

Development of the Urban Wetland Filter for Managing Phosphorus in Stormwater

Shawn E. Rosenquist

Dissertation submitted to the faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Biological Systems Engineering

David H. Vaughan, Co-chair

W. Cully Hession, Co-chair

Theresa M. Wynn

Matthew J. Eick

March 19, 2010

Blacksburg, Virginia

Keywords: Phosphorus, Constructed Wetlands, Sorption, Iron Reduction, Stormwater

Development of the Urban Wetland Filter for Managing Phosphorus in Stormwater

Shawn E. Rosenquist

Abstract

Degradation of surface water quality by excess nutrients in stormwater is a substantial environmental and economic problem in the U.S. Phosphorus (P) is often the limiting nutrient for harmful algal blooms and the best target to prevent degradation. Natural treatment strategies such as constructed wetlands (CW) demonstrate effective and economical P management but obstacles exist to implementation. Biological P removal has large land requirements that limit the use of best management practices (BMP) in high land-value areas. Various BMP also utilize sorption processes (SP) for P removal but variations in performance and finite sorption capacity limit SP as a viable long-term removal strategy. However, by understanding variability and making sorption capacity renewable, SP could provide, with shorter retention times, a space-efficient, long-term removal strategy. This multi-study research program developed the urban wetland filter (UWF), a concept intended to overcome the unique limitations of high land-value areas to natural treatment strategies and provide a low-cost, easily implemented BMP to meet P management goals while harvesting sequestered P for use as a fertilizer. Experimental factors included substrate and influent properties pertinent to understanding performance variation and optimizing microbial iron (Fe) reduction for rejuvenation of sorption capacity. Regarding performance, modeling identified major sources of variability including, by order of importance, magnitude of a solution/substrate concentration gradient, length of the "antecedent dry period" between loadings, and pH. Field-scale results confirmed this multifactor dependence of P-removal while also supporting the inclusion of cast-iron filings in substrate to improve P removal. Regarding rejuvenation, results indicated that microbial Fe reduction is capable of releasing previously sequestered P from substrates. A sufficient carbon source was necessary, but microbial inoculation was not necessary to facilitate Fe reduction, which released most of the previously sequestered P, albeit more slowly than P sequestration. Field-scale results indicated that Fe reduction might occur faster under field conditions, possibly due to humic acids, and that inclusion of cast-iron filings enabled additional P removal after rejuvenation by providing a conservative source of Fe for the creation of new sorption sites; however, cast-iron filings may also limit the release of P during rejuvenation.

This work, in its entirety, is committed to my Lord and Savior Jesus Christ, who, for His purpose and pleasure, has chosen to reveal by the methods of science some of the manifold mysteries of His creation. Let us then, in His service and with this knowledge act as faithful stewards of what has been entrusted to us (Psalm 24, Isaiah 40, Psalm 115, 1 Corinthians 4:1-2).

Acknowledgements

There are many who have taken part in this work in both obvious and unseen ways. Without their contribution this work would not have been possible and I am pleased to acknowledge them here.

I would first like to acknowledge my amazing wife, Meghan, who has selflessly sacrificed of her time and priorities to enable me to complete my course of study and who has been a constant and irreplaceable encourager, companion, and supporter. I cannot thank her enough. I would also like to thank my parents, Joel and Deborah Rosenquist, along with the rest of my family for their love, support, and sacrifice over the years for me and for my education.

I would like to acknowledge my primary advisor, Dr. David Vaughan. He has consistently provided wise counsel, mentoring, and a great example to follow. I also wish to recognize him here for his rich, extensive, and balanced career including dedication and service to his country, his field, his students, and his family and friends. I am very thankful to be among those he has mentored.

I would also like to acknowledge the rest of my advisory committee including: Dr. Cully Hession, co-advisor, for his sizable contributions to this work including technical advice and significant assistance in developing my written communication skills; Dr. Matthew Eick for his critical contributions of technical advise and unique contribution to the committee of a soil chemistry perspective; and last but not least Dr. Tess Wynn for her support through technical advise and the provision of a solid theoretical foundation through her exemplary teaching.

Although they are not directly a part of this work, I would like to acknowledge three secondary school teachers who were inspirational to me in my formative years including: Mrs. Dotty Hoots, who inspired a "math and science kid" to realize the value of literature and good writing to a scientific career; Mr. John Losey, who through significant personal hardship gave selflessly of himself to provide opportunities in advanced science to young men and women who did not at the time fully appreciate the sacrifices he made; and Mr. Richard Welch who inspired me to always give my best, to not waste the abilities I had been given, and to "press onward" when I felt like complaining, feeling sorry for myself, or giving up.

I would like to acknowledge the contribution all of the NSF REU students I was able to work with, particularly those who had direct contributions to this work including Sarah Braman, Cody Newbill, Steven Sell, Cherona Levy, Jonathan Pennington, and Alyse Egner.

I would also like to acknowledge Dan Gallagher, associate professor, as well as Laura Teany, Amy Egan, and Athena Tilley, laboratory technicians, who all gave of their time, effort, and expertise well beyond what was required of them.

. Lastly, I would like to acknowledge the entire BSE faculty, staff, and particularly my fellow graduate students who have all enriched my graduate school experience and contributed in many "statistically" significant ways to the completion of this work.

Table of Contents

Dedication.....	iii
Acknowledgements.....	iv
Table of Contents.....	vi
List of Figures.....	vii
List of Tables.....	xi
List of Terms and Abbreviations.....	xii
1. Introduction.....	1
(i) Background.....	1
(ii) Purpose Statement and Research Objectives.....	6
(iii) Review of Literature.....	8
i. Anthropogenic eutrophication.....	8
ii. Nutrients as non-point source pollution.....	12
iii. Management strategies for NPS pollution in urban areas.....	16
iv. Constructed wetlands for treatment of urban stormwater.....	18
v. Rejuvenation of wetland performance.....	27
2. Variability in adsorptive phosphorus removal by structural stormwater best management practices.....	40
3. Facilitated iron reduction as a means of rejuvenating phosphorus removal performance of filtration substrates.....	61
4. Urban wetland filter: field results in the development of a renewable practice for managing phosphorus in stormwater runoff from high land-value areas.....	82
5. Overall Conclusions and Recommendations.....	110
Appendices	
A. Supplementary Research Studies.....	114
(i) Field-scale study of phosphorus removal by sorption: comparison of substrates and residence times.....	115
(ii) Field-scale study of phosphorus removal by sorption: substrate and residence time study follow-up.....	132
(iii) Effect of humic acid on microbial reduction of iron and release of phosphorus from wetland substrates.....	142
B. Comprehensive Materials and Methods.....	163
C. Primary Data Sets.....	178
D. Comprehensive References.....	192
E. Project Photo Gallery.....	205
F. Copyright Information.....	241

List of Figures

Figure 1.1 - Representative design layout of a UWF system on a typically sized urban retention pond.....	4
Figure 1.2 - The UWF concept for treating urban stormwater can create reductions in land area requirements in several ways.....	5
Figure 1.3 - A vertical, subsurface-flow constructed wetland consistent with the size of an individual UWF cell for an urban application.....	19
Figure 2.1 - The six replicate UWF cells were supplied water from a constant head tank located in the center of the six cells. The CHT had water supplied from a 265-L plastic holding tank that served as a “eutrophic retention pond.”.....	44
Figure 2.2 - An individual UWF cell consisted of horizontal layers from bottom to top including: gravel, sand, and standing water.....	44
Figure 2.3 - During the study, cells increased from below 5% to around 25% of isotherm-derived sorption capacity.....	47
Figure 2.4 - Substrate samples were taken with 5-cm diameter soil coring equipment from top to bottom of the sand layer at three different locations in the filter.....	48
Figure 2.5 - A general increase in cell pH for all wetland cells was observed.....	51
Figure 2.6 - Flow rates observed during runs varied both across and within cells, however, such changes were generally within a factor of two.....	52
Figure 2.7 - Iron-oxide sand filtration demonstrated a significant P removal capability compared to control runs without iron-oxide sand filtration. (plot depicts: Q_1 -1.5 Interquartile Range; Q_1 ; Median; Q_3 ; Q_3 +1.5 Interquartile Range).....	53
Figure 2.8 - Equilibrium pH taken after the 20-h treatment run displays a weak negative correlation to P removal for that run.....	54
Figure 2.9 - Initial concentration gradient was a strong predictor of P removal during the runs.....	55
Figure 2.10 - While a weak vertical spatial gradient in adsorbed P was observed ($R^2 = 0.30$), spatial variation in adsorbed P was better explained by the spatial distribution of Fe ($R^2 = 0.74$).....	56
Figure 3.1 - FTWC cross section showing layers of gravel, sand, and standing water.....	67
Figure 3.2 - Trends in a) pH, b) dissolved oxygen, c) TDP, and d) TDI during the study reveal significant differences between carbon-treated and control cells.....	71
Figure 3.3 - The correlation plot for TDP (mg/L) versus TDI (mg/L) for data after start of Fe reduction contains two distinct slope-regions.....	73

Figure 3.4 - Total desorbed P for the various BRWC treatments (C-Control; S-Sugar; P-Pond; SP=Sugar/Pond) and retention times in days (plot depicts $Q_1-1.5*IQR$; Q_1 ; Median; Q_3 ; $Q_3+1.5*IQR$).....	75
Figure 3.5 - TDI for the various BRWC treatments (C-Control; S-Sugar; P-Pond; SP=Sugar/Pond) and retention times in days (plot depicts $Q_1-1.5*IQR$; Q_1 ; Median; Q_3 ; $Q_3+1.5*IQR$).....	76
Figure 3.6 - Total initially adsorbed P for the various BRWC treatments (C-Control; S-Sugar; P-Pond; SP=Sugar/Pond) and retention times in days (plot depicts $Q_1-1.5*IQR$; Q_1 ; Median; Q_3 ; $Q_3+1.5*IQR$).....	77
Figure 4.1 - Experimental setup of field-scale wetland cells at a Virginia Tech stormwater retention pond...	86
Figure 4.2 - Construction of the small-scale, field-scale wetland cells.....	87
Figure 4.3 - Each of the six, wetland cells ran through three cycles including a pre-rejuvenation filter cycle, the rejuvenation cycle, and a post-rejuvenation filter cycle.....	88
Figure 4.4 - Total phosphorus (TP) trends observed during filtration runs for (A) pre-rejuvenation runs and (B) post-rejuvenation runs.....	92
Figure 4.5 - P-mass removal rate trends observed during filtration runs for (A) pre-rejuvenation runs and (B) post-rejuvenation runs.....	94
Figure 4.6 - pH trends observed during filtration runs for (A) pre-rejuvenation runs and (B) post-rejuvenation runs.....	95
Figure 4.7 - P-Mass Removal Rates (mg/h) between treatments and cells for (A) pre-rejuvenation sand-only cells, (B) pre-rejuvenation iron/sand cells, (C) post-rejuvenation sand-only cells, and (D) post-rejuvenation iron/sand cells.....	96
Figure 4.8 - Correlation of TI to TP in solution during rejuvenation ($R^2=0.90$).....	97
Figure 4.9 - Comparison of rates of (A) Fe reduction and (B) P release between bench-scale and field-scale cells.....	100
Figure 4.10 - Correlation of P-mass removal rate with influent concentration for (A) pre-rejuvenation sand-only cells, (B) pre-rejuvenation iron/sand cells, (C) post-rejuvenation sand-only cells, and (D) post-rejuvenation iron/sand cells.....	102
Figure 4.11 - Correlation of P-mass removal rate with the maximum previous effluent concentration for (A) pre-rejuvenation sand-only cells, (B) pre-rejuvenation iron/sand cells, (C) post-rejuvenation sand-only cells, and (D) post-rejuvenation iron/sand cells.....	103

Figure 4.12 - Correlation of P-mass removal rate with effluent pH for (A) pre-rejuvenation sand-only cells and (B) pre-rejuvenation iron/sand cells.....	104
Figure 4.13 - Correlation of P-mass removal rate with time for (A) pre-rejuvenation sand-only cells, (B) pre-rejuvenation iron/sand cells, (C) post-rejuvenation sand-only cells, and (D) post-rejuvenation iron/sand cells.....	104
Figure A.1 - The tank is located in the top left while the pond is contained just behind the earthen embankment seen across the center of the photograph.....	120
Figure A.2 - Arrangement of field-scale wetland cells.....	121
Figure A.3 – Field-scale experimental wetland cell.....	121
Figure A.4 - Chemical properties for each substrate before filtration; ACCA is the calcium-based substrate, ACFE is the iron-based substrate, and ACYS is the control substrate.....	122
Figure A.5 - Particle size distribution for each substrate.....	122
Figure A.6 - P-load (TP) removal percent data trends for each substrates/HRT combination.....	125
Figure A.7 - Cumulative P-load (TP) removal percentages for the entire study period.....	126
Figure A.8 - P-load (TP) removal percent data trends for each substrates/HRT combination.....	127
Figure A.9 - Cumulative P-load (TP) removal percentages for the entire study period.....	127
Figure A.10 - Cell pH at the beginning (a, left) and towards the end (b, right) of the study period.....	128
Figure A.11 - DRP observed in quality control filtration blanks.....	130
Figure A.12 - Diurnal variation in key properties.....	135
Figure A.13 - Long-term variation in P removal performance for field-scale wetland cells.....	136
Figure A.14 - Measured variables from the long-term data set.....	137
Figure A.15 - Variability in P removal performance across flow rates.....	138
Figure A.16 - Trends in four substrate constituents.....	139
Figure A.17 - Layout of experimental cells including substrate and supernatant.....	145
Figure A.18 - Total Fe Concentrations for the entire study (a, above) and after day 15 with associated regression models (b, below); lines from top to bottom represent T1, T3, C, and T2.....	149
Figure A.19 – Day-28 filter disks after filtration.....	151

Figure A.20 - Fe²⁺ Concentrations for the entire study (a, above) and after day 15 with associated regression models (b, below); lines from top to bottom represent T1, C, T3, and T2..... 152

Figure A.21 - TDP Concentrations for the entire study (a, above) and after day 15 with associated regression models (b, below); lines from top to bottom represent T1, T3, C, and T2..... 154

Figure A.22 - DRP concentrations during the humic acid study..... 155

Figure A.23 - Total organic carbon concentrations during the humic acid study..... 156

Figure A.24 - pH trends during the humic acid study..... 157

Figure B.1 - Chemical and physical properties reports for sand sourced from New Castle, VA..... 175

Figure B.2 - Location and number of samples in the four retention ponds included in this study..... 176

List of Tables

Table 1.1 - Characterization of runoff for various land uses.....	14
Table 1.2 - NRCS curve numbers describing the runoff characteristics for various land uses.....	15
Table 1.3 - Variables of interest for explaining variability in phosphorus removal.....	25
Table 2.1 - Phosphorus concentrations and total loads from four stormwater ponds in Blacksburg, VA.....	45
Table 2.2 - Regression details for first-order model of P removal.....	53
Table 2.3 - Regression details for physical-process model of P removal.....	55
Table 3.1 - Comparison of P concentrations in carbon-treated FTWC.....	74
Table 3.2 - Rejuvenation percentage of carbon-treated FTWC.....	74
Table 4.1 - Flow rates (L/min) observed before and after filtration runs.....	89
Table 4.2 - 95% confidence intervals for mean P-mass removal rates (mg/h).....	96
Table 4.3 - Rejuvenation process effects on pH in wetland cells.....	98
Table 4.4 - 95% confidence intervals for mean of TP in solution (mg).....	98
Table 4.5 - 95% confidence intervals for P-mass removed by filtration (mg).....	99
Table 4.6 - Correlation coefficients for each treatment group.....	101
Table A.1 - Experimentally determined hydraulic conductivities for each substrate.....	123
Table A.2 - Experimentally determined porosity for each substrate.....	124
Table A.3 – Initial cell treatment levels of humic acid.....	146

List of Terms and Abbreviations

Terms

Concentration Gradient – the thermodynamic potential for additional sorption to occur based on the difference between the current concentration of phosphorus in solution and the concentration that previously established sorption equilibrium with the substrate.

Chemisorption – a chemical process that takes place in the context of interaction between water and soil where a dissolved ion attaches strongly to the soil particle through a chemical reaction involving the exchange of ligands

Macrophytes – macroscopic plants or the type of plants that most people are accustomed to calling plants; typical constructed wetland examples are common reed and bulrush

Natural Capital – natural systems that are providing services through a healthy, functioning environment that would require replacement at cost if those natural systems could no longer provide them

NPS Pollution – sometimes referred to as diffuse pollution, it refers to pollutants that enter a water body through flow over land such as stormwater from an agricultural, forested, or urban area; it does not refer to pollutants from a specific source as the in the case of point source pollution with an example being wastewater treatment plants

NRCS Curve Number – a value used to describe the hydrologic properties of a particular land area, specifically regarding the partitioning of soil storage to runoff and ranging from 0 to 100 with 100 representing an impermeable surface such as a roof

Rejuvenation – a process by which the removal capacity of a filtration substrate for a particular pollutant, in this case phosphorus, can be recharged or reestablished without replacement of filtration media

Sorption – the removal of ions from solution by soil particles through chemical processes that involve some complex combination of chemisorption and precipitation

Stormwater – the water that enters lakes and streams through surface and subsurface runoff during or soon after a rain event; the term is often used to distinguish from wastewater in the context of pollution

Urban Areas – land areas that have undergone significant alteration to natural land use, landform, or hydrologic properties based on the construction and development of buildings, roads, golf courses, suburban developments, parking areas, etc

Abbreviations

ACCA – Calcium-based substrate

ACFE – Iron-based substrate

ACYS – Control substrate

BMP – Best management practice

BRWC – Batch-reactor wetland cells

C – Control

CHT – Constant-head tank

cm – Centimeter(s)

CW – Constructed wetland

d - Days

DO – Dissolved oxygen

DP – Dissolved phosphorus

DRP – Dissolved reactive phosphorus

EPA – (US) Environmental Protection Agency

Fe – Iron

Fe⁰ – Zero-valent iron

Fe³⁺ - Oxidized iron

Fe²⁺ - Reduced iron

FTWC – Flow-through wetland cells

g – Gram(s)

h – Hour(s)

ha – Hectare(s)

HRT – Hydraulic residence time

HT – Head tank

IC – Influent concentration

ICPAES – Inductively coupled plasma atomic adsorption spectroscopy

IQR – Inter-quartile range

kg – Kilogram(s)

L – Liter(s)

LOI – Loss-on-ignition (testing)

m – Meter(s)

mg – Milligram(s)

min – Minute(s)

mm – Millimeter(s)

MPEC – Maximum previous effluent concentration

MRR – Mass removal rate

NPS – Non-point source

NRCS – Natural Resources Conservation Service

NSF – National Science Foundation

OM – Organic matter

P – Phosphorus (or "pond" treatment for a few graphs in chapter 3)

Q₁ – First quartile

Q₃ – Third quartile

REU – Research experience for undergraduates

S – Sugar treatment

SC – Sorption capacity

SP – Sorption processes (or "sugar/pond" treatment for a few graphs in chapter 3)

T1 – Treatment level 1

T2 – Treatment level 2

T3 – Treatment level 3

TDI – Total dissolved iron

TDP – Total dissolved phosphorus

TI – Total iron

TOC – Total organic carbon

TP – Total phosphorus

TSS – Total suspended solids

UWF – Urban wetland filter

VF – Vertical flow

Introduction

Background

The effects of certain urban land use practices on water resources, if left unmitigated, will likely contribute to a decline in the health, usefulness, and enjoyment of these valuable resources. Water resources including streams, lakes, and reservoirs provide irreplaceable service to our communities including drinking water, irrigation for agriculture, water for hygiene and sanitation, power generation, and recreational uses. Maintaining the health of these water bodies in terms of water quality is not only imperative of natural resource stewardship, but also essential to the useful continuance of many of these services, while the cost of replacing the services can be significant.

