (Fe2PO4) on ferrihydrite, which may co-exist with different surface species (Arai & Sparks, 2001).
A “Minnesota Filter” trench field test was used to determine the field capacity of an iron filter (up to 10.7% iron, by weight) for phosphorus removal, and results showed up to 85-90% removal of incoming phosphorus over the course of several months (Erickson et al., 2012), without affecting the hydraulic conductivity of the filter. Their calculations reveal that this phosphorus removal filter could be sustained for 3 – 5 years before the media would need to be changed. This study also included a column (5% iron, by weight) studied which reported an average removal of phosphate of 88% for 200 meters of treated depth, capturing 1.29 mg P per gram of Fe, which is an effective method for removing phosphorus, as opposed to traditional sand only filters.

Another column test done by Allred in 2012, demonstrated the ability of porous iron composite (PIC), similar to ZVI, to remove large quantities of phosphorus. The column was flushed with 15 L of influent containing 0.34 ppm PO$_4$-P (total of 5.1 mg of PO$_4$-P), where the effluent concentration of phosphorus was well below the influent concentration, with a very fast reaction time. This is important because in a field application, phosphorus may only have a short contact time with ZVI. However, this study showed that PIC can actually leach phosphorus out before ultimately removing it, needing an initial flushing period to eliminate leaching phosphorus. This does not occur with ZVI granules.

A third column study done by Zhou et. al, in 2014, employed an iron composite, laterite, which is an iron-aluminum-oxide clay mineral, for use in phosphate removal. Concentrations up to 20.0 ppm PO$_4$-P were used in step input
tests, to determine the breakthrough time of the phosphorus solution. It was determined that the adsorption of phosphorous on the laterite was saturated, and that the saturation time was dependent on the influent concentration of phosphorus. In fact, at the highest phosphorus concentration, the adsorption rate was higher, as expected. The authors contribute this to a change in mass transport with change in phosphorus concentration, and faster saturation of the laterite media. Along with this column study, a parallel batch study was conducted to determine the effect of pH and additional ions on phosphorus removal. It was determined that as pH increased from 2.0 to 13.0, the amount of phosphorus adsorbed on to the laterite decreased by a factor of 5, and with the addition of any ions (Cl\(^-\), SO\(_4\)^{2-}, NO\(_3^-\)), the phosphate adsorbed also decreased, with the largest effect coming from NO\(_3^-\). This suggests that at lower pH, where the surface charge of laterite is positive, there will be a stronger affinity for phosphate ions, and with the addition of ions, their adsorption competition effects are coordinated with the ion radius size; NO\(_3^-\) has the smallest radius, indicating the highest competition for adsorption with phosphate ions. Furthermore, XRD analysis showed that after exposure to phosphorus, a measurable amount of Fe\(_3\)(PO\(_4\))\(_2\)(OH)\(_2\) was formed. Since this amount was low, the authors suggest that phosphate was removed by both precipitation and adsorption, as also suggested by Saxe et. al.

2.6 Field Application

Initially, ZVI was employed as use in permeable reactive barriers (PRBs), which are in-situ treatment areas that contain reactive materials capable of removing
contaminants of interest, such as trichloroethylene and hexavalent chromium oxides, for groundwater treatment (U.S. EPA, 1999). Most PRBs use ZVI because of the wide range of contaminant removal, and the ability of ZVI to treat multiple contaminants in a plume, like arsenic, chromate, and phosphate (Su & Puls, 2003).

In addition to groundwater treatment, ZVI has been employed for drinking water and wastewater treatments. Drinking water treatment applications include removal of microorganisms, disinfection by-products, like trihalomethanes and haloacetic acids, and disinfectants, like free chlorine (Chiu, 2013). Wastewater treatment applications include removal of nitroaromatic compounds, like TNT and nitrobenzene, heavy metals, and dyes (Fu et al., 2014).

The use of ZVI for stormwater treatment would be a potential application, and it would be amended into a bioretention cell, as pictured in Figure 2.2. During a rain event, the runoff would infiltrate the cell, and be discharged as treated water. ZVI amendment would be in the anaerobic zone of the ground, thus preventing fast corrosion by both water and oxygen, as well as in the saturated zone, keeping the ZVI consistently exposed to anoxic water. The anaerobic corrosion products, mostly Fe$^{2+}$, as seen in Equation 1, are able to react with incoming phosphorus, as illustrated by Equation 2.

This type of design is beneficial because it would use ZVI plus additional amendments (i.e. biochar) to treat multiple contaminants in one system. It is also useful because of the little amount of land needed to implement this system, as
opposed to current bioretention systems which would require more land to efficiently treat nutrients.

Figure 2.2. Schematic of a potential bioretention filter design for nutrient removal; areas highlighting ZVI addition and phosphorus removal are circled in orange.

2.7 Research Objectives

The long-term goal of this research was to evaluate the feasibility of ZVI for nutrient removal in stormwater treatment systems.

The specific objectives of this study were to:

1. To determine the removal efficiency of phosphate by ZVI.
2. To assess the suitability of the standard advection-dispersion-reaction model to describe phosphate removal by ZVI.
3. To determine the distribution of removed phosphorus in a ZVI treatment system.
Chapter 3

EXPERIMENTAL METHODS

3.1 Sand and ZVI

Sand (Accusand 40/50, particle sizes in desired range of 250 to 500 micron) was treated with citrate to remove excess iron oxides (or manganese oxides, if present). This was done by submerging about 800 mL of dry sand in approximately 250 mL of 10 mM sodium citrate (enough to submerge the sand) and warm temperature (≤ 40°C) for varying time lengths, usually left overnight. Sodium citrate (10 mM) was used as a complexing agent (Deng & Zhou, 2009), with higher temperatures were used to solubilize iron or manganese. 5-mL samples from the aqueous layer were taken and analyzed using the 1,10-phenanthroline method measured on UV-Vis at 510 nm for the amount of iron removed from the sand. These samples were analyzed in triplicate. The sand was then rinsed thoroughly with deionized water. This process was repeated for a total of four times to ensure that the iron oxides were removed from the sand. This was confirmed by a decreasing amount of iron removed during each wash.

Additionally, the sand was tested to ensure that little to no phosphorus would be removed by the sand alone. This was done by using 50 mL of the dried, treated sand in 100 mL of deionized water containing 1.69 ± 0.000123474 mg/L PO₄-P. The
concentration of phosphorus in solution was tested after an hour, using phosphate/molybdate complex (Parsons et al., 1984), and ascorbic acid reduction; measured on UV-Vis at 880 nm (Hach PhosVer 3 reagent). The samples were analyzed in triplicate.

The ZVI used is in the form of scrap iron granules from Peerless Metal Powders and Abrasive, in Detroit MI, and sieved to the desired particle size range of 250 to 500 micron. The ZVI granules were used as is, not pretreated before being packed in columns.

3.2 Solution Preparation

3.2.1 Deionized Water

The solutions used were composed of deionized water that was purged with nitrogen gas for 2 hours (per one liter), then degassed in a vacuum chamber for 20 minutes (up to -27 in. Hg). After degassing, the solution pH was adjusted to between 8.5 and 9.5 by using 6 N NaOH. By choosing a high pH in this study, this ensured that the species of phosphorus would be HPO$_4^{2-}$ for the entirety of the experiment; the high pH would also ensure that ZVI was corroded slowly.

This was used as the “blank” influent, to prepare other solutions, and to pack the columns.

For influent containing phosphorus, the blank solution was spiked with K$_2$HPO$_4$ (final concentration 1.6, 3.2, 8, or 16 mg/L PO$_4$-P).
The concentrations of PO₄-P were chosen as dilutions, starting with 16 ppm – 8 ppm was a two-fold dilution, 3.2 was a five-fold dilution, and 1.6 was a ten-fold dilution. Although even the lowest concentration is still significantly higher than the concentration seen in the field [field concentrations can be greater than 0.4 ppm total phosphorus (Ator, & Denver, 2015)], it was chosen for two reasons: (1) we did not want our PO₄-P concentration too close to the detection limit of our method (0.007 ppm PO₄-P), to ensure confidence in our data, and (2) in order to properly analyze our samples, which are 5 mL total, we need to have enough for pH measurement, PO₄ analysis, and tot Fe analysis. A concentration lower than 1.6 ppm PO₄-P would require all (or more) of the 5 mL sample, leaving nothing left for the additional analyses.

3.2.2 Synthetic Stormwater

The composition of the synthetic stormwater can be seen in Table 4.1. The recipe is modified from Hsieh & Davis (2005), with the addition of sodium bicarbonate (You et al., 2005), and pH adjustment to 9.
Table 3.1 Composition of synthetic stormwater.

<table>
<thead>
<tr>
<th>Component</th>
<th>Final Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO3</td>
<td>2 ppm (as N)</td>
</tr>
<tr>
<td>NH4Cl</td>
<td>2 ppm (as N)</td>
</tr>
<tr>
<td>CaCl2</td>
<td>120 ppm</td>
</tr>
<tr>
<td>NaHCO3</td>
<td>1.5 mM</td>
</tr>
<tr>
<td>6 N NaOH</td>
<td>As needed to adjust pH</td>
</tr>
</tbody>
</table>

First, both nitrogen-containing compounds and the calcium chloride were added to one liter of deionized water. This solution was then purged under nitrogen gas for 2 hours. Next, the solutions were degassed in a vacuum chamber for 20 minutes (up to -27 in. Hg). After degassing, the sodium bicarbonate was added, and solution pH was adjusted to between 8.5 and 9.5 by using 6 N NaOH. This was used as the “blank” influent, as media to prepare other solutions, and to pack the columns.

For influent containing phosphorus, the blank solution was spiked with K$_2$HPO$_4$ (final concentration 1.6, 5.6, or 16 mg/L PO$_4$-P).

3.3 Column Setup

The columns used were acrylic, with a total volume of 114.55 cm$^3$ that were manufactured in the College of Engineering’s Machine Shop. The dimensions are as follows: length, 10.1 cm; inside diameter, 3.8 cm. The columns are fitted with mesh
screens to ensure that no media particles will be eluted from the column, and nylon barbed tube fittings on either side. These fittings are connected to tygon tubing (L/S 16, with inside diameter 3.1 mm). Since the columns are up-flow, the influent enters the bottom of the column, from a 1-L influent reservoir, and out of the top of the column. The solution is pumped through the column using a peristaltic pump.