Nutrients and water quality

Land management practices can result in both avoidable and unavoidable stresses to water quality. One of these stresses is the excessive addition of nitrogen and phosphorus. These nutrients originate from various sources including lawn fertilizers, chemical detergents, and animal excrement. Water running off the land during and after rainfall then picks up and carries these nutrients. This water, referred to as stormwater, makes its way to streams and eventually lakes, reservoirs, and estuaries. It is typically in these relatively still water bodies that the transported nutrients create the most critical water quality problems through a biochemical process called eutrophication (Novotny, 2003).

Parry (1998) cites eutrophication as a significant threat to US water bodies that can create interruptions in the ecological services these water bodies provide. Described in broad terms, eutrophication causes excessive growth of primary producers, such as algae, which eventually die and decompose. This decomposition process uses large amounts of the oxygen normally found dissolved in the water body. The resulting low-oxygen conditions cause many problems including the direct mortality of various aquatic species from suffocation (Novotny, 2003). Other impacts include taste and odor problems for drinking water (Camargo and Alonso, 2006), declines in fish and shellfish populations and outbreaks of the dinoflagellate *Pfiesteria piscicida* or “fish killer” (Shumway, 1990; Boesch et al., 2001). In addition, decrease in aesthetic value for

tourism (Camargo and Alonso, 2006), and even direct human health concerns (Chorus and Bartram, 1999) can result from eutrophication.

Non-point source pollution by nutrients from urban areas

The historical focus on the sources of these excessive nutrient additions has been large agriculture operations and point sources of pollution such as effluent from wastewater treatment plants. However, urban areas have received increased attention more recently due to mounting evidence of their significance as contributors to eutrophication from nutrients in runoff (USEPA, 1983). Improper application of fertilizer and leaky septic systems are typical contributors of nutrients in urban environments, as is erosion of sediments containing large amounts of previously adsorbed phosphorus (Paul and Meyer, 2001). Settings included in this broad categorization of "urban" are urban centers, suburban development, golf courses, and other managed turf environments such as parks and recreational fields.

Many urban areas, such as the Chesapeake Bay, have seen minimal reductions in nutrient export despite efforts made to curtail the export of excess nutrients (Boesch et al., 2001). This shortfall is likely due in part to less than ideal application or complete misfit of best management practices (BMP), such as management of fertilizer application, not originally developed for treating stormwater in the urban environment. In addition, these urban areas are expanding at a steadily increasing rate. Thus, without employing significant efforts to curtail nutrient export, urbanization is an increasingly important driver of eutrophication, eroding natural capital, and increasing costs associated with natural resource use. With an increasing focus on water quality in urban areas, research efforts are needed to develop BMP that are more aptly suited for the specific requirements of water quality protection in urban areas.

Unique constraints to effective stormwater management in urban areas

Stormwater management typically requires the dedicated use of land, and if management includes water quality in addition to water quantity, even more land is typically required. Before water quality in urban areas emerged as a major concern, urban stormwater management often took the form of dry retention ponds, which mainly focused on preventing flooding and stream bank erosion. As interest in protecting water quality increased, the dry detention pond design changed to include a permanent pool of water in the bottom of the pond, creating a wet retention or water quality pond (Ward and Trimble, 2004). These ponds provide modest reductions in

nitrogen and phosphorus in urban stormwater, but the reductions seen are largely dependent on the continued removal of sediment (Comings et al., 2000) and may suffer further decline with long term use (Smith et al., 2005).

Additional efforts to incorporate water quality in urban stormwater management have been subject to two constraints common to many endeavors: money and time. In urban areas, when land-value is high and large land areas are necessary for water quality BMP such as constructed wetlands, the expense of incorporating these additional measures can be difficult to justify. In addition, due to the large amount of impermeable surfaces in urban areas that restrict rainfall from soaking into the ground, urban areas typically have a larger and much faster runoff response to rainfall than other land use categories. This runoff response is comparable to a short, tall wave of water moving through the area instead of a long, short wave more typical of areas with more permeable surface area. The implication of this water quantity factor for stormwater quality is that very little time is available for treatment, usually only hours, necessitating an even larger amount of land to treat urban stormwater adequately.

Urban wetland filter for urban stormwater management

Natural wetlands have demonstrated a effective ecological service of filtering and managing nutrients and have even been described as the kidneys of the natural world (Simeral, 1998). This filtration ability has been recognized and utilized artificially in the form of constructed wetlands, which are often used for low volume wastewater treatment and can be used for treating stormwater as well, but stormwater applications have been somewhat limited due to the large land requirement (Hunt and Wossink, 2003) and lower phosphorus concentrations (Schueler, 1996). For this reason, the adaptation of wetland technology to the constraints of an urban environment while preserving nutrient management function represents a significant gain for urban stormwater quality management. This research project develops a novel nutrient-management practice, the urban wetland filter (UWF), through applying an adapted constructed wetland as a complementary enhancement to existing retention ponds in urban areas (fig. 1.1). The UWF concept places multiple constructed wetlands, of a significantly smaller size than a traditional constructed wetland design, adjacent to an existing wet retention pond. The filter cycles water from the pond continuously, addressing time constraints by filtering

water retained by the pond, enabling continuous treatment, and reducing wetland size by circumventing the need to handle peak flows.

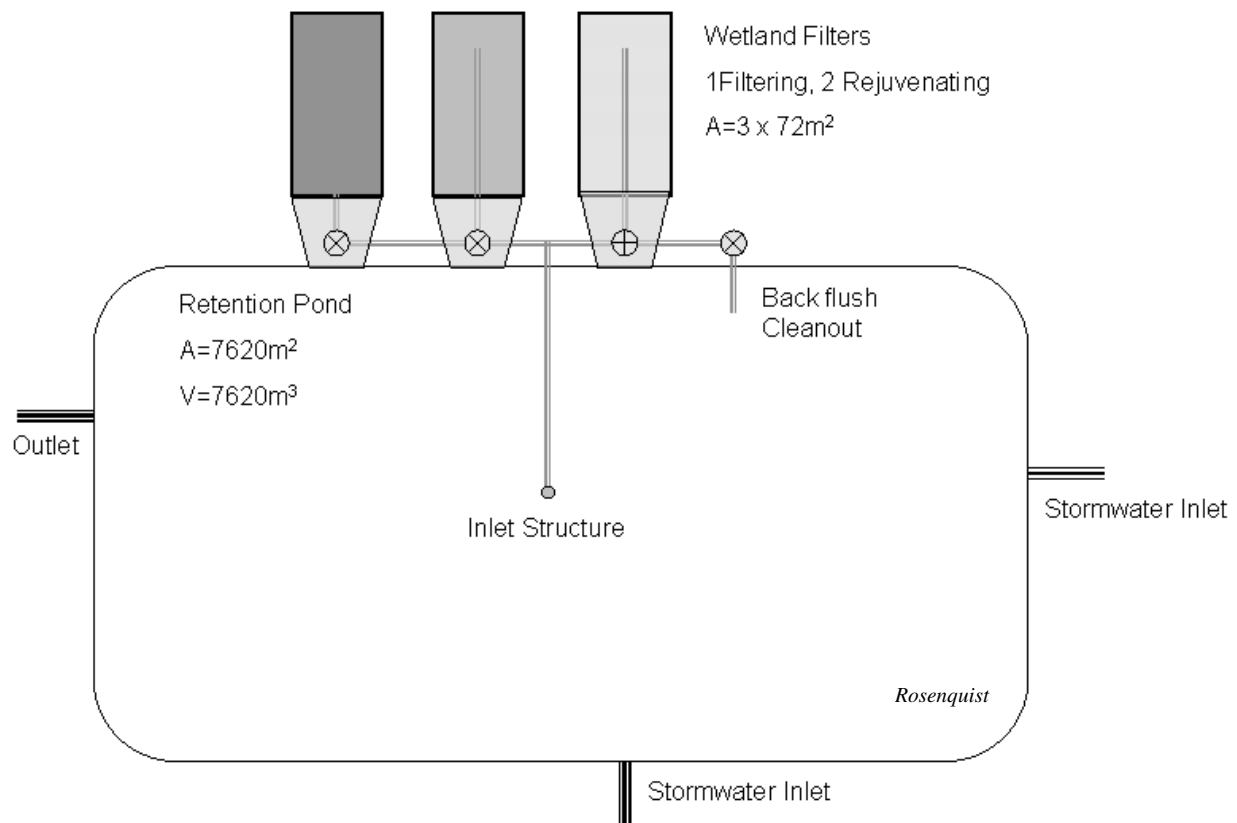
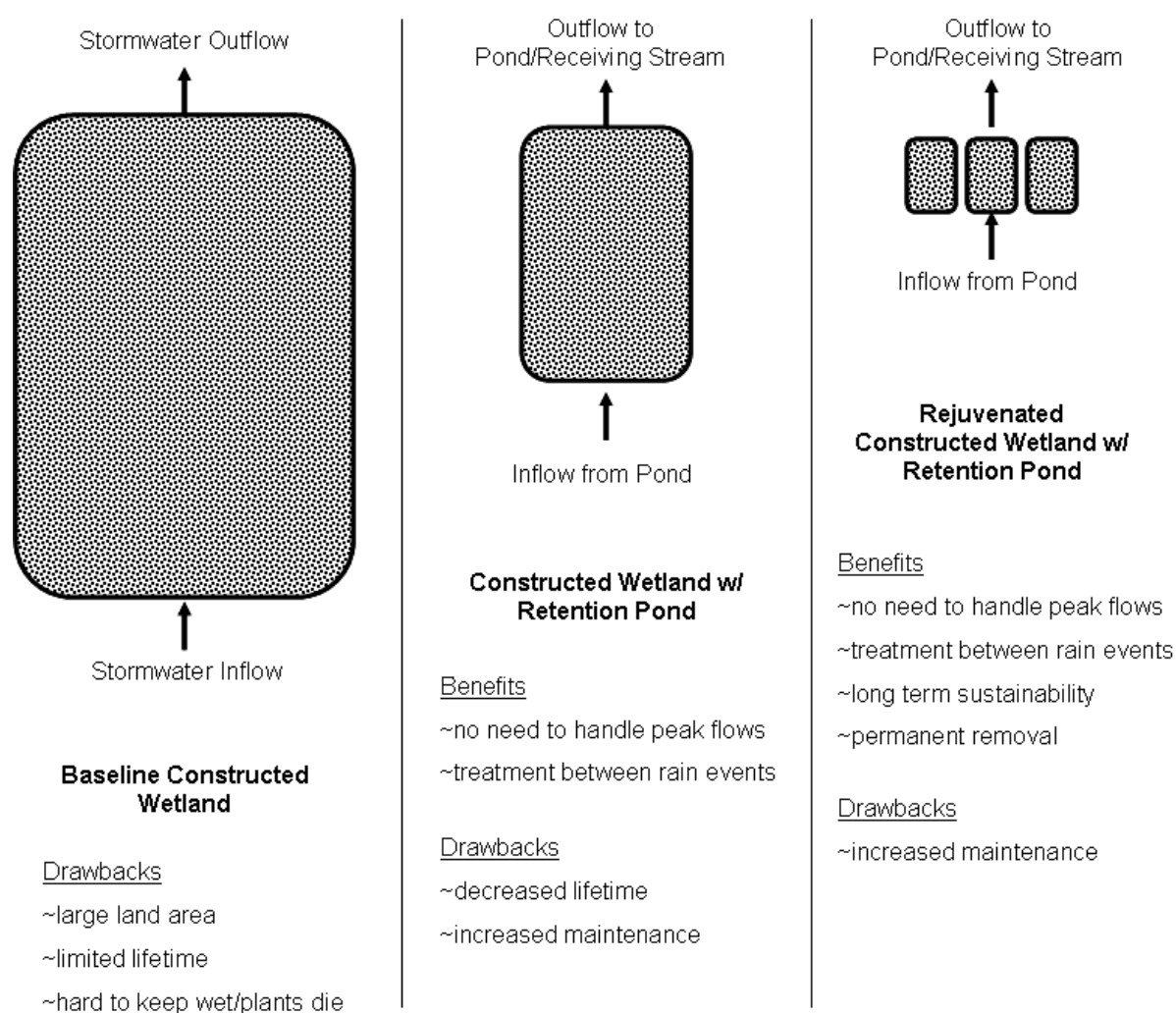


Figure 1.1 - Representative design layout of a UWF system on a typically sized urban retention pond

The UWF enables improvements in urban stormwater quality through significant reductions in dissolved phosphorus, which existing retention ponds do not treat efficiently (Comings et al., 2000), while addressing the necessary adaptation of wetland technologies to the urban environment. Adaptations include minimizing wetland footprint, sustaining removal capacity, and optimizing phosphorus removal performance. The UWF is capable of overcoming urban stormwater management constraints by utilizing existing infrastructure and periodically renewing phosphorus sequestration capability through a constructed wetland rejuvenation cycle. The rejuvenating cycle can further reduce required wetland size (fig 1.2) by eliminating the need to design for a finite sorption lifetime, while harvesting the previously sequestered phosphorus from the system for cost-effective transportation and use elsewhere as a managed nutrient source. And, considering the current dollar estimates placed on phosphorus removal from stormwater

(Sano et al., 2005), this harvesting capability may prove to be an effective financial incentive. Multiple wetlands function in parallel with one or more in the rejuvenation cycle to allow continuous treatment. When the filtering wetland reaches capacity, it switches to rejuvenation and another wetland is ready to start filtering stormwater. The UWF concept addresses the necessity for large land area by periodically rejuvenating a much smaller wetland instead of relying on wetland size to achieve a longer treatment lifetime (Keppler and Martin, 2008), locating the wetland on land already dedicated to stormwater management use, and enabling continuous treatment instead of relying on only storm-event based treatment.



Rosenquist

Figure 1.2 - The UWF concept for treating urban stormwater can create reductions in land area requirements in several ways

Purpose Statement and Research Objectives

The **overall purpose** of this research project is to develop a novel nutrient management practice, the urban wetland filter (UWF) through the application of a optimized and specifically adapted constructed wetland as a complementary enhancement to existing wet retention ponds in urban, low-acreage agricultural or turf-managed land uses such as golf courses. UWF development includes maximizing the mass removal rate for dissolved phosphorus from stormwater filtered from urban retention ponds. Research studies include the construction, development, and monitoring of constructed wetlands scaled and adapted for the UWF concept while investigating processes that enable the necessary adaptation of wetland technologies to the urban environment. Adaptations include minimizing wetland footprint, sustaining removal capacity, and optimizing phosphorus removal performance. The **research objectives** listed below are central to the **overall purpose** of adapting constructed wetlands for use in urban areas through the UWF concept:

1. Identify and quantify sources of variability in phosphorus sequestration by sorption processes in constructed wetland (CW) substrates in order to further understand, predict, and optimize CW performance;
2. Investigate the feasibility of facilitated microbial reduction of Fe-oxyhydroxides as a process to release phosphorus from CW substrates that have reached sorption equilibrium with the intent of continued phosphorus sequestration;
3. Investigate a method of increasing the rate of Fe³⁺ bioreduction with the intent of minimizing UWF land area by matching sequestration and rejuvenation time scales;
4. Investigate a method for regaining Fe-oxyhydroxides in the CW after reduction cycles with the intent of continued sequestration capability by sorption processes after the rejuvenation cycle is complete; and
5. Verify the capability of the UWF concept under field conditions.

To accomplish the adaptation of constructed wetlands to urban environments, it is necessary to identify sources for the high levels of variability among published studies for phosphorus removal by constructed wetlands. Identifying these sources of variability will enable

optimization of wetland performance. In addition, the three-step process of the UWF rejuvenation cycle must be developed and validated for field conditions. These three steps correspond to three specific technological hurdles: decreasing the time associated with microbial reduction to release sequestered phosphorus from sediment, thereby promoting precipitation of high concentration dissolved phosphorus from bulk solution, and enabling the recoating of the filtration material with adsorptive materials once the desorption process is complete in preparation for the next filtration mode. This concept represents an effective new tool for nutrient management in areas where land use is in high demand and where ponds are already available, which describes many urban areas.

In addition to the intellectual merits already described, broader impacts of this research include a greater scientific understanding of constructed wetlands and nutrient removal, significant research experience and involvement of undergraduates through the NSF REU program, and a potential breakthrough for low-cost nutrient management in thousands of urban watersheds across the US through implementation of the UWF concept. The development of an environmental remediation technique that utilizes microorganisms as part of the constructed wetland rejuvenation process represents an additional broader impact. Environmental remediation strategies using microorganisms represent an exciting new frontier in ecological engineering and scientific gains made in this area may serve to enable greater discoveries in the future.

Description of Document Format

This document follows a manuscript format including the following three articles in addition to comprehensive literature review and conclusions/recommendations sections:

1. Chapter 2 - Variability in adsorptive phosphorus removal by structural stormwater best management practices (previously published in *Ecological Engineering*)
2. Chapter 3 - Facilitated iron reduction as a means of rejuvenating phosphorus removal performance of filtration substrates (in review for *Transactions of the ASABE*)
3. Chapter 4 - Urban wetland filter: field results in the development of a renewable practice for managing phosphorus in stormwater runoff from high land-value areas (to be submitted to *Water Research*)

Review of Literature

Anthropogenic eutrophication: sources, processes, and impacts

Eutrophication is the increase in primary productivity in a water body due to an increased availability of either nitrogen or phosphorus depending on which nutrient is most scarce (USEPA, 2000). The process of eutrophication has been discussed in scientific literature from at least the middle of the 20th century (Rohlich, 1969) and has been the focus of many published works since that time.

Characterization of Eutrophication

The process of eutrophication is thought to occur naturally for some water bodies and may describe a natural trajectory from glacial lake towards wetland and potentially, dry land (Novotny, 2003). However, human activities involving the discharge of nitrogen or phosphorus to water bodies can unnaturally cause or accelerate eutrophication. The process is then anthropogenic or cultural eutrophication. Stages along the eutrophication process include, from least nutritious status to most, oligotrophic, mesotrophic, eutrophic, and sometimes hypereutrophic stages. Although the position along these “trophic stages” is fundamentally driven by additions of nitrogen and phosphorus, the stages are also correlated to and measured by other physical and chemical properties of the water body, such as the depth of light penetration or amount of primary production (Novotny, 2003). Total phosphorus concentration may be the most frequently used indicator for the level of eutrophication. Although the boundaries between these states are subjective and sometimes vary, the EPA has developed a widely accepted set of values for these physical and chemical properties. For example, a total phosphorus level of greater than 0.02 ppm or a secchi disk depth of less than 2.0 m is representative of a eutrophic lake (USEPA, 1974). The hypereutrophic condition most commonly describes anthropogenic eutrophication, and can involve nutrient levels and changes in nutrient levels far in excess of those seen in naturally occurring processes.