The columns were wet-packed using the blank influent solution (high pH, degassed DI water) to avoid air bubble formation in the column. The control column was packed with sand only, using the citrate-treated sand. The experimental column was packed in three layers: the first 2 cm was citrate-treated sand, the middle 6.1 cm was a mixture of 5% ZVI/95% Sand, by volume (7.3% ZVI/92.7% citrate-treated sand, by mass), and the final 2 cm was citrate-treated sand. The end sand layers act to even the flow before reaching the reactive center of the column. Column characteristics are summarized in Table 3.2.

The pump was calibrated, and set at 1 mL/min (measured flow rate) for the duration of the experiments.

The column experimental setups can be seen below in Figure 3.2.
Table 3.2  Column setup characteristics

<table>
<thead>
<tr>
<th>Column Type</th>
<th>Porosity</th>
<th>Pore Volume (mL)</th>
<th>Mass of Sand (g)</th>
<th>Mass of ZVI/Sand Mix (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deionized Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>41.0%</td>
<td>47.0037</td>
<td>179.5361</td>
<td>-</td>
</tr>
<tr>
<td>Experimental - 1.6, 16 ppm</td>
<td>39.0%</td>
<td>44.72717</td>
<td>76.5879</td>
<td>120.7784</td>
</tr>
<tr>
<td>Experimental - 3.2 ppm</td>
<td>38.8%</td>
<td>44.4055</td>
<td>75.7513</td>
<td>117.8628</td>
</tr>
<tr>
<td>Experimental - 8 ppm</td>
<td>39.2%</td>
<td>44.95557</td>
<td>73.2433</td>
<td>117.3183</td>
</tr>
<tr>
<td><strong>Synthetic Stormwater</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>39.5%</td>
<td>45.2495</td>
<td>187.3701</td>
<td>-</td>
</tr>
<tr>
<td>Experimental – 1.6, 5.6 ppm</td>
<td>39.4%</td>
<td>45.1594</td>
<td>74.4082</td>
<td>118.6031</td>
</tr>
<tr>
<td>Experimental – 16 ppm</td>
<td>39.8%</td>
<td>45.54101</td>
<td>80.9863</td>
<td>122.9074</td>
</tr>
</tbody>
</table>

Figure 3.2.  Experimental (ZVI) column set up; control (sand only) column setup is the same.
3.4 Phosphate Pulse Tests in Deionized Water

Once assembled, the columns were flushed with blank influent for three pore volumes. After the initial flush, the influent was switched to the solution containing phosphorus, and sample collection began. A pulse of one pore volume of influent solution (containing P) was conducted before switching the influent back to the blank solution for the remainder of sample collection.

For the control column, samples were collected for the first 40 minutes every 10 minutes (each sample, ~10 mL). From 40 to 110 minutes, samples were collected every 5 minutes (each sample, ~5 mL). For the remainder of the time, up to 170 minutes, samples were collected every 10 minutes. During the pulse test, pH was monitored periodically, and PO$_4$-P analysis was performed on every sample. For PO$_4$-P analysis, samples were diluted accordingly to get a measurable concentration, and analyzed using UV-Vis at 880 nm (Hach PhosVer 3 reagent). The phosphorus pulse test in deionized water was repeated four times in total, one for each of the concentrations of phosphorus (1.6, 3.2, 8, and 16 mg/L PO$_4$-P).

For the experimental column, the process for sampling was similar, with the addition of total iron analysis periodically during pulse test. Total iron was analyzed for using the 1,10-phenanthroline method measured on UV-Vis at 510 nm. The first pulse test was the lowest concentration of phosphorus (1.6 ppm PO$_4$-P). There was an additional pulse test performed using this ZVI column, to determine the approximate breakthrough time of phosphate. To do this, the influent solution contained 16 ppm PO$_4$-P (ten times higher than the previous concentration) was introduced to the column.
for one pore volume. After one pore volume, the solution was switched back to the blank influent. Samples were collected every 15 mins (~15 mL) for 8 pore volumes total.

Second and third ZVI columns were set up following the conclusion of the 16 mg/L PO₄-P pulse test, one for the 3.2 mg/L PO₄-P pulse and the other for the 8 mg/L PO₄-P pulse. Sampling for both columns followed the same procedure as the sand columns.

3.5 Phosphate Pulse Tests in Synthetic Stormwater

The columns were assembled in the same manner as the previous studies (Chapter 3). The methodology is also the same - after assembly, the columns were flushed with blank influent for three pore volumes, then the influent was switched to the solution containing phosphorus, and sample collection began. A pulse of one pore volume of influent solution (containing P) was conducted before switching the influent back to the blank solution for the remainder of sample collection. Sampling protocol (Chapter 3) was also the same, and continued for 3.78 pore volumes.

During the control column pulse test, pH was monitored periodically, and PO₄-P analysis was performed on every sample. For PO₄-P analysis, samples were diluted accordingly to get a measurable concentration, and analyzed using UV-Vis at 880 nm (Hach PhosVer 3 reagent). The control column phosphorus pulse test was done only using one concentration (1.6 ppm PO₄-P).
For the experimental column, the process for sampling was similar, with the addition of total iron analysis periodically during pulse test. Total iron was analyzed for using the 1,10-phenanthroline method measured on UV-Vis at 510 nm. The first pulse test was the lowest concentration of phosphorus (1.6 ppm PO$_4$-P), followed by the middle concentration (5.6 ppm PO$_4$-P). The highest concentration (16 ppm PO$_4$-P) pulse was performed on a new, freshly packed column. After one pore volume of phosphorus-containing compound had entered the column, the solution was switched back to the blank influent.

At the conclusion of sampling from the 16 ppm pulse test, the column was dissected and extracted, as discussed in the next section.

3.6 Phosphorus Extractions

A total of three extractions were selected in order to determine how the phosphate was trapped in the column. First, the experimental (ZVI) column used in synthetic stormwater experiments was dissected as shown in Figure 3.3. The column used was exposed to three pulses of phosphate influent, 1.6, 5.6 and 16 ppm PO$_4$-P. Five layers were chosen because the two sand layers were each 2 cm long, and in order to get approximately the same amount of column media in each layer, five-2 cm long layers were used. This would help to determine the spatial distribution in the column of the trapped phosphorus, as well as the extractable fraction in each layer. Following the layer dissection, each layer was split into 6 subsamples, two for each extraction.
Figure 3.3. Column dissection schematic illustrating different layers.

The three extractions used were as follows: a salt extraction, to determine exchangeable and soluble phosphorus; a complexation extraction, to determine chelated phosphorus; and an acid extraction, to determine inorganic (Fe-bound) phosphorus. The salt extraction was modified from Walna et. al (2005), to use MgCl₂ instead of KCl, and at a lower concentration, due to previous preliminary tests to determine the ideal salt solution to extract a measurable amount of phosphorus. The EDTA and acid extractions are both modified from Uchimiya et. al (2015), to appropriate concentrations and times. A shorter time was, as compared to other studies in the literature, because acid and EDTA will also extract iron, and excess iron interferes with phosphorus analysis by UV-Vis.
The salt extraction used 30 mL of 0.01 M MgCl\textsubscript{2} in DI water for 2 hours, with periodic shaking. The supernatant was decanted, and an aliquot was diluted for phosphorus analysis by UV-Vis. The complexation extraction used 30 mL of 1 mM EDTA in DI water for 1 hour, and the acid extraction used 30 mL of 0.01 M HCl in DI water for 1 hour, with periodic shaking, both following the same procedure as the salt extraction.

### 3.7 Data Analysis and Modeling

To model the observed effluent concentrations, the 1D Advection-Dispersion-Reaction Equation, with first order rate kinetics was used:

\[
D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C = \frac{\partial C}{\partial t} \quad \text{(6)}
\]

Where \( \lambda \) is the first order rate constant, with units \( \text{time}^{-1} \); \( v \) is the velocity of the phosphorus pulse, with units \( \text{length time}^{-1} \); \( D \) is the dispersion coefficient, with units \( \text{length}^2 \text{time}^{-1} \); \( dx \) refers to the distance along the length of the column; \( dC \) is the concentration of the traveling phosphorus pulse. The first term in the equation describes the mass transport by diffusion, the second term describes the mass transport by advection, and the third term describes the first-order reaction (Domenico and Schwartz, 1998).

The analytical solution for Equation 6 (Wexler – USGS, 1992) is given as follows, Equations 7-10:
\[ C(x, t) = \frac{C_o}{2} \left\{ \exp \left[ \frac{x}{2D} (v - U) \right] \cdot \text{erfc} \left[ \frac{x - Ut}{2\sqrt{Dt}} \right] + \exp \left[ \frac{x}{2D} (v + U) \right] \cdot \text{erfc} \left[ \frac{x + Ut}{2\sqrt{Dt}} \right] \right\} \]

\[ U = \sqrt{v^2 + 4\lambda D} \]

\[ v = \frac{\text{velocity of water in column}}{R_f} \]

Where \( C_o \) is the initial influent concentration of the influent phosphorus pulse, with units mass volume\(^{-1}\); \( x \) is the length of the column; \( \text{erfc} \) is the complementary error function; and \( R_f \) is the retardation factor, defined as linear actual velocity of water divided by linear transport velocity of phosphorus in solution, which is a dimensionless number (Bouwer, 1991).

For a conservative tracer (\( \lambda = 0 \)), as in the case of the sand only column, the solution condenses to:

\[ C(x, t) = \frac{C_o}{2} \left\{ \text{erfc} \left[ \frac{x - vt}{2\sqrt{Dt}} \right] + \exp \left[ \frac{xV}{D} \right] \cdot \text{erfc} \left[ \frac{x + vt}{2\sqrt{Dt}} \right] \right\} \]

Since the conditions in the experiments were pulse tests, Equation 10 applies during the phosphorus-containing influent pulse, when \( 0 > t \geq 45 \) minutes. After the pulse, the influent is switched back to anaerobic, DI water, and the “\( t \)” in the analytical solution becomes \( t - 45 \) minutes; the entire set of equations as follows:
\[ C(x, t) = \begin{cases} \frac{C_o}{2} A(x, t) & \text{for } 0 < t \leq 45 \\ \frac{C_o}{2} [A(x, t) - A(x, t - 45)] & \text{for } t > 45 \end{cases} \]  \hspace{1cm} \text{(11)}

\[ A_{ZVI}(x, t) = \left\{ \exp \left[ \frac{x}{2D} (v - U) \right] \cdot \text{erfc} \left[ \frac{x - Ut}{2\sqrt{D}t} \right] + \exp \left[ \frac{x}{2D} (v + U) \right] \right. \\
\left. \cdot \text{erfc} \left[ \frac{x + Ut}{2\sqrt{D}t} \right] \right\}, \hspace{1cm} \text{........................................ (12)}