Process of Eutrophication

A number of aquatic species including algae and cyanobacteria are growth-limited by nitrogen or phosphorus. In some cases growth rates can be extreme resulting in algal mats that significantly increase turbidity thereby cutting off light to submerged plant life (USEPA, 2000). The eventual dieback and decomposition of these algal mats can create huge oxygen demand on the water body. Even without dieback, the diurnal switching between respiration and photosynthesis can cause huge swings in dissolved oxygen and create problems for aquatic life that are sensitive to low oxygen conditions. In fact, hypolimnetic oxygen saturation by itself can be used as an indicator of a water body's "trophic status" (Novotny, 2003).

Impacts of Eutrophication

In addition to purely ecological impacts, if such a condition even exists, anthropogenic eutrophication may result in economic and human health impacts. Direct fish kills from low oxygen saturation can occur in some situations where oxygen-sensitive species are present and anoxia persists for a sufficient time (USEPA, 2000). Indirect causes are responsible for more subtle, yet serious detriments to populations of various species. Anoxic conditions resulting from eutrophication can cause increases in various toxins including nitrite (Comeau et al., 2001). Also, interruptions in the food web at many levels can cause additional stresses that cause declines in populations over time (Camargo and Alonso, 2006). These pathways to population decline in aquatic species have exacerbated stresses from unrelated factors such as overfishing leading to significant economic detriments on coastal economies. Shumway (1990) described major distress in the shellfish economy of the Gulf of Mexico due in part to cultural eutrophication. In addition to fisheries, economic detriment can be realized from increased cost of water treatment due to taste and odor problems typically associated with cyanobacteria (Chorus and Bartram, 1999). Treatment of taste and odor problems is a particularly good example of a decline in natural capital and the associated cost of replacement.

Research on human health concerns stemming from eutrophication has received less attention than ecological detriments, but some published work exists relating blooms of cyanobacteria to human health (Chorus and Bartram, 1999). Sometimes referred to as blue-green algae, cyanobacteria are, as their true name implies, a phylum of the taxonomic domain bacteria. They produce toxins that, in addition to causing the taste and odor problems cited earlier, may

lead to sickness in human beings. While skin, eye, and gastro-intestinal maladies are well associated with contact or ingestion of cyanobacteria toxins, even fatality is considered possible with sufficient dosing (Chorus and Bartram, 1999).

The Chesapeake Bay as a Case Study

The Chesapeake Bay provides a good case study on the effects of eutrophication. This water body has received an enormous amount of study that will not be covered here, but the main points from a selected work on the Chesapeake Bay, Boesch et al. (2001), are addressed. The Chesapeake Bay contains many of the impacts cited for anthropogenic eutrophication, including reductions in submerged vegetation, significant algal blooms, and declines in fishery populations. Various factors have confounded a determination of the exact causes for these impacts, especially overfishing. These confounding factors may partially explain the minimal improvement to water quality seen in the bay despite significant work done to reverse the existing impacts. This situation exemplifies an inherent problem in issues of environmental impact, that the level of interdependency and multifactor processes in natural systems makes it very difficult to trace a path back to a historical condition, even if such a path is consistent with the un-impacted trajectory for the system. Therefore, it is of critical importance to move toward a proactive strategy of preserving natural capital by preventing further additions of excess nutrients both to water bodies already affected in order to preserve remaining water quality and to currently healthy systems with anticipated impacts.

Concept of Natural Capital

Natural capital has been described as the services provided by a healthy, functioning environment that would have to be replaced at some cost if possible if the environment could no longer provide them (Wheeler and Beatley, 2004). Attempts to estimate these costs typically reach into the hundreds of millions of dollars. These figures provide perspective for the value of a protected environment, and enhanced appreciation for the brilliant design of natural systems and their relatively high capacity to not only provide services that are often taken for granted but also to absorb and attenuate imbalances without complete and catastrophic collapse (Swenson and Catchpoole, 2000; Jones and Schmitz, 2009). However, ecological service can greatly

diminish even before a complete collapse, as seen in the Chesapeake Bay, highlighting the need for proactive stewardship.

Nutrient Cycling and Sources of Imbalance

Since excess nutrient additions drive anthropogenic eutrophication and since control of this stressor is so vitally important to the health of aquatic ecosystems, a characterization of the anthropogenic imbalances in nutrient cycling is critical to understanding the problem of eutrophication. One of the ways that natural nutrient cycles are affected is in the transport of high value goods from one location to another as described by Lijklema (1995). High-value goods such as grain feedstock extracted from one location are often rich in nutrients from that location. Upon use of that high-value good at a distant location, many of the nutrients end up in a low-value waste product, such as animal or human excrement. This waste, with its associated nutrient load, remains close to the consuming location, seldom returning to the place of origin. In this sense one can imagine a steady flow of nutrients from producing locations to consuming locations with an associated deprivation of nutrients in the producing locality and excess of nutrients in the consuming locality (Lijklema, 1995). This concept is important in this study because urban areas are generally consuming localities and must manage the steady influx of nutrients in such a way as to prevent damage to the surrounding environment. A study based on this principle found that a mass-flow model of phosphorus movement was a good predictor of water quality problems in the Chesapeake Bay (Russell et al., 2008).

Another imbalance comes from the mining of phosphorus to restore fertility to the soils of producing locations or to enhance soil fertility or landscaping aesthetics in consuming locations. This nutrient transfer often takes the form of application of rapidly bioavailable, inorganic fertilizers (Lijklema, 1995). Locations for the application of these fertilizers are often agricultural areas or managed turf areas such as golf courses or lawns (Parry, 1998; Novotny, 2003). Generally, the full amount of nutrients applied do not fully incorporate into the soil, and with rainfall, nutrient rich runoff is produced, increasing nutrient loads in water bodies downstream from where nutrients are applied. Inorganic fertilizer is used extensively in urban areas as well as agricultural areas, its use is subject to much less regulation than in agricultural areas, and it is generally used by individuals less informed about best management practices for fertilizer application and who are more prone to over-apply the product. The result is a

systematic tendency favoring anthropogenic eutrophication in urban areas and an accompanying need for methods that can economically remove and recycle these nutrients back to producing localities.

Cause to Focus on Phosphorus Management over Nitrogen

Although nitrogen and phosphorus are both critical to the discussion of eutrophication, there are some reasons to concentrate remediation and prevention efforts on phosphorus. First, phosphorus is of particular concern since it lacks a process equivalent to denitrification, where nitrogen can be transferred to the atmosphere, alleviating the excesses in water (Lijklema, 1995). Also, phosphorus is usually the limiting nutrient for algal growth in freshwater systems, and under some situations can also be limiting in saltwater systems (Fisher et al., 1992). Characterization as a limiting nutrient means that the plant has sufficient availability to all other nutrients (such as nitrogen) for further growth, but cannot grow further without the limiting nutrient (such as phosphorus). Furthermore, from a supply perspective, natural resources for mined inorganic phosphorus are becoming increasingly scarce, and any technique that can sequester phosphorus and harvest it for productive use could decrease demand for mined phosphorus (Abelson, 1999). Lastly, water quality regulators are choosing phosphorus as the target pollutant for the increasing regulation of stormwater quality (Dowling, 2009) creating increased interest from municipalities on the phosphorus-removal performance of water quality BMP.

Nutrients as non-point source pollution

Water pollution issues categorize into two broad categories based on the pollutant source. The first category includes point sources of pollution such as wastewater treatment plants and industrial processing plants. Much of the efforts of the past couple of decades have been directed towards this category and researchers have made significant gains toward reducing nutrients loads (Boesch et al., 2001).

The other broad category includes non-point sources (NPS) or diffuse sources of pollution, which consist mostly of pollutant loads in surface runoff and shallow subsurface flow from areas as diverse as agricultural operations, leaky septic systems, and urban development areas. Pollution, including nutrient excess, from NPS sources is likely a major detrimental impact

for up to 50% of US waterways (Hammer, 1992). More recently, nutrient control efforts have focused on non-point sources of pollution, but they have proven to be much more difficult to manage, while often contributing 50% or more of the nutrient load (Hammer, 1992; Boesch et al., 2001). The difficulties rise from a variety of reasons including near impossibility of complete monitoring (Novotny, 2003), regulatory difficulties, spatial scale of sources, higher water volumes to treat, and technological difficulties in further reducing stormwater concentrations that are near or below the “irreducible minimums” proposed by Schueler (1996).

Within non-point sources there have been and continue to be a great number of pollutant reduction strategies, often generally referred to as best management practices (BMP). Although originally meant to describe ways to manage a resource through methodology, the term also represents many structural practices, such as constructed wetlands, retention ponds, and infiltration trenches. These BMP, intended for control of non-point source pollution, separate further into three general categories including source control, transmission blockage, and endpoint remediation (Novotny, 2003). An example of source control would be requiring proper management of the land application of animal manures to ensure that minimal nutrients are lost to runoff. An example of transmission blockage would be constructed wetlands for treating runoff (Hammer, 1992) and an example of endpoint remediation would be bioaccumulation of nutrients in oysters intentionally placed into a eutrophic water body. Multiple examples of source control and transmission blockage are given by Ward and Trimble (2004). Some of the source control strategies include reduction in impervious surface, better construction practices, and soil erosion control. Transmission blockage strategies include constructed wetlands as well as retention and detention systems. In general, the implementation cost of these BMP probably increases from source control to endpoint remediation, making remediation strategies generally undesirable. Source control strategies are ideal, but often illusive due to enforcement difficulty and scale of implementation. Transmission blockage techniques have become very common, possibly due to a balance between cost and ease of implementation. While the UWF BMP falls within this category, its developmental goals include both minimizing cost and maximizing ease of implementation.

Specifically in regards to the cost of pollutant treatment through various BMP, the newly developing market for nutrient credits may significantly alter the decision-making process. A study that attempted to apply a market cost for phosphorus removed from stormwater found that,

depending on influent and effluent concentrations, phosphorus removal value ranged from \$24 to \$1,346 per kg of phosphorus removed (Sano et al., 2005). Numbers such as these could quickly offset implementation costs associated with the BMP. Furthermore, a BMP such as the UWF that provides a means of harvesting phosphorus from stormwater, a tangible and quantifiable measure of nutrient removal, will likely command an even higher value on the nutrient trading market.

Characterization of NPS Runoff

It is necessary to characterize runoff from various non-point source locations in order to determine where remediation efforts are most beneficial and how to best achieve remediation in a particular area. Specifically, characterization of phosphorus yield in runoff from a particular area must include consideration of both phosphorus concentration in runoff and the total amount of runoff. Table 1.1, based on data from the Nationwide Urban Runoff Program (USEPA, 1983), describes the medians and ranges of concentrations typical for various land uses, including various types of urban land use.

Table 1.1 – Characterization of runoff for various land uses

Type of land use	Range in mean TP observations (ppm)	Median TP across all sites (ppm)	Number of sites
Residential	0.22 – 4.09	0.38	39
Urban Open and Non-Urban	0.03 – 0.49	0.12	8
Light Industrial	0.11 – 0.54	-	100
Commercial	0.11 – 0.70	0.20	10

In regards to the total amount of runoff, hydrologic modeling such as the NCRS curve number method can provide estimations of the relative amount of rainfall that becomes overland runoff. In the curve number method, higher curve numbers correspond to areas where more of the rainfall becomes runoff, placing a higher weighting factor on the concentration of any pollutant in these areas. Table 1.2 contains information from USDA (1986) with example curve numbers for various land use areas, including urban land uses.

Table 1.2 – NRCS curve numbers describing the runoff characteristics for various land uses

Type of land use	Curve number
Residential (half-acre lots)	80
Forested	70
Roads	90
Pasture	74
Commercial	90
All values are given assuming a hydrologic soil group of C, good conditions, and antecedent soil moisture condition II	

While agriculture is often cited as the major contributor of nutrient pollution (Boesch et al., 2001), the rapid increase in urban sprawl and the significant nutrient concentrations associated with urban land uses, such as golf courses and other managed turf applications, create an increasing need for nutrient management in stormwater. Both the rate and percent of urbanization have been studied and correlated to increased water quality detriments (Atasoy et al., 2006)

NPS Runoff in Urban Areas

While the sources of phosphorus in runoff from agricultural areas are relatively well recognized (soil loss and the application of inorganic fertilizer and animal manure) it is often less obvious how urban areas contribute to nutrient excess. In a general sense, urban areas can be characterized as a source of nutrients under the Lijklema (1995) paradigm as a consuming locality. Urban and suburban areas have a large volume of high-value nutrient containing goods brought in, and very seldom export many of those nutrients apart from wastewater effluents. Although regulators often consider wastewater effluent a point source, many suburban areas with septic systems could be contributing significantly to NPS nutrient loads. Paul and Meyer (2001) describe this septic groundwater discharge to gaining streams along with illicit sewer discharges as significant sources of phosphorus loading. In the same study, urban areas were as high in terms of phosphorus concentration and yield as agricultural areas. This finding was echoed by Osborne and Wiley (1988) in a watershed that was mostly agricultural. Similarly, in a NPS

modeling study by Winter and Duthie (2000), urban areas contributed over 50% of the phosphorus load transported by streams from the watershed while making up less than 50% of the land area. Improper lawn fertilization is another typical source of nutrient contamination in urban areas, even with organic fertilizers (Baker et al., 2007).

While the identification of lawn fertilization and septic discharge as contributing nutrient sources may not be surprising, impacts to predevelopment urban hydrology as a source for nutrient pollution may be surprising. An increase in phosphorus delivery based on hydrologic impacts alone may not be immediately obvious, but is connectable. When urban runoff is channelized and rerouted either for rapid transmittance to a water body or through stormwater BMP such as detention ponds, natural filtrations functions can be removed, so that a larger percentage of nutrients initially picked up by runoff water are transmitted to the water body (WEF, 1998; Hogan and Waldbridge, 2007). In addition, Paul and Meyer (2001) discuss the condition of urban soils that were previous agricultural and highly enriched with phosphorus becoming “chemical time bombs” that can contribute huge phosphorus loads when eroded or permanently saturated due to hydrologic changes.

Management strategies for NPS pollution in urban areas

Attenuation efforts on of the impacts of urbanization on water quality have seen varying degrees of success and some unintended side effects. In general, urban stormwater management divides in two areas, quantity and quality, with the former being historically more readily and more successfully managed. Hogan and Waldbridge (2007) cite a range of stormwater management techniques and structures that have been used over time in urban areas along with the various studies that have evaluated them. These techniques range from the historical curb and gutter with large diameter pipes intended to transmit flow quickly to receiving streams with no treatment whatsoever, to more recent approaches with BMP such as water quality ponds, stormwater wetlands, and bioretention areas. These last designs include long-term water retention by providing surface storage and promoting infiltration. This approach intends to decrease the total volume of runoff and decrease peak flows by flattening the stormwater response wave after an urban rain event. In addition, these newer techniques also attempt to include some water quality treatment for pollutants such as organics, sediment, and nutrients. One of the most common stormwater management techniques of the last few decades has been

the stormwater detention pond or “dry pond,” which include no intentional provision for water quality improvement.

Wet Retention Ponds as a Stormwater Quality Strategy

As water quality, including nutrient concentrations, have become more of a concern, some pond designs have been replaced or existing ponds retrofitted to water quality retention ponds or “wet ponds” (Smith et al., 2005; Hogan and Waldbridge, 2007). The main difference between a detention pond and a retention pond is that the retention pond has a permanent pool of water that can promote increased settling of solids along with some attached pollutants and the ability to provide a sustained habitat for aquatic species. This permanent pool can sometimes increase aesthetic appeal compared to a dry pond, although problems with algal growth, which provides obvious visual confirmation of the reality of the nutrient problem in urban areas, can decrease aesthetics. Another point that has been made regarding wet ponds and other water quality treatments based on natural processes, including constructed wetlands, is the increased efficacy and cost savings associated with the utilization of these natural processes to achieve treatments compared to more traditional treatment techniques exemplified by mechanical wastewater treatment plants (Comeau et al., 2001; Luederitz et al., 2001).

While the increasingly ubiquitous “wet pond” does attempt to provide some water quality treatment, much of this treatment occurs by sedimentation, and is directly limited by the pollutants that can settle to the bottom of the pond during the designed retention time and be retained there (Comings et al., 2000). Sedimentation can be a very effective means of pollutant removal, especially for sediment carried by stormwater, often measured as total suspended sediment (TSS). This process occurs due to gravitational force acting upon particles that are heavier than water, and is most effective when particle size is larger, retention times are longer, and short-circuiting becomes minimal. Under ideal conditions, removal percentages for TSS in retention ponds can be well over 50%. However, dissolved pollutants may be largely untreated (Comings et al., 2000) creating a significant opportunity for media filtration strategies such as constructed wetlands or bioretention cells.

Constraints to Stormwater BMP Use in Urban Areas

The technological availability along with the economic value of these “natural treatment” techniques has led to increased interest for applications such as wastewater treatment and stormwater management. However, constructed wetland use in urban areas has been somewhat restricted by several specific constraints including: limited availability of large areas of land needed for constructed wetlands, high land cost for land that is available, and limited treatment time due to the rapid hydrologic response in urban watersheds (Hunt and Wossink, 2003; Birch et al., 2004). In regards to the last constraint, a “typical” watershed may experience a ten-fold increase in peak discharge accompanying an increase from 25% to 75% urban land use (Ward and Trimble, 2004).

Constructed wetlands for treatment of urban stormwater

Natural wetlands are a significant part of the natural nutrient cycling process and can function both as a source and a sink for phosphorus (Fisher and Reddy, 2001). Wetland soils have shown ability significantly beyond that of uplands to remove and sequester phosphorus (Axt and Walbridge, 1999). However there has been a significant degradation of natural wetlands by either complete loss or significant disturbance to the extent that only about 50% of historical US wetlands remain intact (Mitsch and Gosselink, 2000). The realization of this loss along with the current understanding of the vital processes that wetlands play in the water cycle are part of the significant interest in efforts to replace wetland function. Replacement of lost wetland function either can include restoration efforts on historically wetland areas, creation of wetlands from historically upland areas, or constructed wetlands designs. The intention of the two former techniques, though not always attained, is to develop the look, feel, and function of a natural, undisturbed wetland. On the other hand, constructed wetlands, typically used to treat wastewater or stormwater in highly impacted land use areas, typically bear less resemblance to natural wetlands (Mitsch and Gosselink, 2000). Constructed wetlands seek to mimic some of the functions of natural wetlands either to replace lost ecosystem service or to provide additional treatment to remediate water quality impacts. This study focused on constructed wetlands.