\[ A_{ZVI}(x, t - 45) \]
\[ = \left\{ \exp \left[ \frac{x}{2D} (v - U) \right] \cdot \text{erfc} \left[ \frac{x - U(t - 45)}{2\sqrt{D}(t - 45)} \right] + \exp \left[ \frac{x}{2D} (v + U) \right] \right. \\
\left. \cdot \text{erfc} \left[ \frac{x + U(t - 45)}{2\sqrt{D}(t - 45)} \right] \right\}, \hspace{1cm} \text{................................. (13)}

\[ A_{sand}(x, t) = \text{erfc} \left[ \frac{x - vt}{2\sqrt{D}t} \right] + \exp \left[ \frac{xV}{D} \right] \cdot \text{erfc} \left[ \frac{x + vt}{2\sqrt{D}t} \right], \hspace{1cm} \text{.............. (14)}

\[ A_{sand}(x, t - 45) \]
\[ = \text{erfc} \left[ \frac{x - v(t - 45)}{2\sqrt{D}(t - 45)} \right] + \exp \left[ \frac{xV}{D} \right] \cdot \text{erfc} \left[ \frac{x + v(t - 45)}{2\sqrt{D}(t - 45)} \right] \hspace{1cm} \text{..... (15)}

In order to confirm the observed effluent concentrations from the sand column, two parameters (R_f and D) were fitted using solver to minimize the sum of the residuals squared (RMSE). For the ZVI column, the same two parameters were fitted first, with λ = 0, and C_o as a percent of influent concentration, determined by dividing the highest effluent concentration by the influent concentration. This percentage was modified until the smallest RMSE was obtained. Once the optimal R_f and D
parameters were obtained, the $C_o$ fraction was set to 1 (100% of the influent concentration), and solver was used to fit $\lambda$. 
4.1 Control Column (Sand Only) – Deionized Water

Breakthrough curves for the four concentrations of phosphate (1.6, 3.3, 8, and 16 ppm PO₄-P) for the sand-only columns are presented in Figure 4.1. As seen in the effluent concentration of the column, the pulse of phosphate-containing solution comes out later than expected; a pulse of contaminant for one pore volume is expected to elute from a column starting at one pore volume of collected effluent, and end at two pore volumes. Our pulse is shifted to the right, so this indicates some retardation by the sand on the phosphate. Additionally, the shape of the influent pulse indicates there is some dispersion in the column. Using the model as described earlier, the dispersion coefficient and retardation factor were calculated to confirm the observational data. These fitted parameters are summarized in Table 4.1a. Although the phosphate pulse was retarded in the column, due to some surface interaction with the sand, there this was a reversible retention, leading to a percent recovery of about 100%. The percent removals are shown in Table 4.1a.

In order to calculate the percent removal, the ADR equation was integrated over the entire time of the pulse test, and this area was compared to the influent phosphorus area. This ratio yielded a percent mass breakthrough and percent removal.
Upon comparing the dispersion coefficients for the four different influent concentrations, it can be seen that they are quite similar. This is because the four pulses were performed using the same column. The same observation can be made for the retardation factors. The retardation of the phosphorus could be due to an interaction with the negative surface charge of the sand, but this doesn’t affect the discharge of the entire pulse from the column.

Furthermore, our assumption that influent phosphate will not be removed by sand was confirmed by having percent recoveries of over 99.9% for each concentration. This proves to be a good control column, since nearly all of the influent phosphorus is recovered, and there is no reaction between sand and phosphorus. More importantly, the data suggest clean sand would be ineffective at removing phosphate in clean water.

**4.2 Experimental Column (ZVI + Sand) – Deionized Water**

Breakthrough curves for the four concentrations of phosphate (1.6, 3.3, 8, and 16 ppm PO\textsubscript{4}-P) for the ZVI + sand columns are presented in Figure 4.2. Similar observations as the sand column results can be made about these data sets: the pulse of phosphorus-containing solution comes out later than expected, suggesting that the transport of phosphate through the ZVI-sand mixed media was retarded and dispersed to similar extents as in the sand only column (Table 4.1b). The three fitted parameters for the ZVI experiments are summarized in Table 4.1b, along with the percent recoveries. Note that in Figure 4a (1.6 ppm), there is no breakthrough curve, and thus,
a model could not be constructed for this data, but the few breakthrough points gathered were manually integrated to provide an estimate of percent removal. Also, it can be seen that the pulse height is lower than the influent height for all four concentrations, confirming that a reaction with the ZVI was occurring, and the need for a reaction term in the model equation.

Additionally, the total iron concentration was measured periodically during each pulse test. The highest concentration observed was 0.56 ppm of total iron (Appendix B). This low concentration does not interfere with phosphorus analysis, and does not contribute any color (rust) to the effluent solution.

Comparing the dispersion coefficients for the four different influent concentrations, it can be seen that they are again, similar, like the sand columns. However, when comparing the retardation factors and reaction coefficients for each concentration, the trend is with increasing concentration, the retardation and reaction coefficients both decrease. The retardation changed due to the increase in concentration, which decreases the distribution coefficient, and, in turn, decreases the retardation factor (Hutchinson et. al, 2003).

With increasing influent concentration, the percent removal decreases, until the highest concentration of 16 ppm PO₄-P, where the percent removal is higher than it was for 8 ppm PO₄-P. This could be due to the 16 ppm pulse being performed on an aged column, whereas the 3.2 and 8 ppm pulses were each performed on freshly packed columns. We can say that the phosphate removal is most likely associated with the corrosion products. Since the corrosion of ZVI is continuous over time, and the 16
ppm PO$_4$-P pulse test was performed on an aged column and resulted in good removal, this suggest the corrosion products are responsible for the retention of phosphorus.

It is also important to again note the importance of the concentrations used. The most significant concentration for field application is 1.6 ppm PO$_4$-P, since the field concentration is typically around 0.4 ppm PO$_4$-P. Since almost all of the phosphorus was retained in the column at 1.6 ppm, at field concentrations, we would also expect all of the incoming phosphorus to be retained.
Figure 4.1. All data from control (sand only) column for 4 different concentrations: (a) 1.6 ppm PO₄-P, (b) 3.3 ppm PO₄-P, (c) 8 ppm PO₄-P, and (d) 16 ppm PO₄-P.
Figure 4.2. All data from experimental (5% ZVI by volume/95% sand) column for 4 different concentrations: (a) 1.6 ppm PO$_4$-P, (b) 3.3 ppm PO$_4$-P, (c) 8 ppm PO$_4$-P, and (d) 16 ppm PO$_4$-P.
Table 4.1  Deionized water results. (a) Summary of fitted model parameters for control column, at different influent concentrations of PO$_4$-P; (b) Summary of fitted model parameters for experimental (ZVI) column, at different influent concentrations of PO$_4$-P. Note: No parameters are included for the lowest PO$_4$-P concentration in the ZVI column because no breakthrough curve was observed. *Manual integration performed to estimate percent removal.

**a. Control Column Model Parameters**

<table>
<thead>
<tr>
<th>Influent Concentration mg/L</th>
<th>Dispersion Coefficient $cm^2/\text{min}$</th>
<th>Retardation Factor</th>
<th>Percent Removal %</th>
<th>Mass of P Removed mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>2.15E-02±0.002</td>
<td>1.46±0.009</td>
<td>0.004</td>
<td>3.23E-6</td>
</tr>
<tr>
<td>3.3</td>
<td>2.15E-02±0.0029</td>
<td>1.46±0.013</td>
<td>0.01</td>
<td>1.97E-5</td>
</tr>
<tr>
<td>8</td>
<td>2.15E-02±0.0021</td>
<td>1.416±0.0086</td>
<td>0.03</td>
<td>1.02E-4</td>
</tr>
<tr>
<td>16</td>
<td>1.76E-02±0.0017</td>
<td>1.352±0.0066</td>
<td>0.05</td>
<td>3.85E-4</td>
</tr>
</tbody>
</table>

**b. Experimental Column Model Parameters**

<table>
<thead>
<tr>
<th>Influent Concentration mg/L</th>
<th>Dispersion Coefficient $cm^2/\text{min}$</th>
<th>Retardation Factor</th>
<th>Rate Constant $1/\text{min}$</th>
<th>Percent Removal %</th>
<th>Mass of P Removed mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>98.42*</td>
<td>0.0714</td>
</tr>
<tr>
<td>3.2</td>
<td>1.32E-02±0.0035</td>
<td>2.01±0.044</td>
<td>1.33E-02±0.0011</td>
<td>69.92</td>
<td>0.101</td>
</tr>
<tr>
<td>8</td>
<td>1.15E-02±0.0014</td>
<td>1.70±0.0095</td>
<td>4.15E-03±0.00035</td>
<td>27.46</td>
<td>0.0991</td>
</tr>
<tr>
<td>16</td>
<td>1.77E-02±0.0049</td>
<td>1.48±0.022</td>
<td>6.77E-03±0.00067</td>
<td>36.34</td>
<td>0.265</td>
</tr>
</tbody>
</table>

4.3  Control Column (Sand Only) – Synthetic Stormwater

Graphical results of the control column (1.6 ppm PO$_4$-P) can be seen in Figure 4.3a, and tabulated model parameters are summarized in Table 4.2. The pulse is shifted farther to the right (more retarded) than the pulse in deionized water. This leads to the assumption that the multi-valent ions, such as Ca$^{2+}$, present in the solution will increase the retardation factor of the pulse.
The ions may act as a bridge between the surface of sand and phosphate molecules. With the DI water solution, the retardation factor was approximately 1.5, whereas in synthetic stormwater, it had increased to 2.0. Due to this increase, at the conclusion of sampling, it is very possible that not all of the phosphorus pulse eluted from the column, shown in Figure 4.3a, where the right-hand side of the pulse has not reached a zero concentration yet. To compensate, the model for this pulse was extended to time = 200 minutes (4.44 PV’s), seen in the figure were the dashed orange line extends beyond the observed data points. This extension was also used in the integration and percent removal calculation.

Furthermore, the dispersion of the pulse in the column was also affected by the introduction of synthetic stormwater solution. The dispersion coefficient in DI water was 2.15E-2, and in synthetic stormwater was 4.86E-2, an increase of a factor of 2. This linear relationship between dispersion and retardation was also demonstrated by Hutchison et al. (2003), where when dispersion had increased, so had retardation factor. Since dispersion is an intrinsic property of the packing media (sand, in this case), the sand must be affected by the solution composition, varying the molecular diffusion of phosphate, which, in turn varies the dispersion coefficient and retardation factors calculated from the model.

Due to the high recovery (>99%) of the phosphorus pulse, it can be assumed that there is no reaction inside the column, and no rate constant fitted in the model, just as was assumed in the DI water models.