Categorization of Constructed Wetland Types

Within constructed wetlands, a distinction can be made between constructed wetlands for wastewater treatment (Shilton et al., 2005) and constructed wetlands for stormwater treatment (Carleton et al., 2000). The requirements of these two types of systems are so different due to the type and concentrations of pollutants associated, that they typically look and act very different. This study focused mainly on constructed wetlands for stormwater treatment, while a few wastewater studies have been included to provide supporting information. Another classification of constructed wetlands is between free surface wetlands and subsurface flow wetlands. Free surface wetlands include some combination of floating vegetation, emergent vegetation, and submerged vegetation types and prioritize flow through the vegetation (Kadlec, 2005). Alternatively, subsurface wetlands prioritize flow through the substrate, while vegetation may be included for aesthetics or to provide additional treatment (Reed and Brown, 1995). Within subsurface flow wetlands, further distinction can be made between vertical and horizontal flow wetlands (Luederitz et al., 2001) while vertical flow wetlands can have either upward or downward flow (Arias et al., 2003; Langergraber et al., 2003). This study focused on vertical subsurface flow wetlands in order to maximize flow rates, minimize land area usage, and focus on rapid removal processes (fig. 1.3).

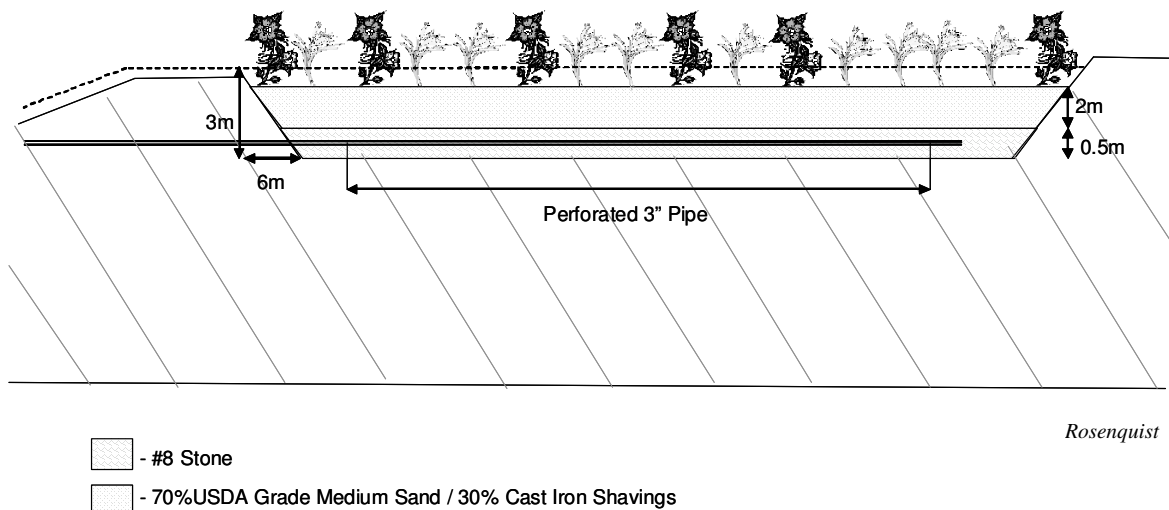


Figure 1.3 – A vertical, subsurface-flow constructed wetland consistent with the size of an individual UWF cell for an urban application

Metrics for Constructed Wetland Performance

Also important to the study of constructed wetlands are the metrics used to compare nutrient removal performance. Typically, pollutant-removal efficacy metrics for wetlands are removal percentages based on either the percent change in concentration or the percent decrease in mass load. Several studies included in this review use one or both of these methods. However, recently the EPA and others (Strecker et al., 2001) have become somewhat critical of this approach as it may include biases in reported pollutant removal. The biases include bias from water volume decreases between inlet and outlet of the BMP that are problematic for percent decrease in mass load, and variability across ranges of concentrations that are problematic for percent decrease in concentrations. In the first case, reported performance can be artificially high because not all flow out of the BMP is accounted. In the second case, a high removal percentage from a study at high concentrations may have little or no bearing on the removal percentage at a lower concentration (USEPA, 2002). In addition, reporting a removal percentage tends to foster an assumption that the reported removal percentage remains constant and is capable of providing estimates of effluent concentrations or mass removal under different conditions than the study where the removal percentage was calculated. Even an average taken from many studies is of little value due to the large variation between studies. For these reasons, this study used total mass removal as a performance metric while also reporting concentrations in order to convey the most information.

Phosphorus Removal Mechanisms in Constructed Wetlands

The mechanisms of phosphorus removal by wetlands categorize into three areas: sorption to existing substrate, uptake by plants, and sedimentation and incorporation into new substrate (Kadlec, 2005). The last process differentiates from the first in that a chemical reaction, described below in detail, is taking place whereas in the latter the removal process is only a physical filtering or settling of material (mineral or organic) that already has the nutrients associated. In other words, the first process removes dissolved phosphorus while the latter does not. While an understanding exists for the ability of constructed wetlands to remove phosphorus through a combination of these processes (Reddy et al., 1999), significant variation exists between studies (Kadlec and Wallace, 2009).

Variability in Removal Performance by Constructed Wetlands

In regards to the removal percentages reported, Lantzke (1999) reviewed studies that ranged from 34% removal of TP to 99% removal of TP. These studies focused on wastewater performance. One stormwater study found removal percentage for TP as low as 12% (Birch et al., 2004). Another study reported removal performance for dissolved phosphorus from 0% - 66% for unplanted wetlands and 27% - 100% in planted wetlands suggesting that significant variation exists both within and across the different P removal mechanisms (Regimi et al., 2003). Such variation raises questions as to why such differences occur and this review covers many possibilities. Lantzke (1999) also compares performance between removal mechanisms for dissolved phosphorus, the particular speciation of concern in this study. The study found that rates of removal were higher for substrate sorption than for removal by macrophytes and total mass removal was higher for chemical sorption than for macrophytes in the short term. However, this trend reverses if the time scale considered is more than a couple months (Lantzke et al., 1998; Lantzke et al., 1999). This last condition is likely due to a decrease in sorption over time without some rejuvenation of sorption capacity. Non-process specific, macroscopic variables of importance suggested in the literature for phosphorus removal include mixing, temperature, and a general “age” of the filter (Lantzke et al., 1998; Lantzke et al., 1999), as well as size relative to the catchment area (Birch et al., 2004).

Phosphorus Removal by Macrophytes

Phosphorus is a macronutrient and essential for plant growth, which explains its extensive use in agricultural applications and problematic nature for algal growth. However, macrophytes, in addition to algae, can provide appreciable removal of dissolved phosphorus from stormwater given that enough planted area is available and hydraulic residence time is sufficient (Kadlec, 2005). One of the major sources of removal by macrophytes is during the initial states of wetland development when plants are still “growing in” to achieve full coverage. This removal can decrease sharply to a much lower steady state amount after complete coverage has occurred (Kadlec, 2005). Some further inference from this finding would support the decreased importance of removal by macrophytes during times of plant dormancy in seasonal climates. In another sense, macrophytes serve a critical role where the harvest of biomass or accretion of dead plant material with associated nutrients as humus represent “sustainable”

removal mechanisms (Kadlec and Wallace, 2009), as opposed to temporary sequestration where the removal mechanism can be reversible and act as a phosphorus source at other times (Kadlec, 2005). It is important to note, however, that the sustainable nutrient sequestration in humus represents only 10 – 20% of the nutrients removed from stormwater by the living plants (Kadlec, 2005). Overall, for stormwater systems where space is at a premium, phosphorus removal by macrophytes probably does not represent a major dependable process, but rather a seasonal or temporary augmentation to other mechanisms. This conclusion is supported by Drizo et al. (2000) and by Naylor et al. (2003), who suggested an unplanted wetland unit process where substrates were used that were not optimal for plant growth but were more optimal for phosphorus removal by sorption. Thus, phosphorus removal by macrophytes was not a central part of this study, although macrophytes will likely be a valuable component of a final UWF design by providing necessary organic carbon and beneficial humic acid for the rejuvenation process (Brady and Weil, 2002) and improving the overall aesthetic of the UWF.

Phosphorus Removal by Physical Filtration

Secondly, physical filtration can remove phosphorus already attached to sediments or phosphorus in organics carried by stormwater by of the sediment or organic material by wetlands. In addition to gravitational sedimentation and physical exclusion due to particle size and pore space, the presence of macrophytes, especially in free surface wetlands may promote physical filtration by providing structure both in terms of living and dead organic matter for particles to adhere to (Anderson and Mitsch, 2006). The ability of wetlands versus ponds to filter lighter and smaller materials provides some additional benefit. However, there are some drawbacks to this process. Anaerobic conditions are typical in wetlands, and under these conditions, phosphorus release from settled upland sediments can occur (Masscheleyn et al., 1992; Coveney et al., 2002; Aldous et al., 2007). This finding highlights a potential benefit of maintaining an unnaturally oxidized state throughout the constructed wetland. In addition to phosphorus, some studies show that the ability of wetlands to filter organics is somewhat lower than might be expected (Kadlec, 2005). Substrate clogging of vertical subsurface flow constructed wetlands has also been cited as a major problem associated with physical removal, with one of the side effects being decreased oxygen to sediment, further exacerbating the problem of dissolved phosphorus being released from storage in sediments (Langergraber et al.,

2003). While sedimentation may be more important to surface flow wetlands, for the reasons stated here and since retention ponds already show a great ability for sedimentation, the approach adopted in this study involved restricting the flow of suspended solids into subsurface wetlands. Instead, efforts are concentrated on removal mechanisms for dissolved phosphorus that the ponds currently demonstrate less ability to treat.

Phosphorus Removal by Sorption

Thirdly, substrate sorption, a general term that incorporates both chemisorption and precipitation due to the practical difficulty in separating the two, is another mechanism in constructed wetlands capable of removing appreciable amounts of phosphorus (Bubba et al., 2003). The shorter retention times required for this removal process (Zhu et al., 2003) along with the specific ability to remove dissolved phosphorus make sorption appealing for minimizing BMP footprint for urban areas and are thus the focus of this study. To describe this removal process in technical terms, the chemisorption reaction is a ligand exchange reaction, involving replacement of a hydroxide ion located on a particle surface by a dissolved phosphate anion. The particle surface is often a Fe or Al oxyhydroxides. Chemisorption is distinct but not unrelated to the precipitation reaction, where the phosphate ion combines with a cation, sometimes Fe, to form a very insoluble precipitate (McBride, 1994). The sorption process is the focus of study for several reasons. First, it is generally a very fast process with theoretical kinetics in the range of minutes or seconds (McBride, 1994) and experimental studies showing equilibrium times for sorption of as little as 20 minutes (Oguz, 2005). This low reaction time allows for sustained efficacy even at very high flow rates, which enable smaller wetlands and promote aerobic conditions. Secondly, sorption is a major mechanism for removal of dissolved phosphorus (Comings et al., 2000; Maynard et al., 2009). In addition to dissolved reactive phosphorus, some dissolved organic phosphorus may be adsorbed by these processes as well (Anderson and Magdoff, 2005). Two important caveats to the sorption removal process is its finite capacity and documented reversibility under certain conditions (McBride, 1994). As described above for natural wetlands, the phosphorus sorption process may be reversible if the constructed wetland becomes anaerobic and reduced. Under anaerobic conditions, Fe^{3+} can serve as a terminal electron acceptor for microbial metabolism, reducing Fe^{3+} to a more soluble Fe^{2+} and simultaneously releasing the phosphorus that was adsorbed to the Fe^{3+} (Lovley, 1991). This mechanism may also be at work

in the benthic regions of retention ponds and explain the “confusing” results of several authors concerning the phosphorus export of wetlands and retention ponds during certain periods (Calder et al., 2006; Holley et al., 2007). Although decreases in bulk water concentration have sometimes been implicated for the release of phosphorus, results from Zhu et al. (2003) contradict such implication in favor of the redox theory. Ironically, one limitation may function to eliminate the other as the rejuvenation process, based on the release of phosphorus during anaerobic conditions and developed through this study, is a targeted attempt to remove the finite capacity limitation.

Variability in Removal Performance by Sorption Mechanisms

As discussed for studies of constructed wetlands in general, studies focusing on the sorption process alone include significant variability. Previous studies have submitted many potential factors to explain the variability in removal by sorption process (Table 1.3). Of the variables listed this study investigated flow rate (which is inversely proportional to retention time for a static treatment volume), changes in concentration, redox conditions, pH, wetland "age," spatial variations, and stopped-flow time which is somewhat analogous to an antecedent dry period. Regarding variability related to substrate, Cucarella and Renman (2009) reviewed various studies that used an empirical method, the batch isotherm experiment, to investigate and compare sorption performance of various substrates for phosphorus removal in wetlands. Some of the studies had also attempted to estimate performance lifetime for phosphorus removal by sorption based on the isotherm information. The review concludes that a high degree of dependence on external variables such as concentration and loading ratios limits the isotherm approach for estimating phosphorus removal performance of potential substrates. This conclusion is probably especially relevant to materials used in treating stormwater, as concentrations are much lower and potentially more variable than wastewater streams.

Table 1.3 – Variables of interest for explaining variability in phosphorus removal

Variable	Effect on Removal	Pertinent Studies
Redox Potential	Reducing conditions favor phosphorus release from sediments and decreased overall removal	(Redshaw et al., 1990; Carleton et al., 2000)
Retention Time	Possible non-linear correlation with removal	(Chick and Mitchell, 1995; Shilton et al., 2005; Line et al., 2008)
Flow Rate	Increased flow rate may favor more adsorption, hence more removal	(Farahbakhshazad and Morrison, 2003)
Fe in Substrate	Increased concentrations favored more sorption lifetime and more removal	(Naylor et al., 2003; Arias and Brix, 2005; Shilton et al., 2005; Maynard et al., 2009)
pH	Several values have been presented as optimal for removal	(Redshaw et al., 1990; Shilton et al., 2005)
Wetland Age	Substantial decrease in removal with age	(Redshaw et al., 1990; Prochaska and Zouboulis, 2006)
Temperature	Increased temperature may favor increased removal	(Redshaw et al., 1990)
Substrate Size	Smaller Particles provided increased sorption, hence increased removal	(Zhu et al., 2003; Maynard et al., 2009)
Stopped-Flow Time	Longer periods of stopped-flow may increase removal possibly due to a kinetically limited diffusion process	(Farahbakhshazad and Morrison, 2003)
Influent P Concentration	Higher influent concentrations may favor increased removal, also possible importance of a thermodynamic gradient between adsorbed and dissolved phosphorus	(Schueler, 1996; Drizo et al., 2000)

First-order vs. Physical-process Models for Phosphorus Removal in Constructed Wetlands

There has been a general historical precedent in the applied science of structural BMPs including stormwater wetlands of modeling performance as a first-order or black-box model with a set removal percentage that does not change based on location, influent water characteristics, or time. The first-order model is typified by the Virginia Stormwater Management Handbook (VDCR, 1999) among other documents and published papers (Zhang et al., 2008). While this

approach might be convenient, it can also be very misleading, and there is significant evidence, including a study by Kadlec (2000) to suggest that a first-order model does not fully explain the process. First, the large range of reported removal percentages alone provides doubt to the suitability of relying on some average value to represent all wetlands under all circumstances.

While variability outside of a first-order model most likely occurs from several removal processes, the numerous variables cited above for sorption processes alone indicate the presence of multiple factors that would influence a phosphorus removal percentage. Several studies including Maynard et al. (2009) have shown that removal by sorption in constructed wetlands decreases over time. Many of these variables, such as pH and influent concentration, remain relevant even if the BMP design was constructed the same every time. If design or construction is not the same then almost all of these variables could become important. Some studies have moved away from the first-order model in favor of analyses based on the thermodynamics and kinetics associated with removal processes. Additional studies at least recognize a future state of sorption equilibrium (Redshaw et al., 1990; Oguz, 2005).

This "physical-process" approach is not entirely novel. Soil chemists have been analyzing sorption processes based on thermodynamic and kinetic models for years (McBride, 1994). Two techniques used by soil chemists to describe sorption behavior in soils are the isotherm curve and the breakthrough curve. The isotherm curve relates the mass of adsorbed material per mass of substrate at various concentrations (thermodynamics), while the breakthrough curve describes the time it takes for the effluent concentration of the adsorbed constituent in a soil column to reach the concentration of the influent (thermodynamics and kinetics). Bubba et al. (2003) used the isotherm approach to study various substrates for phosphorus sorption in wetlands while Arias and Brix (2005) attempted to use this parameter as a main performance indicator for wetlands. Its success was probably limited in part by not including the historically adsorbed P as discussed by Zhang et al. (2009). Georgantas (2006) used isotherm and kinetic analysis including x-ray diffraction to study sorption on phosphorus adsorbing substrates. Thermodynamic and kinetic evaluation of substrate sorption has also been included in a number of additional studies (Zhu et al., 2003; Zeng et al., 2004; Namasivayam et al., 2005).

Rejuvenation of wetland performance for sustainable water quality treatment

Although various effective phosphorus removal processes in constructed wetlands exist, these processes are usually finite or reversible paths. Some “sustainable” paths have been suggested, specifically organic accretion (Kadlec, 2005); however, the percentage retained is low and reducing conditions have demonstrated the ability to release sequestered phosphorus from sediment. This lack of permanent sequestration and occurrence of reducing conditions may strongly affect phosphorus removal efficacy of the entire wetland system (Komatsu et al., 2006). The lack of a reliable and efficient, permanent removal mechanism along with the finite capacity of removal by sorption processes has led to the development of the rejuvenation strategy through this research project. The ideal rejuvenation procedure as part of the overall UWF concept consists of four main steps: 1) the reduction of iron and accompanying release of previously sequestered phosphorus into solution; 2) the temporary removal of water from the wetland; 3) aeration and precipitation of Fe-phosphates; and 4) the reestablishment of sorption capacity from Fe⁰ contained in the wetland substrate. A decreased redox potential has shown great ability to release sequestered phosphorus into solution in natural wetlands as previously discussed. Since Fe-oxyhydroxides, a significant adsorption surface for phosphorus, are redox active and redox active under natural conditions in wetlands, this mechanism might function as part of a removal process. With water contained in the wetland, facilitated reducing conditions could reduce Fe, releasing adsorbed phosphorus in much higher concentrations than typical, even for stormwater. Then, the resident water with high concentrations of dissolved phosphorus and iron is removed either for direct use or to promote a precipitation of Fe-phosphates before the water is returned to the wetland. This precipitated Fe-P solid allows for efficient transport and productive use elsewhere such as fertilizer for agriculture, lawns, or ornamental plants.

Microbial Nature of Fe-Reduction in Constructed Wetlands

The phosphorus desorption process associated with reducing conditions has also been associated directly with Fe (Redshaw et al., 1990; Zhang et al., 2003; Komatsu et al., 2006). This desorption process may, however, be significantly slower than the adsorption process due to the fact that it is microbial driven while the adsorption process occurs abiotically. The process of microbial reduction of Fe is well understood by microbiologists, as indicated by the extensive review of these processes provided by Lovley (1991). Generalizing the findings made through

the field of biology for this application provides a series of requirements for this microbial process to occur efficiently. The reduction of Fe by microbes is a direct causal effect of their metabolism, where Fe serves as the terminal electron acceptor for electrons gained from the microbes' energy source, typically organic carbon (Martinko and Madigan, 2006). Martinko and Madigan (2006) also describe the requirements for effective microbial metabolism to take place, including: 1) the existence and presence of a microbe capable of the stated microbial process; 2) a bioavailable terminal electron donor, usually organic carbon; 3) the presence of a terminal electron acceptor such as Fe or an intermediate electron shuttle such as humic acid; and 4) favorable environmental conditions for the particular microbe(s) to thrive.