4.4 Experimental Column (ZVI + Sand) – Synthetic Stormwater

Graphical results of the experimental column pulses (1.6, 5.6, and 16 ppm PO₄-P) can be seen in Figure 4.3b,c,d, and tabulated model parameters are summarized in Table 4.2. As in the
columns using DI water, there is no breakthrough curve seen at the lowest concentration. However, during the middle concentration pulse, there was also no breakthrough curve, even though during the columns using DI water, both 3.2 and 8 ppm PO$_4$-P had breakthrough curves. This indicates that the composition of the influent affects the corrosion of ZVI in order to promote the removal of incoming phosphorus. This is enforced by the measurements of effluent iron from the column: the effluent total iron concentration was as high as 1.2 ppm, about double the concentration of total iron seen in DI water experiments (Appendix B). Since more iron is being corroded by the presence of bicarbonate inside the column, it is allowing for more phosphorus to be bound, up until a certain point, seen at the highest concentration of 16 ppm PO$_4$-P. Although these two pulses did not have breakthrough curve, there were still a handful of breakthrough data points, which were used to estimate percent removal via manual integration.

The highest concentration had a breakthrough curve, which is similar to the one using DI water, with the removal percentage in synthetic stormwater being about 10%. The fitted parameters are also similar (Table 4.3) to those in deionized water at this concentration, with the exception of the rate constant, which is much lower. This confirms the low removal of phosphorus under these conditions, which could have to do with using “fresh” ZVI for this column, as opposed to ZVI that has been aging inside a column for several days. Relative to the DI water results, the percent removal was lower and the rate constant was slower in synthetic stormwater because of the interference of the other ions in solution, since the other factors were the same.

Finally, it is important to note the potential longevity of this treatment system. This small column was used for three pulses of increasing phosphorus concentration, plus continuous flushing of blank synthetic stormwater, over a span of a week, and was still capable of removing
large amounts of phosphorus. In the field, since the phosphorus concentration can be quite low (~0.4 ppm PO$_4$-P), the longevity of ZVI for phosphorous removal is very promising.

4.5 Extractions

Figure 4.4 summarizes the results of the extractions done on the sections of the column. It should be noted that since phosphorus actually broke through during the column experiments, it would suggest that phosphorus would be removed throughout the column, not just near the inlet. It was calculated that after the 16 ppm PO$_4$-P pulse, 0.080 mg of P remained in the column. The total extracted from the layers is 0.059 mg of P (~74% extracted), suggesting that there is still more phosphorus retained very strongly in the column, which was not extracted during the one hour acid extraction time. It should be noted that each extraction was cumulative, not in sequence, so the complexed fraction includes both complexed phosphorus and loosely-bound/aqueous phosphorus, and acid-extractable fraction includes all three extractions.

From the breakdown of the different extractants used, it can be seen that most of the phosphorus extracted was strongly held (acid-extractable). This phosphorus is likely associated with iron, either the surface of ZVI, or ZVI corrosion products – if most of the incoming phosphorus is strongly held by the ZVI corrosion products, it will likely not be leached out in the next storm event. There were similar amounts of phosphorus extracted both with salt and complexing agent, but slightly more was extracted with the complexing agent.

Comparing the different layers dissected from the column, the aqueous and complexed phosphorus was evenly distributed between all the ZVI layers and the end sand layer. However, most of the acid extractable sand was found in the end sand layer, most likely associated with the ZVI pieces trapped in the end of the column, or associated with ZVI corrosion products (i.e.
coating of sand surface by iron oxy-hydroxides, which then served as sorption/surface complexation sites) that have migrated with the flow towards the end of the column, but had not eluted from the column. The next highest fraction of acid extractable phosphorus occurred in the beginning of the ZVI portion of the column, where any residual oxygen would be depleted by the ZVI pieces, and therefore would be corroded faster. Upon moving upwards in the column layers, it was shown that less acid-extractable phosphorus was found. The extracted phosphorus found in the inlet sand layer was likely due to the interface between the sand and the first ZVI layer, where some ZVI particles were responsible for removing phosphate.
Figure 4.3. All data from both control and experimental columns using synthetic stormwater.
Table 4.2  Synthetic stormwater results. Summary of fitted model parameters [using equations (14) and (15)] for control (sand only) column, at influent concentration of 1.6 ppm PO$_4$-P. Also including fitted model parameters [using equations (12) and (13)] for experimental (7.33% ZVI/92.7% sand, by volume) column, at different influent concentrations of PO$_4$-P. Note: There are no parameters included for the two lowest concentrations of phosphorus in the experimental column because no breakthrough curve was observed. *Manual integration performed to estimate percent removals.