Conditions Necessary for Microbial Growth in Constructed Wetlands

The existence of microbes capable of reducing Fe is well documented and has been observed in many places including aquatic sediments (Lovley et al., 1991) and “waterlogged soils, bogs, and anoxic lake sediments” (Martinko and Madigan, 2006). Also, the decrease in concentration of an electron donor has been shown to correspond to the growth of known Fe-reducing bacteria (Lovley, 1991). In the study cited, acetate was used, but other forms of naturally occurring organic carbon also indicate suitability and acetate is a common byproduct of many natural fermentation processes (Martinko and Madigan, 2006). The criticality of this organic carbon-source to Fe reduction may explain some of the decrease in phosphorus removal by constructed wetlands seen between indoor studies where organic carbon may not be present and pilot studies where organic carbon is likely to be present. In the context of this research, the presence of a electron acceptor, Fe, can be assumed to a degree, although the bioavailability of that Fe to the microbes deserves further consideration (Martinko and Madigan, 2006). Some Fe-oxyhydroxides in the wetland may be located in micropores and other spaces that allow for the diffusion of phosphorus for adsorption, but disallow access by microbes for direct use as a terminal electron acceptor.

Electron Shuttles to Speed and Increase Total Phosphorus Release from Sediments

The presence of an electron shuttle may overcome this lack of bioavailability by serving as a terminal electron acceptor for the microbe, and then reaching the Fe locations unavailable to the microbe and reduce them abiotically. The efficacy of humic acids as such an electron shuttle

has been documented extensively (Lovley et al., 1998; Nevin and Lovley, 2000; Chen et al., 2003; Kappler et al., 2004; Rakshit et al., 2009) and may have a significant role in both the rate and extent of Fe reduction in saturated soils and transported sediments. The viability of this process has also been documented specifically for natural wetlands (Coates et al., 1998). In addition to electron shuttling, humic acids have been shown to increase the rate of Fe bioreduction by complexation with Fe to dissolve Fe^{3+} directly (Rakshit et al., 2009). The last requirement of the metabolic process, suitable environmental conditions, may also function to enhance metabolic rate for Fe reducers. Kostka et al. (1996) reported optimal conditions for Fe bioreduction in smectite clays as pH of 5 to 6 and a temperature of 25-37 C.

Bulk Removal of Phosphorus from the Reduced Wetland

Once microbial reduction releases phosphorus from the substrate, it is necessary to remove it from the filter, preferably through a management process that is as quick and inexpensive as possible. A promising possibility for this requirement is the precipitation of Fe-phosphates. The microbial reduction step of the rejuvenation process provided not only a high concentration of dissolved P, but also a high concentration of dissolved Fe. This condition of both a high concentration of Fe and a high concentration of phosphorus may provide an excellent starting condition for the formation of Fe-phosphate. Reduced Fe (Fe^{2+} or ferrous iron) has a much higher solubility limit than oxidized Fe (Fe^{3+} or ferric iron). Thus, with temporary removal and oxidation of the water contained in the wetland it may be possible to precipitate Fe-phosphates. Hupfer et al. (1998) indicated that for benthic sediments in a eutrophic mining lake, thermodynamic calculations favored the formation of vivianite, a hydrated Fe-phosphate. The presence of Fe-phosphates including vivianite has been documented in studies of flocculated wastewater sludges (Frossard et al., 1997) and in wetland sediments (Kaplan, 2004). Thermodynamic probability may favor the formation of strengite versus that of vivianite for conditions similar to those seen in the UWF rejuvenation process (Lindsay, 1979).

Reestablishing Fe-oxyhydroxides in the Wetland for Continued Sorption Capacity

The third step to rejuvenation involves restoring sorption capacity in the sediment that was lost due to the reduction and removal of Fe in the first step. Inclusion of Fe^0 (zero-valent iron), may accomplish this restoration in the form of cast iron shavings serving as some

percentage of the substrate. Under aerobic conditions, during filtration, the Fe^0 will oxidize and provide sorption capacity in the form of additional Fe-oxyhydroxides. Under anaerobic conditions during rejuvenation, the underlying Fe^0 will remain while bacteria reduce Fe^{3+} to Fe^{2+} . This underlying Fe^0 represents a long-term reservoir for providing Fe to the system after each successive rejuvenation cycle. Luederitz and Gerlach (2002) used iron filings and found them to be more beneficial for phosphorus removal than Ca-soil additions. Kaplan (2004) found that additions of Fe^0 studied in a dynamic natural environment created significant additional sorption sites and also provided evidence for possibility of Fe^0 additions forming sorption sites across the soil substrate in bulk. In addition, Maynard et al. (2009) found evidence that redox transformation of Fe in saturated constructed wetland sediments favored the formation of additional sorption sites. Heal et al. (2005) studied the use of ochre from mine drainage treatments as an additive to constructed wetlands for increasing sorption capacity; however, since ochre consists mainly of oxidized Fe, it would not have the ability to persist through rejuvenation cycles and would require replenishment after each cycle. For this reason, Fe^0 is as an ideal candidate for replacing iron coatings on substrate and was a focus of investigation in this study.

Aside from enabling sorption capacity rejuvenation, there may be additional benefits of including zero-valent iron through its capacity as a strong reducer. Fe^0 has been studied and proven successful for the remediation of hexavalent chrome, other heavy metals including lead and copper, hydrocarbons, and possibly viruses (Puls et al., 1999; Janda et al., 2004; Daniels et al., 2006; Noubactep and Woafu, 2008) in groundwater and surface water applications. One study of a groundwater application of Fe^0 additions for the removal of arsenic from groundwater found that P in treatment influent water competed effectively for sorption sites and that the iron nails used in the study may have had limited effectiveness due to limited contact with the water (Chiew et al., 2009). This finding favors the use of finer materials for additions to substrate.

References

- Abelson, P. H. 1999. A potential phosphate crisis. *Science* 283 (5410): 2015.
- Aldous, A. R., C. B. Craft, S. J. Carla, M. J. Barry, and B. B. Leslie. 2007. Soil phosphorus release from a restoration wetland, Upper Klamath Lake, Oregon. *Wetlands* 27 (4): 1025–1035.
- Anderson, B. H., and F. R. Magdoff. 2005. Relative movement and soil fixation of soluble organic and inorganic phosphorus. *J. Environ. Qual.* 34 (6): 2228-2233.
- Anderson, C. J., and W. J. Mitsch. 2006. Sediment, carbon, and nutrient accumulation at two 10-year-old created riverine marshes. *Wetlands* 26 (3):
- Arias, C. A., H. Brix, and N. H. Johansen. 2003. Phosphorus removal from municipal wastewater in an experimental two-stage vertical flow constructed wetland system equipped with a calcite filter. *Water Sci. Technol.* 48 (5): 51-58.
- Arias, C. A., and H. Brix. 2005. Phosphorus removal in constructed wetlands: can suitable alternative media be identified? *Water Sci. Technol.* 51 (9): 267-273.
- Atasoy, M., R. B. Palmquist, and D. J. Phaneuf. 2006. Estimating the effects of urban residential development on water quality using microdata. *J. Environ. Manage.* 79: 399-408.
- Axt, J. R., and M. R. Walbridge. 1999. Phosphate removal capacity of palustrine forested wetlands and adjacent uplands in Virginia. *Soil Sci. Soc. Am. J.* 63 (4): 1019-1031.
- Baker, B. J., K. W. King, and H. A. Torbert. 2007. Runoff losses of dissolved reactive phosphorus from organic fertilizer applied to sod. *Trans. ASABE* 50 (2): 449-454.
- Birch, G. F., C. Matthai, M. S. Fazeli, and J. Suh. 2004. Efficiency of a constructed wetland in removing contaminants from stormwater. *Wetlands* 24 (2): 459-466.
- Boesch, D. F., R. B. Brinsfield, and R. E. Magnien. 2001. Chesapeake bay eutrophication: scientific understanding, ecosystem restoration, and challenges for agriculture. *J. Environ. Qual.* 30: 303-320.
- Brady, N. C., and R. R. Weil. 2002. *The Nature and Properties of Soils*. Upper Saddle River, N.J.: Prentice Hall.
- Bubba, M. d., C. A. Arias, and H. Brix. 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. *Water Res* 37 (14): 3990-3400.

- Calder, N., B. C. Anderson, and D. G. Martin. 2006. Field investigation of advanced filtration for phosphorus removal from constructed treatment wetland effluents. *Environ. Technol.* 27 (10): 1063-1071.
- Camargo, J. A., and A. Alonso. 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. *Environ. Int.* 32: 831-849.
- Carleton, J. N., T. J. Grizzard, A. N. Godrej, H. E. Post, L. Lampe, and P. P. Kenel. 2000. Performance of a constructed wetlands in treating urban stormwater runoff. *Water Environ. Res.* 72 (3): 295-304.
- Chen, J., B. Gu, R. Royer, and W. Burgos. 2003. The roles of natural organic matter in chemical and microbial reduction of ferric iron. *The Science of the Total Environment* 307: 167-178.
- Chick, A. J., and D. S. Mitchell. 1995. A pilot study of vertical flow wetlands at Coffs Harbour, New South Wales, Australia. *Water Sci. Technol.* 32 (3): 103-109.
- Chiew, H., M. L. Sampson, S. Huch, S. Ken, and B. C. Bostick. 2009. Effect of groundwater iron and phosphate on the efficacy of arsenic removal by iron-amended biosand filters. *Environ. Sci. Technol.* 43 (16): 6295-6300.
- Chorus, I., and J. Bartram. 1999. Toxic Cyanobacteria in Water: A Guide to their Public Health Consequences, Monitoring, and Management. London & New York: E & FN Spon.
- Coates, J. D., D. J. Ellis, E. L. Blunt-Harris, C. V. Gaw, E. E. Roden, and D. R. Lovley. 1998. Recovery of humic-reducing bacteria from a diversity of environments. *Appl. Environ. Microbiol.* 64 (4): 1504-1509.
- Comeau, Y., J. Brisson, J. P. Réville, C. Forget, and A. Drizo. 2001. Phosphorus removal from trout farm effluents by constructed wetlands. *Water Sci. Technol.* 44: 55-60.
- Comings, K. J., D. B. Booth, and R. R. Horner. 2000. Storm water pollutant removal by two wet ponds in Bellevue, Washington. *J. Environ. Eng.* 126 (4): 321-330.
- Coveney, M. F., D. L. Stites, E. F. Lowe, and R. C. Battoe. 2002. Nutrient removal from eutrophic lake water by wetland filtration. *Ecol. Eng.* 19: 141-159.
- Cucarella, V., and G. Renman. 2009. Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments - A comparative study. *J. Environ. Qual.* 38: 381-392.
- Daniels, J. L., G. P. Das, and M. T. S. Hernandez. 2006. Coastal pollution mitigation with lime and zero valent iron. *Marine Georesources and Geotechnology* 24: 183-191.

- Dowling, D. C. 2009. Virginia Stormwater Management Program (VSMP) Permit Regulations. 4VAC50-60. Richmond, VA: Virginia Soil and Water Conservation Board, Virginia Code Commission.
- Drizo, A., C. A. Frost, J. Grace, and K. A. Smith. 2000. Phosphate and ammonium distribution in a pilot-scale constructed wetland with horizontal subsurface flow using shale as a substrate. *Water Res* 34 (9): 2483-2490.
- Farahbakhshazad, N., and G. M. Morrison. 2003. Phosphorus removal in a vertical upflow constructed wetland system. *Water Sci. Technol.* 48 (5): 43-50.
- Fisher, M. M., and K. R. Reddy. 2001. Phosphorus flux from wetland soils affected by long-term nutrient loading. *J. Environ. Qual.* 30: 261-271.
- Fisher, T. R., E. R. Peele, J. W. Ammerman, and L. W. Harding. 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Mar. Ecol. Prog. Ser.* 82 (1): 51-63.
- Frossard, E., J. P. Bauer, and F. Lothe. 1997. Evidence of vivianite in FeSO₄-flocculated sludges. *Water Res* 31 (10): 2449-2454.
- Georgantas, D. A., V. M. Matsis, and H. P. Grigoropoulou. 2006. Soluble phosphorus removal through adsorption on spent alum sludge. *Water Sci. Technol.* 27 (10): 1081-1088.
- Hammer, D. 1992. Designing constructed wetlands systems to treat agricultural nonpoint source pollution. *Ecol. Eng.* 1 (1/2): 49-82.
- Heal, K. V., K. E. Dobbie, E. Bozika, H. McHaffie, A. E. Simpson, and K. A. Smith. 2005. Enhancing phosphorus removal in constructed wetlands with ochre from mine drainage treatment. *Water Sci. Technol.* 51: 275-282.
- Hogan, D. M., and M. R. Waldbridge. 2007. Best management practices for nutrient and sediment retention in urban stormwater runoff. *J. Environ. Qual.* 36: 386-395.
- Holley, J. W., R. M. Chambers, and G. S. Hancock. 2007. *Water quality in headwater streams: A test of best management practices*. Virginia/West Virginia Water Research Symposium. Blacksburg, VA: Virginia Water Resources Research Center.
- Hunt, W. F., and A. Wossink. 2003. The Economics of Structural Stormwater BMPs in North Carolina. UNC-WRRI-2003-344. Raleigh, NC: UNC-WRRI.
- Hupfer, M., P. Fischer, and K. Friese. 1998. Phosphorous retention mechanisms in the sediment of an eutrophic mining lake. *Water Air Soil Pollution* 108: 341-352.

- Janda, V., P. Vasek, J. Bizova, and Z. Belohlav. 2004. Kinetic models for volatile chlorinated hydrocarbons removal by zero-valent iron. *Chemosphere* 54: 917-925.
- Jones, H. P., and O. J. Schmitz. 2009. Rapid Recovery of Damaged Ecosystems. *Plos ONE* 4 (5): e5653.
- Kadlec, R. H. 2000. The inadequacy of first-order treatment wetland models. *Ecol. Eng.* 15: 105-119.
- Kadlec, R. H. 2005. Phosphorus removal in emergent free surface wetlands. *J. Environ. Sci. Health, Pt. A: Environ. Sci. Eng. Toxic Hazard. Subst. Control* 40 (6): 1293-1306.
- Kadlec, R. H., and S. D. Wallace. 2009. *Treatment Wetlands*. Boca Raton, FL: CRC Press.
- Kaplan, D. 2004. Enhanced contaminant desorption induced by phosphate mineral additions to sediment. *Environ. Sci. Technol.* 38 (11): 31-53.
- Kappler, A., M. Benz, B. Schink, and A. Brune. 2004. Electron Shuttling via humic acids in microbial iron (III) reduction in a freshwater sediment. *FEMS Microbiol. Ecol.* 47: 85-92.
- Keppler, A. M., and J. F. Martin. 2008. Investigating the performance of a laboratory-scale ecological system to treat dairy wastewater. *Trans. ASABE* 51 (5): 1837-1846.
- Komatsu, E., T. Fukushima, and H. Shiraishi. 2006. Modeling of P-dynamics and algal growth in a stratified reservoir - mechanisms of P-cycle in water and interaction between overlying water and sediment. *Ecol. Model.* 197 (3/4): 331-349.
- Kostka, J. E., J. W. Stucki, K. H. Nealson, and J. Wu. 1996. Reduction of structural Fe(III) in smectite by a pure culture of shewanella putrefaciens strain MR-1. *Clays Clay Miner.* 44 (4): 522-529.
- Langergraber, G., R. Haberl, J. Laber, and A. Pressl. 2003. Evaluation of substrate clogging processes in vertical flow constructed wetlands. *Water Sci. Technol.* 48 (5): 25-34.
- Lantzke, I. R., A. D. Heritage, G. Pistillo, and D. S. Mitchell. 1998. Phosphorus removal rates in bucket size planted wetlands with a vertical hydraulic flow. *Water Res.* 32 (4): 1280-1286.
- Lantzke, I. R., D. S. Mitchell, A. D. Heritage, and K. P. Sharma. 1999. A model of factors controlling orthophosphate removal in planted vertical flow wetlands. *Ecol. Eng.* 12 (1): 93-105.
- Lijklema, L. 1995. Development and eutrophication: experiences and perspectives. *Water Sci. Technol.* 31 (9): 11-15.
- Lindsay, W. L. 1979. *Chemical Equilibria in Soils*. New York: John Wiley and Sons.

- Line, D. E., G. D. Jennings, M. B. Shaffer, J. Calabria, and W. F. Hunt. 2008. Evaluating the effectiveness of two stormwater wetlands in North Carolina. *Trans. ASABE* 51 (2): 521-528.
- Lovely, D. R., E. J. P. Phillips, and D. J. Lonergan. 1991. Enzymatic versus nonenzymatic mechanisms for Fe(III) reduction in aquatic sediments. *Environ. Sci. Technol.* 25 (6): 1062-1067.
- Lovley, D. R. 1991. Dissimilatory Fe(III) and Mn(IV) Reduction. *Microbiological Reviews* 55 (2): 259-287.
- Lovley, D. R., J. L. Fraga, E. L. Blunt-Harris, L. A. Hayes, E. J. P. Phillips, and J. D. Coates. 1998. Humic Substances as a Mediator for Microbially Catalyzed Metal Reduction. *Acta Hydrochim. Hydrobiol.* 26: 152-157.
- Luederitz, V., E. Eckert, M. Lange-Weber, A. Lange, and R. M. Gersberg. 2001. Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. *Ecol. Eng.* 18: 157-171.
- Luederitz, V., and F. Gerlach. 2002. Phosphorous removal in different constructed wetlands. *Acta Biotechnology* 22 (1/2): 91-99.
- Martinko, J. M., and M. T. Madigan. 2006. *Brock Biology of Microorganisms*. Pearson, Prentice Hall.
- Masscheleyn, P. H., J. H. Pardue, R. D. DeLaune, and W. H. Patrick, Jr. 1992. Phosphorus release and assimilatory capacity of two lower Mississippi Valley freshwater wetland soils. *Water Resources Bulletin* 28 (4): 763-773.
- Maynard, J. J., A. T. O'Geen, and R. A. Dahlgren. 2009. Spatial relationships of phosphorus sorption in a seasonally saturated constructed wetland soil. *Soil Sci. Soc. Am. J.* 73 (5): 1741-1753.
- McBride, M. B. 1994. *Environmental Chemistry of Soils*. New York, NY: Oxford.
- Mitsch, W. J., and J. G. Gosselink. 2000. *Wetlands*. New York, NY: Wiley.
- Namasivayam, C., A. Sakoda, and M. Suzuki. 2005. Removal of phosphate by adsorption onto oyster shell powder - kinetic studies. *J. Chem. Technol. Biotechnol.* 80 (3): 356-358.
- Naylor, S., J. Brisson, M. A. Labelle, A. Drizo, and Y. Comeau. 2003. Treatment of freshwater fish farm effluent using constructed wetlands: the role of plants and substrate. *Water Sci. Technol.* 48 (5): 215-222.

- Nevin, K. P., and D. R. Lovley. 2000. Potential for nonenzymatic reduction of Fe(III) via electron shuttling in subsurface sediments. *Environ. Sci. Technol.* 34: 2472-2478.
- Noubactep, C., and P. Woaf. 2008. Elemental Iron for Better Drinking Water in Rural Areas of Developing Countries. Uranium, Mining and Hydrogeology. Springer Berlin Heidelberg.
- Novotny, V. 2003. *Water Quality*. Hoboken, NJ: John Wiley and Sons, Inc.
- Oguz, E. 2005. Thermodynamic and kinetic investigations of PO adsorption on blast furnace slag. *J. Colloid Interface Sci.* 281 (1): 62-67.
- Osborne, L. L., and M. J. Wiley. 1988. Empirical relationships between land use/cover and stream water quality in an agricultural watershed. *J. Environ. Manage.* 26: 9-27.
- Parry, R. 1998. Agricultural phosphorous and water quality: A US environmental protection agency perspective. *J. Environ. Qual.* 27: 258-261.
- Paul, M. J., and J. L. Meyer. 2001. Streams in the urban landscape. *Annu. Rev. Ecol. Syst.* 32: 333-365.
- Prochaska, C. A., and A. I. Zouboulis. 2006. Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate. *Ecol. Eng.* 26 (3): 293-303.
- Puls, R. W., C. J. Paul, and R. M. Powell. 1999. The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test. *Appl. Geochem.* 14: 989-1000.
- Rakshit, S., M. Uchimiya, and G. Sposito. 2009. Iron(III) bioreduction in soil in the presence of added humic substances. *Soil Sci. Soc. Am. J.* 73 (1): 65-71.
- Reddy, K. R., R. H. Kadlec, E. Flaig, and P. M. Gale. 1999. Phosphorus retention in streams and wetlands: a review. *Critical Review is Environmental Science and Technology* 29 (1): 83-146.
- Redshaw, C. J., C. F. Mason, C. R. Hayes, and R. D. Roberts. 1990. Factors influencing phosphate exchange across the sediment-water interface of eutrophic reservoirs. *Hydrobiologia* 192: 133-245.
- Reed, S. C., and D. Brown. 1995. Subsurface flow wetlands: A performance evaluation. *Water Environ. Res.* 67 (2): 244-248.

- Regimi, T. P., A. L. Thompson, and D. M. Sievers. 2003. Comparative studies of vegetated and non-vegetated submerged-flow wetlands treating primary lagoon effluent. *Trans. ASAE* 46 (1): 17-27.
- Rohlich, G. A. 1969. *Eutrophication: Causes, Consequences, Correctives*. Washington, DC: National Academy of Sciences.
- Russell, M. J., D. E. Weller, T. E. Jordan, K. J. Sigwart, and K. J. Sullivan. 2008. Net anthropogenic phosphorus inputs: spatial and temporal variability in the Chesapeake Bay region. *Biogeochemistry* 88: 285-304.
- Sano, D., A. Hodges, and R. Degner. 2005. Economic Analysis of Water Treatments for Phosphorus Removal in Florida. Gainesville, FL: Florida Cooperative Extension Service.
- Schueler, T. R. 1996. Irreducible pollutant concentrations discharged from urban BMPs. *Watershed Protection Techniques 2*: 369-372.
- Shilton, A., S. Pratt, A. Drizo, B. Mahmood, S. Banker, L. Billings, S. Glenny, and D. Luo. 2005. 'Active' filters for upgrading phosphorus removal from pond systems. *Water Sci. Technol.* 51: 111-116.
- Shumway, S. E. 1990. A review of the effects of algal blooms on shellfish and aquaculture. *Journal for the World Aquaculture Society* 21: 65-104.
- Simeral, K. D. 1998. Using constructed wetlands for removing contaminants from livestock wastewater. A-5-98. Columbus: The Ohio State University Extension Office.
- Smith, J. T., W. F. Hunt, and S. Jadlocki. 2005. *Conversion of an urban pond to a water quality treatment pond*. World Water and Environmental Resources Congress. Anchorage, AK: ASCE.
- Strecker, E. W., M. M. Quigley, B. R. Urbonas, and J. J. Jones. 2001. Determining urban storm water BMP effectiveness. *Journal of Water Resources Planning and Management* 127 (3): 144-149.
- Swenson, K., and D. Catchpoole. 2000. After devastation...the recovery. *Creation ex nihilo*. 22 (2): 33-37.
- USDA. 1986. Urban Hydrology for Small Watersheds. Technical Release No. 55. Washington, DC: Soil Conservation Service, US Government Printing Office.

- USEPA. 1974. The Relationships of Phosphorus and Nitrogen to the Trophic State of Northeast and North-Central Lakes and Reservoirs. Working Paper No. 23. Corvallis, OR: US Environmental Protection Agency, Office of Water.
- USEPA. 1983. Results of the Nationwide Urban Runoff Program. EPA 832-R-83-112. Washington, DC: US Environmental Protection Agency, Office of Water.
- USEPA. 2000. Nutrient Criteria Technical Guidance Manual. EPA-822-B00-001. Washington, DC: US Environmental Protection Agency, Office of Water.
- USEPA. 2002. Urban Stormwater BMP Performance Monitoring. EPA 821-B-02-001. Washington, DC: US Environmental Protection Agency, Office of Water.
- VDCR. 1999. Virginia Stormwater Management Handbook. Richmond, VA: Department of Conservation and Recreation, Division of Soil and Water Conservation.
- Ward, A. D., and S. W. Trimble. 2004. *Environmental Hydrology*. Boca Raton, FL: Lewis Publishers.
- WEF. 1998. Urban Runoff Quality Management. Manual of Practice No. 87. Reston, VA: ASCE.
- Wheeler, S. M., and T. Beatley. 2004. *The Sustainable Urban Development Reader*. New York, NY: Routledge.
- Winter, J. G., and H. C. Duthie. 2000. Export coefficient modeling to assess phosphorus loading in an urban watershed. *Journal of the American Water Resources Association* 36 (5): 1053-1061.
- Zeng, L., X. Li, and J. Liu. 2004. Adsorptive removal of phosphate from aqueous solutions using iron-oxide tailings. *Water Res.* 38 (5): 1318-1326.
- Zhang, W., G. O. Brown, D. E. Storm, and H. Zhang. 2008. Fly-ash-amended sand as a filter media in bioretention cells to improve phosphorus removal. *Water Environ. Res.* 80 (6): 507-516.
- Zhang, W., J. W. Faulkner, S. K. Giri, L. D. Geohring, and T. S. Steenhuis. 2009. Evaluation of two langmuir models for phosphorus sorption of phosphorus-enriched soils in New York for environmental applications. *Soil Science* 174 (10): 523-530.
- Zhang, Y., X. Lin, and W. Werner. 2003. The effect of soil flooding on the transformation of Fe oxides and the adsorption/desorption behavior of phosphate. *J. Plant Nutr. Soil Sci.* 166 (1): 68-75.

Zhu, T., T. Maehlum, P. D. Jenssen, and T. Krogstad. 2003. Phosphorus sorption characteristics of a light-weight aggregate. *Water Sci. Technol.* 48 (5): 93-100.

Variability in adsorptive phosphorus removal by structural stormwater best management practices

S.E. Rosenquist, W.C. Hession, M.J. Eick, D.A. Vaughan

Abstract

Various best management practices (BMPs) utilizing sorption processes (SP) have demonstrated effectiveness for phosphorus (P) management in stormwater. However, the widespread use of these BMPs in urban areas has been limited by large land requirements and limited P removal capacity. Central to this study is the development of the urban wetland filter (UWF), a concept intended to overcome these limitations and provide a low-cost, easily implemented BMP that can meet urban P-management goals. Performance variation along with finite sorption capacity has limited the reliability of SP as a primary removal strategy. However, if variability were better-understood and capacity made renewable, sorption of P to substrates could provide the option of a more rapid and (with less required retention time) more space-efficient sustainable removal strategy than biological uptake. The goal of this study was to identify and model major sources of variability in P removal by sorption, enabling better prediction and optimization of sorption performance and ultimately the development of a small-footprint stormwater BMP with efficient P removal ability. Experiments were conducted in bench-scale reactors with an iron-oxide sand substrate. Results included a physical-process model developed by considering the thermodynamic and kinetic properties of SP. Significant sources of variability included, by order of importance, magnitude of a solution/substrate concentration gradient, length of the “antecedent dry period” between loadings, and pH. Most importantly, results indicate the critical importance of a thermodynamic gradient between solution P and previously adsorbed P to achieve continued removal.

Introduction

Eutrophication, driven largely by excess nutrients in surface runoff, is a significant problem in US surface waters (Parry, 1998). Eutrophication can cause environmental degradation and also has significant economic impacts on coastal fisheries and municipal drinking water supplies (Camargo and Alonso, 2006). Phosphorus (P) is often the target nutrient for preventing eutrophication because it is the limiting factor for algal growth in some saltwater and almost all freshwater systems (Fisher et al., 1992) and because it does not have a process analogous to denitrification to prevent buildup in surface water through transition to the atmosphere.

Urban areas are of particular interest for non-point source P management as adverse water quality has been correlated to both the density and speed of urbanization (Atasoy et al., 2006). Urban P loads can rival those of agricultural land uses (Paul and Meyer, 2001) and urban environments have unique constraints such as high land-value and rapid hydrologic response that complicate stormwater treatment. Traditional urban stormwater management often utilized dry detention ponds and focused on peak flow attenuation while doing little to address nutrient impacts. More recently, wet retention ponds designed with permanent pools have been introduced in an effort to address stormwater quality along with quantity (Carleton et al., 2000; Hogan and Waldbridge, 2007). These stormwater ponds are ubiquitous in the American urban landscape with an estimated 2.6 million such ponds across the contiguous US (Smith et al., 2002). Retention ponds provide some water quality treatment, mostly by sedimentation, but remove little dissolved phosphorus (DP) (Comings et al., 2000). However, retention ponds do provide a unique opportunity to extend available treatment time for the water retained. This extended treatment time can be utilized more productively by incorporating an add-on BMP positioned off-line from stormwater flow, optimized for removing DP, and continuously filtering retained water. This strategy is similar to one used by Coveney et al. (2002) with a wetland on Lake Apopka, but with a decentralized, smaller-scale approach.

Other BMP have been investigated for urban stormwater treatment, including stormwater wetlands (Carleton et al., 2000; Kadlec and Wallace, 2009) and have performed effectively, but land availability is a common limitation. Traditional designs are often land-intensive and not economically feasible in urban areas (Hunt and Wossink, 2003). Biological uptake followed by organic accretion in sediments is the typical strategy for long-term P removal in these BMP (Kadlec and Wallace, 2009) but it also drives the large land

requirements (Lantzke et al., 1999). This process is not, however, the only P removal process involved. Sorption processes (SP), mainly adsorption at stormwater concentrations, can effectively sequester DP and do so more rapidly than biological uptake (Kadlec and Wallace, 2009). A rapid removal mechanism can enable shorter residence times for treatment, increase allowable flow rates, and decrease required BMP size. However, reliance on SP for removal has limitations including large variability in performance and finite sorption capacity (USEPA, 2002). While some of this variability can be attributed to performance metrics, including volume reductions (Kadlec and Wallace, 2009) significant variability remains.

Though understood to be based on saturation processes (VDCR, 1999), P removal by BMPs that rely on SP is often conceptualized by practitioners as a first-order model with a constant removal percentage at stormwater concentrations (Carleton et al., 2000; Pant et al., 2001; Farahbakhshazad and Morrison, 2003; Naylor et al., 2003; Arias and Brix, 2005; Shilton et al., 2005). This removal percentage is assumed constant regardless of changes in internal parameters (such as substrate type, redox potential, and pH) or external parameters (such as flow rate and "antecedent dry period") that have been suspected of causing variation (McBride, 1994).

Alternatively, P removal by SP could be conceptualized with a physical-process model using the thermodynamic and kinetic principles associated with SP and the internal and external parameters subject to variation. Thermodynamics involved in P removal by SP are described by isotherm curves, which are used extensively in soil chemistry to provide often-published sorption capacities for various substrates. Isotherm curves represent the thermodynamic possibility for a reaction to occur based on the nature of the adsorbent and given concentration of the adsorbate (2007). Therefore, it is reasonable to conclude that influent concentration, representing the concentration of the adsorbate, as well as pH and P sorption history, representing the nature of the adsorbent, may function interactively to determine the thermodynamic probability of further P removal.

Kinetics associated with SP have been described by Arai and Sparks (Lovley, 1991) who divide the kinetics of specific adsorption into two reactions: 1) rapid (hours or less) adsorption limited by the ligand exchange process; and 2) slower (days to months) adsorption limited by diffusion into pore spaces and the subsequent enabling of further ligand exchange. Therefore, it is also reasonable to include diffusion-related variables such as filter age, flow rate, or the timing of loadings to predict P removal.

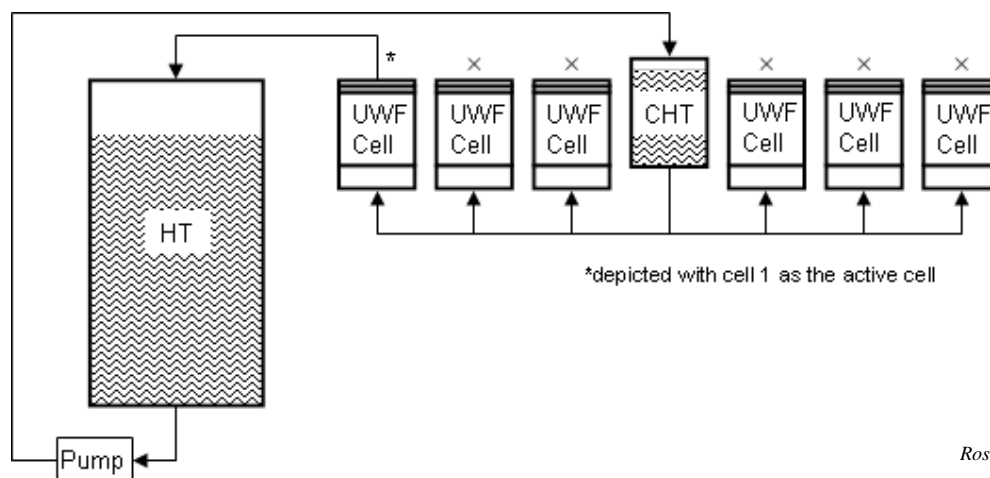
The objectives of this study were: 1) to validate DP removal by SP using iron-oxide sand substrate; 2) to identify major sources of variability in P removal by SP; and 3) to determine

whether a physical-process model can provide significantly better P removal prediction than a first-order model. These objectives are part of the multi-study development of a novel stormwater BMP for urban P management, the urban wetland filter (UWF). The UWF concept pairs small ($<140 \text{ m}^2$), vertical-flow (VF) wetland cells with an existing retention pond. The off-line cell does not need to be sized for peak flows and can either re-circulate water from the pond (with pumping) or serve as the low-water outlet for the pond (without pumping). Cell size is decreased compared to a typical stormwater wetland by a periodic rejuvenation process based on microbial reduction of iron (Fe) enabling controlled release of adsorbed P from the substrate (Comings et al., 2000). In addition, the ability of the retention pond to sequester sediment-bound P (Darke and Walbridge, 2000) is incorporated, allowing the UWF cells to be optimized for DP removal. Further design choices for the UWF seek to optimize SP, including: 1) use of substrate high in iron-oxides to provide adsorptive capacity and ability for rejuvenation (Luederitz et al., 2001); 2) upward, VF for minimum size (Farahbakhshazad and Morrison, 2003), maximum mixing, and minimal clogging (Farahbakhshazad and Morrison, 2003); and 3) low residence time ($<1 \text{ h}$) to promote aerobic conditions (2006).

Materials and methods

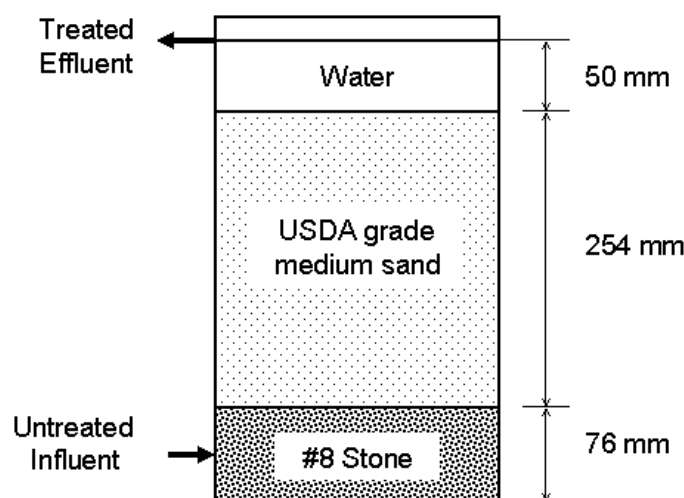
Experimental setup

Six experimental UWF cells (fig. 2.1) were set up in a climate-controlled laboratory space, which maintained a temperature of $22 \pm 4^\circ\text{C}$. Water for the cells was supplied from a constant head tank (CHT) located in the center of the cells. The CHT received water from a 265-L plastic holding tank (HT) that served as the “eutrophic retention pond” for this study. The cells were similar in construction and scale to those used by Prochaska and Zouboulis (Kadlec and Wallace, 2009). Some scaling problems have been associated with field applicability of bench-scale studies on SP, specifically in regards to quantification of performance (2007). While all quantitative results should be viewed in this perspective, the objectives of this study also led to qualitative conclusions that should be more resistant to scaling problems. Cells contained the following horizontal layers, listed from bottom to top: a 76-mm layer of medium-sized gravel (#8 stone), where the inlet structure was located; a 254-mm layer of USDA-grade medium sand (0.5-1% Fe by mass); and a 50-mm layer of standing water (fig. 2.2). Sand was sourced from a pit quarry in New Castle, VA.



Rosenquist

Figure 2.1 - The six replicate UWF cells were supplied water from a constant head tank located in the center of the six cells. The CHT had water supplied from a 265-L plastic holding tank that served as a “eutrophic retention pond.”