<table>
<thead>
<tr>
<th>Influent Concentration mg/L</th>
<th>Dispersion Coefficient cm$^2$/min</th>
<th>Retardation Factor</th>
<th>Rate Constant 1/min</th>
<th>Percent Removal %</th>
<th>Mass of P Removed mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6 (Control)</td>
<td>4.86E-02±0.0032</td>
<td>2.01±0.02</td>
<td>0</td>
<td>0.9</td>
<td>6.99E-4</td>
</tr>
<tr>
<td>1.6 (ZVI)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>98.89*</td>
<td>0.0715</td>
</tr>
<tr>
<td>5.6 (ZVI)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>77.05*</td>
<td>0.253</td>
</tr>
<tr>
<td>16 (ZVI)</td>
<td>1.79E-02±0.0028</td>
<td>1.69±0.01</td>
<td>1.45E-03±0.00054</td>
<td>10.57</td>
<td>0.56</td>
</tr>
</tbody>
</table>
Table 4.3 Side-by-side comparison of all ZVI column fitted model parameters. (S.S. = synthetic stormwater)

<table>
<thead>
<tr>
<th>ZVI Columns</th>
<th>Influent Concentration</th>
<th>Dispersion Coefficient</th>
<th>Retardation Factor</th>
<th>Rate Constant</th>
<th>Percent Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>cm^2/min</td>
<td>1/min</td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>1.6 (S.S.)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>98.89</td>
<td></td>
</tr>
<tr>
<td>1.6 (DI water)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>98.42</td>
<td></td>
</tr>
<tr>
<td>3.2 (DI water)</td>
<td>1.24E-02</td>
<td>2.013</td>
<td>1.34E-02</td>
<td>69.93</td>
<td></td>
</tr>
<tr>
<td>5.6 (DI water)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>77.05</td>
<td></td>
</tr>
<tr>
<td>8 (DI water)</td>
<td>1.15E-02</td>
<td>1.700</td>
<td>4.15E-03</td>
<td>27.46</td>
<td></td>
</tr>
<tr>
<td>16 (DI water)</td>
<td>1.77E-02</td>
<td>1.475</td>
<td>6.77E-03</td>
<td>36.34</td>
<td></td>
</tr>
<tr>
<td>16 (S.S.)</td>
<td>1.79E-02</td>
<td>1.693</td>
<td>1.45E-03</td>
<td>10.57</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.4. Summary of phosphorus extractions.
Chapter 5
CONCLUSIONS AND FUTURE RESEARCH

As initially hypothesized, ZVI has the capability of removing and retaining phosphorus in a stormwater runoff treatment cell. With removal efficiencies as high as 98% at low phosphorus concentrations in synthetic stormwater, this treatment can be proposed in field sites to treat stormwater runoff. Even more surprising, ZVI has the capability of retaining over 30% of a pulse of high concentration phosphorus of 16 ppm PO₄-P, a concentration never seen in the field.

Additionally, the phosphorus retained in the column is mostly strongly-bound to iron, and only extractable by acid. Since such low pH conditions do not exist in stormwater, the phosphorus will not be leached out over time, or over different rain events. This Fe-bound phosphate could potentially form vivianite (Fe₃(PO₄)₂ · 8H₂O) aggregates over time, as seen in literature (Rothe et al., 2014), which are very stable under anoxic conditions. This is consistent with our extraction data, as most of the extracted phosphorus was iron-bound.

This study showed that the ADR equation could successfully model predicted data, and can provide values for removal efficiencies, as well as important modeling parameters, including rate constant, dispersion coefficient, and retardation factor. These could be of use when trying to understand the transport and behavior of phosphate through a bioretention cell that is amended with ZVI.
An issue that arises when using ZVI amendment is the potential for soluble iron to leach out into the water. The values recorded in this study were slightly higher than 1 ppm of total Fe, as compared to the EPA’s secondary drinking water standard for Fe being 0.3 ppm (U.S. EPA, 2016).

For future research, it would be suggested to study the effect of both pH and flow rate on the phosphorus removal by ZVI. Both of these factors may play a large role in how the phosphorus interacts with the surface of ZVI and ZVI corrosion products, and how well the removal can be. The flow rate affects the contact time, or retention time, the phosphorus has with ZVI in the column, which can influence the reaction. It would be expected that a slower flow rate would increase removal, while a faster flow rate could reduce the removal. A different pH may change the association of the phosphate ion with the surface of ZVI or its corrosion products, since the influent phosphate form is pH dependent. Furthermore, it would be advisable to study the long term effects of phosphate removal by ZVI, including X-ray diffraction to determine any surface formation, and extractions to determine how much phosphorus is held over longer time periods. Finally, the implementation of ZVI into a field site should be studied, to monitor phosphorus levels over different periods of rain events to judge the performance of ZVI.
REFERENCES


Figure A1. Residual plots for DI water pulse with 1.6 ppm PO₄-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Figure A2. Residual plots for DI water pulse with 3.2 ppm PO$_4$-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Figure A3. Residual plots for DI water pulse with 8 ppm PO$_4$-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Figure A4. Residual plots for DI water pulse with 16 ppm PO$_4$-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Figure A5. Residual plots for DI water pulse with 3.2 ppm PO₄-P in the experimental column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Figure A6. Residual plots for DI water pulse with 8 ppm PO$_4$-P in the experimental column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Figure A7. Residual plots for DI water pulse with 16 ppm PO₄-P in the experimental column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Figure A8. Residual plots for synthetic stormwater pulse with 1.6 ppm PO₄-P in the control column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Figure A9. Residual plots for synthetic stormwater pulse with 16 ppm PO$_4$-P in the experimental column, a. residuals vs. measured phosphorus concentration and b. residuals vs. pore volume.
Appendix B

MEASURED TOTAL IRON CONCENTRATIONS IN EFFLUENT

Figure B1. Total iron concentrations in effluent over time in ZVI + sand columns; a. deionized water and; b. in synthetic stormwater. In deionized water, total iron measurements were limited due to some samples having undetectable iron levels (detection limit = 0.03 mg/L total Fe).