Rosenquist

Figure 2.2 - An individual UWF cell consisted of horizontal layers from bottom to top including: gravel, sand, and standing water

The experiment included a series of 20-h runs of the six cells, including both treatment and control runs, with only one cell receiving flow during a particular treatment run while the other cells remained saturated without flow. During treatment runs, flow started in the holding tank where a submersible pump brought water to the CHT. A hydraulic head of 5.5 cm in the CHT drove the water through one UWF cell and back into the holding tank. Water entered the UWF cell in the gravel layer at the bottom of the cell through a bulkhead fitting for horizontal distribution before flowing upward through the sand layer. This bottom to top, VF regime is similar to that used by Evans and Rusch (2001) except for the fixed

boundaries in this study. During control runs, flow proceeded from the HT to the CHT, and directly back to the HT, completely bypassing the UWF cell. In this way, any unanticipated P removal in the experimental setup, apart from that due to P removal in the cell, could be identified. Fifteen treatment runs were performed with each cell for 90 total treatment runs. Four control runs were performed after the treatment runs. Water used was a synthetic stormwater created by adding an inorganic P solution to distilled water to achieve concentrations between 0.1 mg/L and 0.6 mg/L. These concentrations were consistent with samples taken from stormwater ponds in the Blacksburg, VA, area that represented a range in both depth and distance between inlet and outlet (Table 2.1). P concentrations in the synthetic stormwater, mostly DP, were consistent with TP concentrations in the ponds. The water in the HT was periodically augmented during the study with additional inorganic P solution to maintain concentrations in the desired range, and distilled water to offset evaporation.

Table 2.1 – Phosphorus concentrations and total loads from four stormwater ponds in Blacksburg, Va

Pond	# of Samples	Average TP (mg/L)	Estimated Volume (L)	Total Resident Load (kg)
1	6	0.19	2.9E+06	0.56
2	4	0.18	5.8E+06	1.04
3	5	0.26	2.4E+06	0.63
4	5	0.24	2.3E+06	0.55

All concentrations given as mass of P, not PO₄⁻

Experimental design

Independent variables included the filtration “age” of the cell, initial DP concentration in the HT, and "antecedent dry period" between flow events. The dependent variable was the mass of P removed by the wetland cell during a given filtration run, measured by changes in HT concentration. Results are presented as mass removed instead of removal percentage because it proved more useful towards identifying sources of variability. Additional monitored, but uncontrolled, variables of interest included cell pH and flow rate. These variables were included in anticipation that they may prove to be of interest in explaining the results of the experiment.

Isotherm testing

To describe the “age” of the filter, a theoretical sorption maximum was established for the substrate to serve as a reference point. The total mass of P removed in each cell compared the calculated maximum, thus providing a filter “age” as the percent of the maximum that had been reached (fig. 2.3). This isotherm procedure was conducted with the sand substrate according to standard soil testing procedures similar to those described by Arias et al. (Li and Davis, 2009). Key differences from the cited study were that 10 g of substrate were used for each 200-mL sample container, samples were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and no containers were included for analysis without substrate. The theoretical maximum was determined with the linear form of the Langmuir equation:

$$C/q = 1/kb + C/b \quad (1)$$

where C is the equilibrium concentration of the adsorptive, q is the adsorbed quantity, k is a constant related to the binding strength, and b is the sorption maximum. The result was a sorption maximum of 45 mg-P/kg which relates to approximately 1125 mg-P for each 25-kg sand filter. For comparison, a recent study of two small (<1 ha), highly urbanized catchments in the Chesapeake Bay watershed found contributions of 900 mg-P/ha/yr and 3600 mg-P/ha/yr (Sonzogni et al., 1980). A study from the Great Lakes observed urban watersheds contributing as much as 23000 mg-P/ha/yr during development and 300-4800 mg-P/ha/yr after development (Drizo et al., 2000).

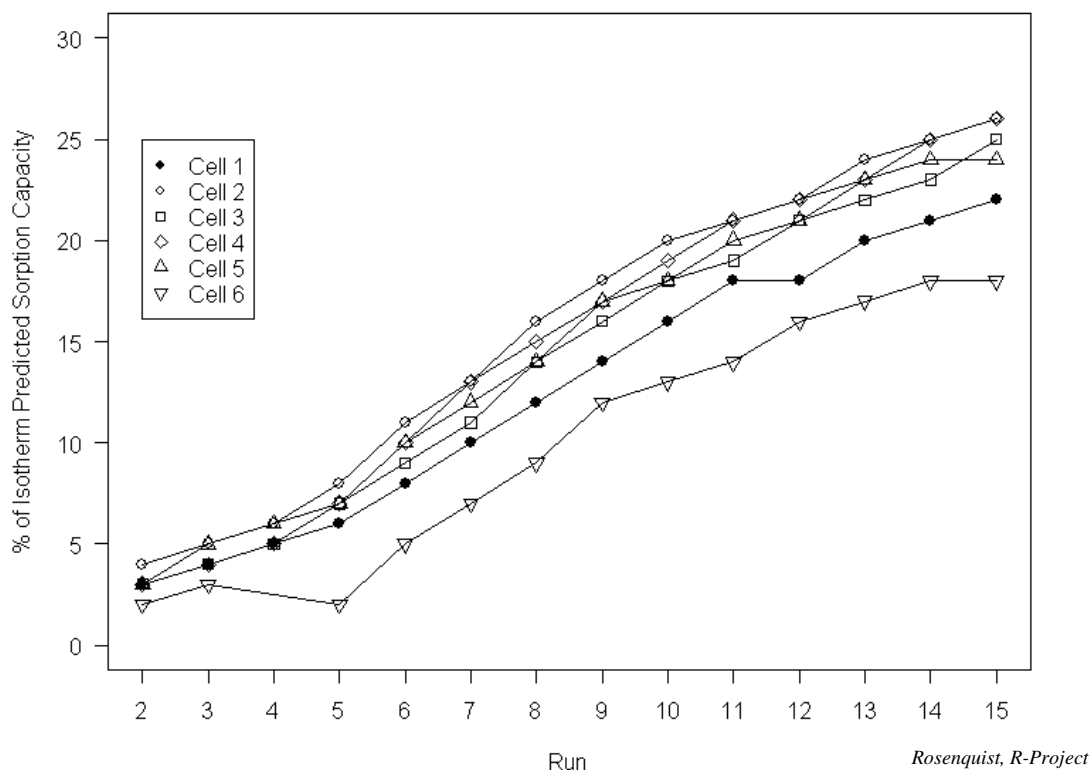


Figure 2.3 - During the study, cells increased from below 5% to around 25% of isotherm-derived sorption capacity

Sampling procedure

Data collection for this study took place between January 2008 and January 2009. All water samples were taken from the HT. Samples were taken before, after, and in some cases throughout the 20-h runs and analyzed for DP to track removal in each run of each cell. An automated sampler (ISCO 3700, Lincoln, NE) was used for the first 33 runs sampling from the HT at 5-h intervals throughout the run to ensure a proper sampling interval. Once temporal trending was well established, samples were collected by hand from the HT at the beginning and end of each run. The mass of P removed during each specific run was determined with the known volume of the HT.

The initial flow rate was set near 0.2 L/min. This flow rate was chosen based on trial runs conducted in conjunction with this study. It represented a safe maximum to avoid disruption of the sand media by fluidization. Flow rate was estimated by volumetric capture into a graduated cylinder (500 mL) while timing with a stopwatch. Two measurements were averaged with the previously calculated flow rate to estimate a representative flow rate

for a given run. Two pH measurements were taken for each run with a handheld pH pen (Hanna Instruments, Woonsocket, RI) in the standing water portion at the top of the UWF cell, once before flow was started and once at the end of the run. The pH pen was periodically calibrated with standard buffer solutions.

Spatial distribution procedure

Previous studies have indicated the existence of spatial gradients of adsorbed P in substrates with the amount of adsorbed P decreasing in the direction of flow (McBride, 1994). An existing spatial gradient of P could coincide with an existing thermodynamic gradient and continued capacity for P removal. By this theory, little or no spatial gradient would be expected if a quasi-equilibrium thermodynamic condition had been reached. A condition of no existing spatial gradient would be indicated by very little or no statistical difference from samples taken in spatial positions ranging from inlet to outlet of the UWF cells following completion of the last run.

After the filtration runs, substrate samples were taken on a three-dimensional grid in the UWF cell (fig. 2.4). Samples were taken with 5-cm soil coring equipment through the entire depth of the sand layer at three cell locations, two at the side and one in the middle. Samples were taken 6 months after removal runs. After coring, samples were oven dried for 24 h, then analyzed for Fe and P with supernatant analysis by ICP-AES after extraction with sulfuric and hydrochloric acids.

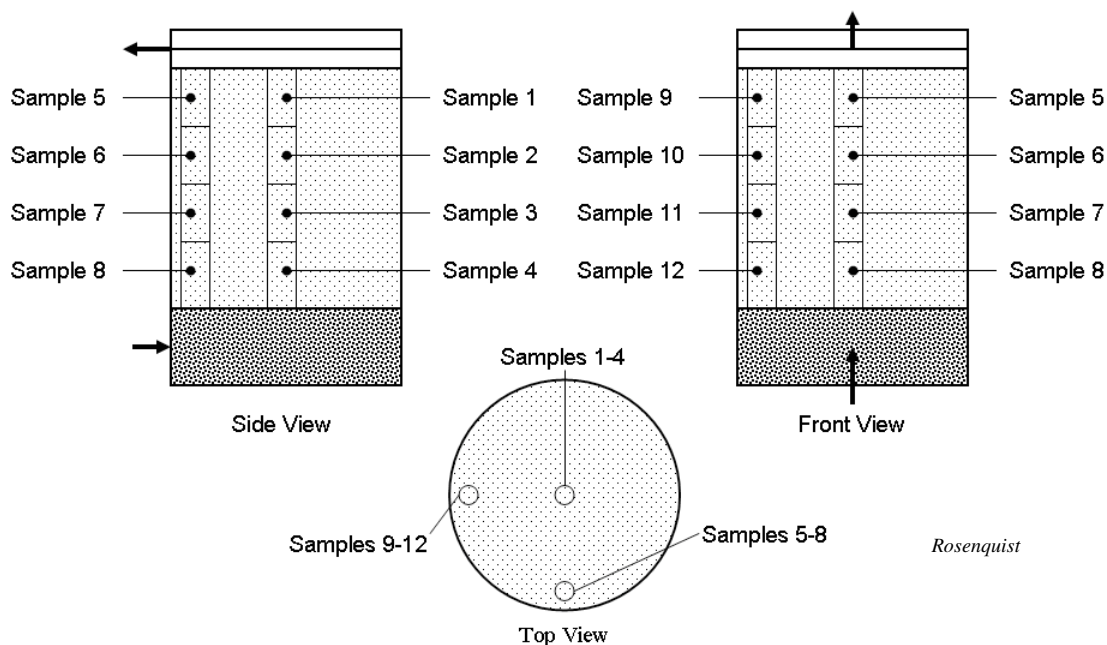


Figure 2.4 - Substrate samples were taken with 5-cm diameter soil coring equipment from top to bottom of the sand layer at three different locations in the filter.

Modeling

Data from the experiment were used to test two different models: 1) a first-order model; and 2) a physical-process model. Regressor variables for the first-order model included influent concentration, filter “age,” pH, and flow rate. If P removal percentages were consistent, then mass removal should have a positive linear correlation with influent concentration, but not with pH or flow rate. Correlation with filter “age” might be expected as sorption sites are filled.

The physical-process model included the following regressor variables: 1) concentration gradient, where P removal may be positively correlated with a concentration gradient between the previous adsorption equilibrium of the adsorbent and current influent concentration of adsorptive (larger increases in influent concentration from previous equilibrium would favor more adsorption); 2) pH, where P removal may be inversely correlated with pH (adsorption of stronger acid anions in soils is generally favored at lower pH values (USEPA, 1994)); 3) flow rate, where P removal may be correlated with flow rate (lower flow rates might favor additional adsorption if the process is diffusion-controlled, or alternatively lower flow rates might favor anaerobic conditions and less adsorption) and; 4) "antecedent dry period", where P removal may be positively correlated with the time between runs (kinetic limitation based on diffusion between runs opening additional adsorption sites).

The key difference between these two models is that in the physical-process model additional adsorption may not occur even though there are still “available” sites as predicted by the theoretical maximum based on isotherm testing. Additional concentration gradient might be established by the following methods: 1) introducing additional free sorption sites as with new substrate; 2) removing adsorbed P from the media and into solution; 3) increasing the influent concentration of DP; or 4) diffusion of P into micropores, thereby freeing the original sorption sites. Testing this model made use of two variables calculated from the data set. The first variable, “concentration gradient”, quantified the increase in the influent concentration between the end of the previous run (assumed quasi-equilibrium) and the beginning of the following run, for which the removal mass is to be predicted. The second variable, "antecedent dry period", quantified the length of time between runs of a given cell. This variable represents a kinetic effect such as diffusion of P into micropores, freeing up external sorption sites and increasing the thermodynamic gradient.

Data management

Sampling complications occurred on two runs, including a battery failure on the automated sampler and a valve failure resulting in water leakage. The battery failure run was excluded from the data set since no data were available. Data were gathered for the valve failure run and were included since the P removal could be adequately estimated. Also, without direct comparison of the influent and effluent concentrations, it was somewhat difficult to determine whether complete equilibrium had been reached at the end of the 20-h run and the term quasi-equilibrium is used. However, any expected error based on this assumption should under-predict the effect of the gradient since runs with lower calculated gradients would be biased more heavily than runs with higher calculated gradients by any carryover between runs.

Sample analysis

Samples from the first two treatment runs were analyzed with a colorimetric technique involving premeasured reactants, while samples from the remaining 13 treatment runs and the control runs were analyzed by ICP-AES. This procedure was conducted in accordance with EPA Method 200.7 (R Development Core Team, 2009). After direct comparison of samples analyzed by both methods, the ICP-AES method reported equivalent concentrations with less standard error and more quality control than the available colorimetric technique.

P in the samples was differentiated as DP by gravimetric settling and could include some suspended forms of P. However, this differentiation is probably more consistent with P not removed by sedimentation.

Statistical analysis

Data analysis was conducted using the “R” statistical software package (McBride, 1994). The Shapiro–Wilkes test for normality and Welch’s t-test were used for comparing means of P mass removal between control and treatment runs.

Analyses of the various proposed sources of variability utilized multivariable regression analysis and backward model selection. The associated model assumptions were verified by graphical residual analysis.

Results and discussion

pH and flow rate trends

During the study, pH values were neutral to alkaline and increased in general (fig. 2.5). This was expected because the specific adsorption of P is a ligand exchange reaction, which includes a release of hydroxide ions (Schueler, 1996; Strecker et al., 2001). The tendency to increase pH may be an important factor for BMP designers, and supports the inclusion of pH buffering materials. Flow rates varied both between and within cells (fig. 2.6). A general trend was also noted, with most cells experiencing a decrease in flow rate over time. Since TSS was not a factor in this experiment, any decrease was probably due either to settling of the substrate or biofouling.

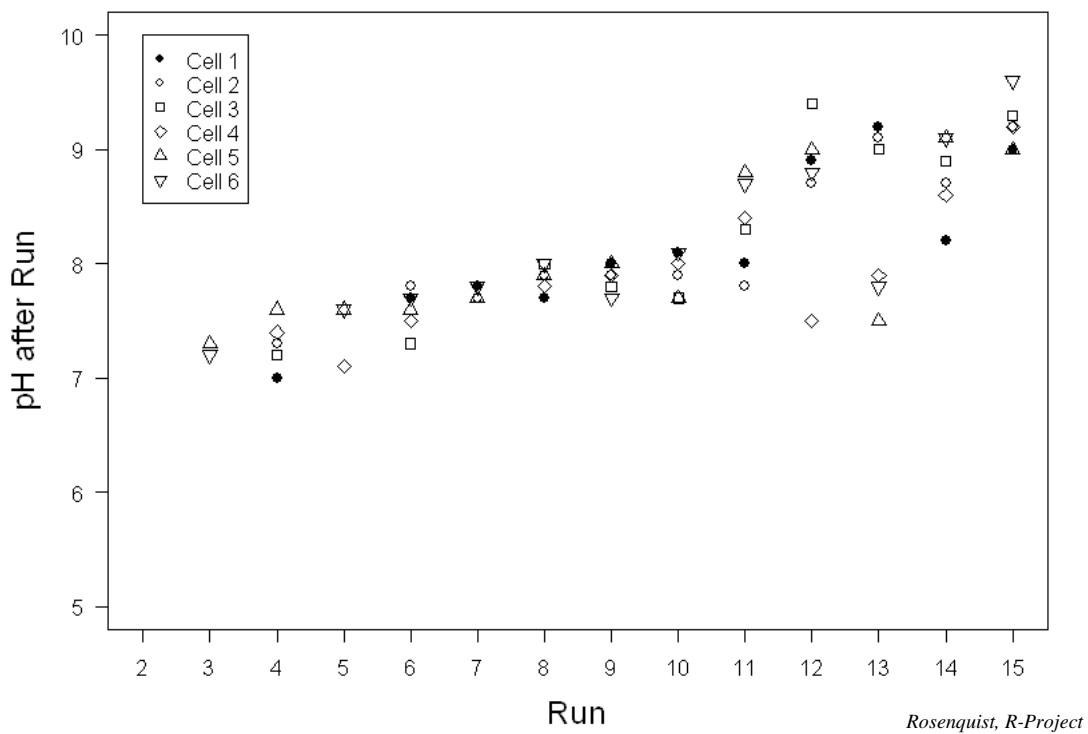


Figure 2.5 – A general increase in cell pH for all wetland cells was observed.

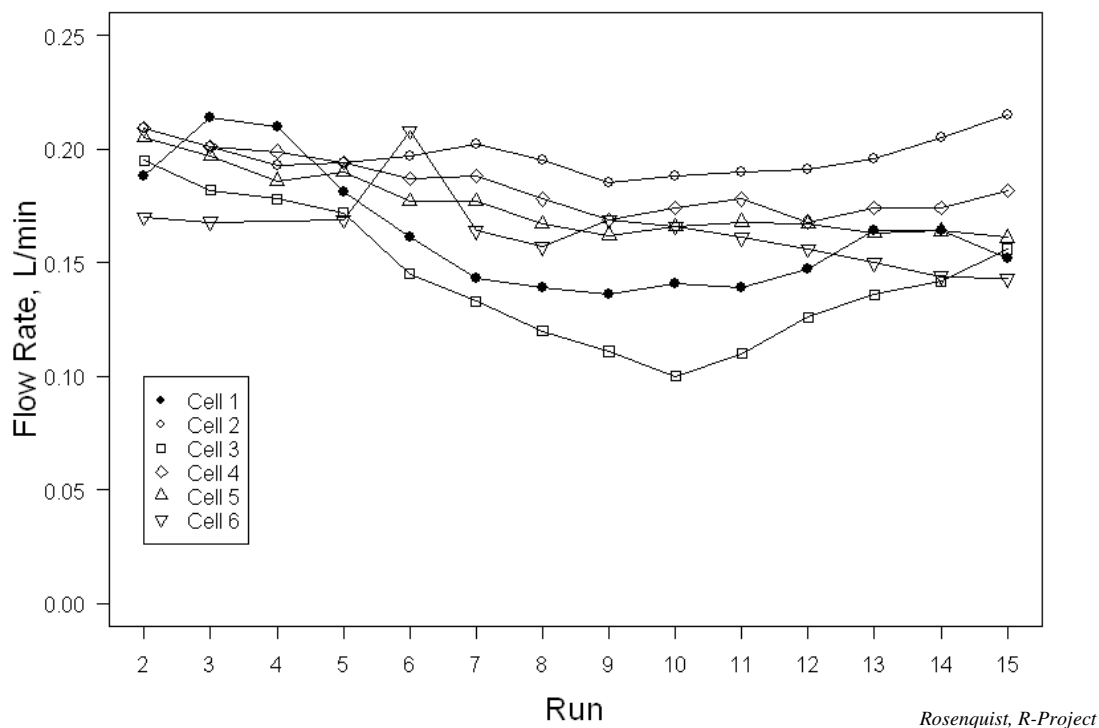


Figure 2.6 - Flow rates observed during runs varied both across and within cells, however, such changes were generally within a factor of two

Validation of P removal by iron-based substrate

Comparison of data from treatment and control runs verified the ability of an iron-based media filter to remove DP (fig. 2.7; $p=0.025$; Welch's two-sample t-test). On average, the iron-based media filterers removed 18.16 mg-P per run while the average removal for the control runs was not statistically different from 0 mg-P per run. Any removal during control runs could be due to biological uptake by microorganisms or sorption to plastic containers and tubing. These results support the use of iron-substrates in BMP design for increased P removal performance by SP.

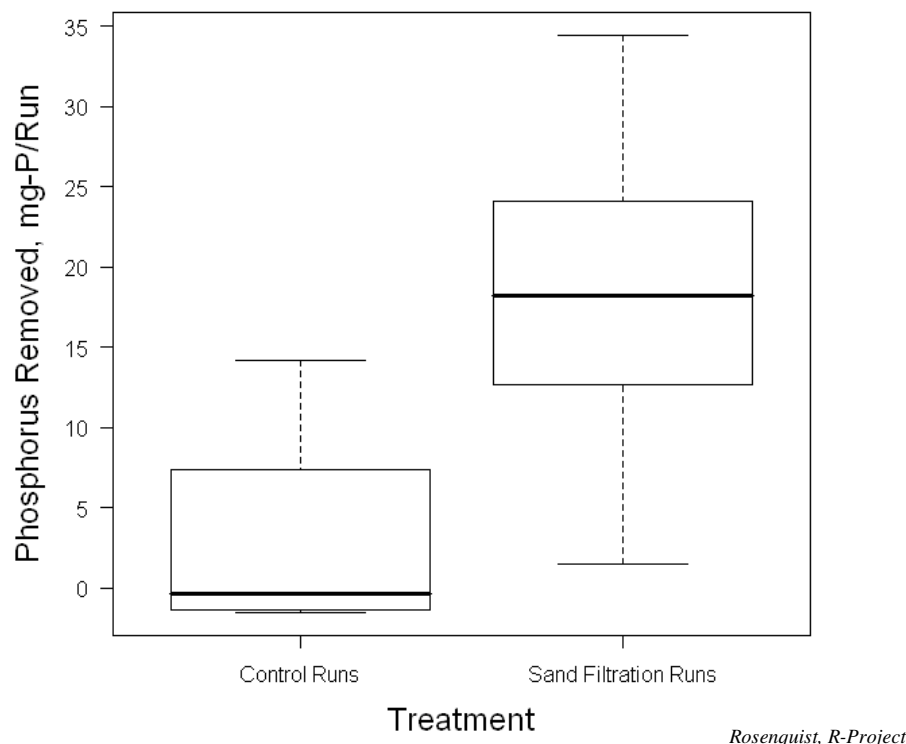


Figure 2.7 - Iron-oxide sand filtration demonstrated a significant P removal capability compared to control runs without iron-oxide sand filtration. (plot depicts: $Q_1-1.5*$ Interquartile Range; Q_1 ; Median; Q_3 ; $Q_3+1.5*$ Interquartile Range)

First-order model

Of the four variables included in this model (Table 2.2), only pH was significant ($p=0.0208$), and provided limited explanation for variability (fig. 2.8). It is notable that neither influent concentration nor filter “age” was significant in the model, indicating that a constant removal percentage was not demonstrated and that current influent concentrations alone may be a weak predictor of P removal by SP. Results also show that the percent of sorption capacity filled is a poor predictor of removal decay.

Table 2.2 – Regression details for first-order model of P removal

Coefficient	P-value	Estimate
Intercept	0.0006	58.9
Filter age (%SC)	0.9715	N/A
Initial influent concentration (mg/L)	0.7173	N/A
pH	0.0208	-2.37
Flow Rate (L/min)	0.8078	N/A
R^2	N/A	0.14

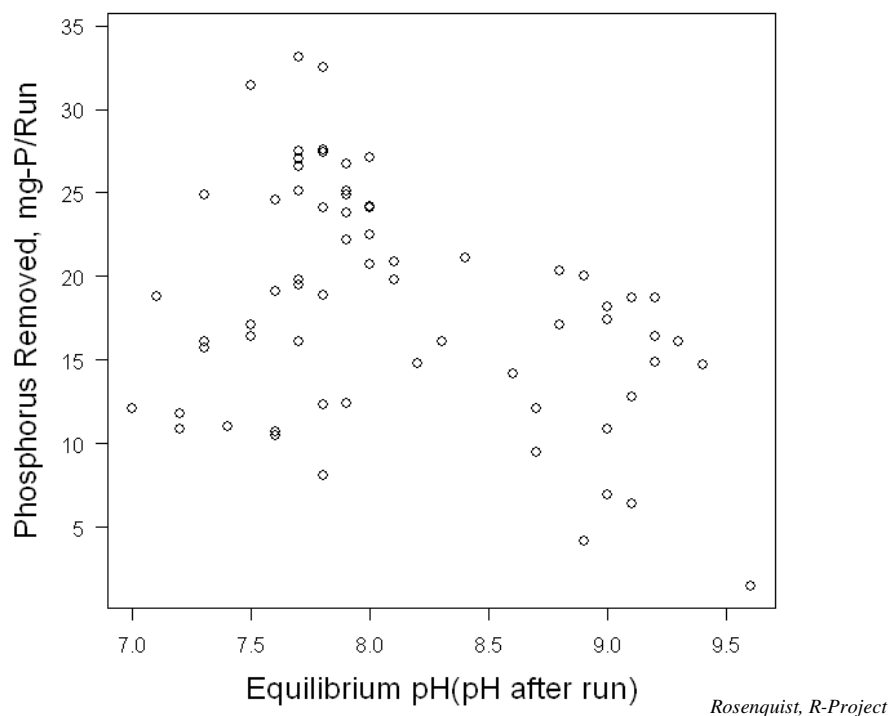


Figure 2.8 - Equilibrium pH taken after the 20-h treatment run displays a weak negative correlation to P removal for that run.

Physical-process model

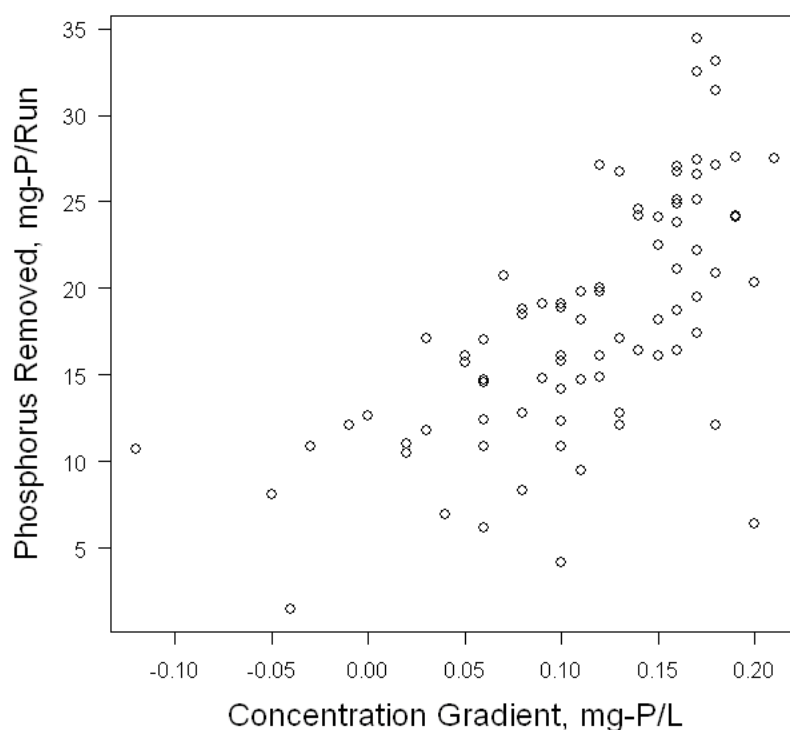
In addition to a significant negative correlation with pH, “concentration gradient” and “antecedent dry period” demonstrated significant positive correlation to P removal in this model (Table 2.3). Of particular interest, the “concentration gradient” variable may, at least partially, explain the mechanism associated with “irreducible concentrations” reported in previous studies (Schueler, 1996; Strecker et al., 2001). Significance of the “antecedent dry period” variable is consistent with a study which also predicted a positive correlation with flow rate using bench-scale studies with VF wetland cells (Farahbakhshazad and Morrison, 2003). The absence of a correlation with flow rate in this study could be due to the relatively small range in flow rates. The negative correlation with pH is consistent with the findings of Zeng et al. (2004) and a field-based study by Redshaw et al. (1990). Regarding the relative influence of the significant variables, “concentration gradient” had by far the largest effect, followed by pH, and lastly the diffusion-related, “antecedent dry period” variable.

The significant amount of variability explained by the “concentration gradient” variable (fig. 2.9) indicates that it may be the major source of variability observed in P removal by SP and possibly a significant factor for variability in P removal for stormwater

BMP overall. Residual analysis performed on the model indicated no obvious problems with regression assumptions.

Table 2.3 – Regression details for physical-process model of P removal

Coefficient	P-value	Estimate
Intercept	1.78E-06	5.28
Concentration Gradient (mg/L)	2.56E-15	10.46
Rest (days)	1.12E-02	2.62
pH	1.26E-05	-4.75
R ²	N/A	0.70



Rosenquist, R-Project

Figure 2.9 - Initial concentration gradient was a strong predictor of P removal during the runs

Spatial distribution of removal

There was no apparent spatial gradient of adsorbed P in the direction of flow; however, a weak spatial gradient against the direction of flow was observed (fig. 2.10A). When a linear regression model was applied to this gradient, the coefficient of determination was low ($R^2=0.30$). Iron concentrations also exhibited a spatial gradient against the direction of flow, which could be due to slower settling velocities for finer particles while loading the

substrate into standing water. The association of P sorption with particle size is consistent with Zhu et al (2003). Further regression analysis strongly indicated Fe concentration as significant for explaining variation in P concentration (fig. 2.10B, $R^2=0.74$). Adding spatial position as a regressor provided no further explanation for P concentration variability, lending support to the lack of a spatial gradient, and hence a state of thermodynamic quasi-equilibrium.

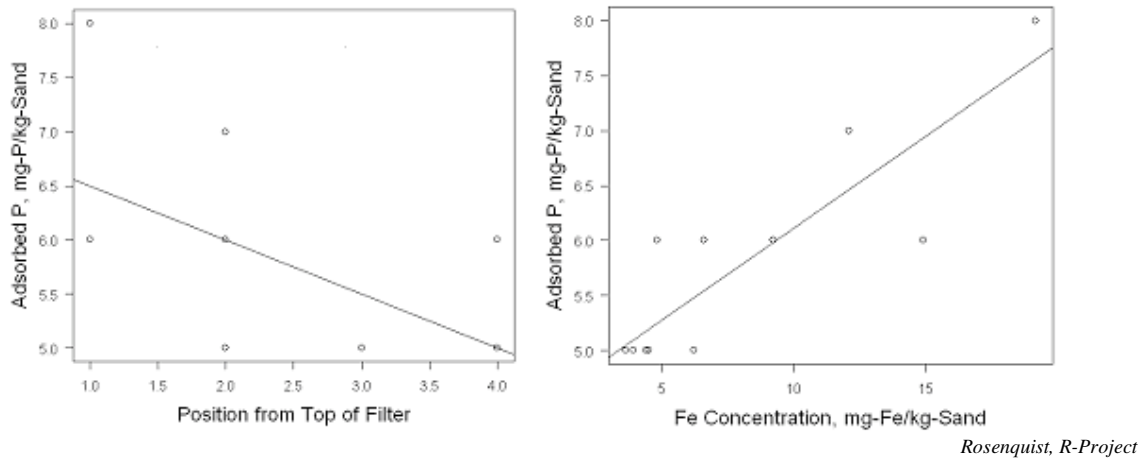


Figure 2.10 - While a weak vertical spatial gradient in adsorbed P was observed ($R^2 = 0.30$), spatial variation in adsorbed P was better explained by the spatial distribution of Fe ($R^2 = 0.74$)

Conclusions

Results indicate that P removal by SP depends strongly on the relative equilibrium between solution P and adsorbed P in the substrate. Direct conclusions from this research include the following: 1) iron-oxide sand filtration is capable of removing DP; 2) filter "age" based on percent of theoretical sorption capacity is a poor predictor of the lifetime of P removal in the CW; 3) P removal may not occur even with theoretical sorption sites remaining as predicted by isotherm testing if no concentration gradient exists; 4) P removal is inversely correlated with pH; and 5) P removal is dependent on and directly correlated to the concentration gradient present between solution and adsorbed P.

If an experimental run is considered analogous to a storm event, P removal by SP during a given event is likely dependent on previous loadings to the BMP in terms of mass and concentration from past events. As a general trend, effluent concentrations will likely converge with influent concentrations over time, assuming that no additional concentration gradient is established. This convergence may help explain the "irreducible concentrations" seen in field studies of stormwater BMPs and may explain any variation in the level of this concentration between sites due to different loading histories. Estimates of future effluent

concentrations or load reductions from SP should include information about both average and maximum influent concentrations, sorption capacity of the media, and the amount of P currently adsorbed. In addition, pH of the system and the timing of hydrologic loadings may provide additional value for estimation.

Potential design considerations from this model include the following: 1) for the same BMP design, less P removal by SP may occur for a lower influent concentration than for a higher influent concentration; 2) for the same influent, P removal in a BMP with less available sorption sites (less total volume or less sorption site density) will likely decrease and/or become negligible more quickly; 3) if influent concentration decreases significantly from a sustained higher level, P removal by SP may become negligible or even reverse; 4) substrates will likely gain additional concentration gradient slowly as P diffusion into micropores occurs; 5) concentration gradient may also be driven by influent concentration increase, addition of more sorption sites, or by harvesting P from the substrate; and 6) spatial gradients of P in substrate may be a better indicator of remaining sorption potential than isotherm-derived maximums.

Future Work

The rejuvenation process described involves at least three areas of future research: 1) dissolution of adsorbed P into solution by promoting microbial reduction of iron oxides; 2) precipitation and harvest of phosphate solids from the CW; 3) and renewal of iron oxide coatings in the substrate for further adsorption. In addition, further research may validate the relationship between existing spatial gradients of adsorbed P in substrates and remaining sorption potential and validate the physical-process model and associated conclusions with cells in field conditions.

Acknowledgements

The authors would like to thank the National Science Foundation for providing support for students who worked on the project as a part of the NSF Research Experiences for Undergraduates grant. In addition, the authors would like to acknowledge assistance from exceptional faculty (Dr. Tess Wynn and Dr. Daniel Gallagher), staff (Laura Teany and Julie Jordan), and students (Molly Julian (including photos), Gina Hayes, Yemi Ojumu, Cody Newbill, Sarah Brahman, Cherona Levy, and Steven Sell). Lastly, the authors would like to acknowledge the contributions of Ecosolutions, LLC in the development of the UWF concept.

References

- Arai, Y., and D. L. Sparks. 2007. Phosphate reaction dynamics in soils and soil components: A multiscale approach. *Advances in Agronomy* 94: 136-179.
- Arias, C. A., M. d. Bubba, and H. Brix. 2001. Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. *Water Res.* 35 (5): 1159-1168.
- Arias, C. A., and H. Brix. 2005. Phosphorus removal in constructed wetlands: can suitable alternative media be identified? *Water Sci. Technol.* 51 (9): 267-273.
- Atasoy, M., R. B. Palmquist, and D. J. Phaneuf. 2006. Estimating the effects of urban residential development on water quality using microdata. *J. Environ. Manage.* 79: 399-408.
- Camargo, J. A., and A. Alonso. 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. *Environ. Int.* 32: 831-849.
- Carleton, J. N., T. J. Grizzard, A. N. Godrej, H. E. Post, L. Lampe, and P. P. Kenel. 2000. Performance of a constructed wetlands in treating urban stormwater runoff. *Water Environ. Res.* 72 (3): 295-304.
- Comings, K. J., D. B. Booth, and R. R. Horner. 2000. Storm water pollutant removal by two wet ponds in Bellevue, Washington. *J. Environ. Eng.* 126 (4): 321-330.
- Coveney, M. F., D. L. Stites, E. F. Lowe, and R. C. Battoe. 2002. Nutrient removal from eutrophic lake water by wetland filtration. *Ecol. Eng.* 19: 141-159.
- Darke, A. K., and M. R. Walbridge. 2000. Al and Fe biogeochemistry in a floodplain forest: implications for P retention. *Biogeochemistry* 51 (1): 1-32.
- Drizo, A., C. A. Frost, J. Grace, and K. A. Smith. 2000. Phosphate and ammonium distribution in a pilot-scale constructed wetland with horizontal subsurface flow using shale as a substrate. *Water Res* 34 (9): 2483-2490.
- Evans, E. A., and K. A. Rusch. 2007. Phosphorus treatment capability of the marshland upwelling system under low background salinity conditions. *Ecol. Eng.* 30: 250-263.
- Farahbakhshazad, N., and G. M. Morrison. 2003. Phosphorus removal in a vertical upflow constructed wetland system. *Water Sci. Technol.* 48 (5): 43-50.
- Fisher, T. R., E. R. Peele, J. W. Ammerman, and L. W. Harding. 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Mar. Ecol. Prog. Ser.* 82 (1): 51-63.
- Hogan, D. M., and M. R. Waldbridge. 2007. Best management practices for nutrient and sediment retention in urban stormwater runoff. *J. Environ. Qual.* 36: 386-395.

- Hunt, W. F., and A. Wossink. 2003. The Economics of Structural Stormwater BMPs in North Carolina. UNC-WRRI-2003-344. Raleigh, NC: UNC-WRRI.
- Kadlec, R. H., and S. D. Wallace. 2009. Treatment Wetlands. Boca Raton, FL: CRC Press.
- Lantzke, I. R., D. S. Mitchell, A. D. Heritage, and K. P. Sharma. 1999. A model of factors controlling orthophosphate removal in planted vertical flow wetlands. *Ecol. Eng.* 12 (1): 93-105.
- Li, H., and A. P. Davis. 2009. Water quality improvement through reduction of pollutant loads using bioretention. *J. Environ. Eng.* 135 (8): 567-576.
- Lovley, D. R. 1991. Dissimilatory Fe(III) and Mn(IV) Reduction. *Microbiological Reviews* 55 (2): 259-287.
- Luederitz, V., E. Eckert, M. Lange-Weber, A. Lange, and R. M. Gersberg. 2001. Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. *Ecol. Eng.* 18: 157-171.
- McBride, M. B. 1994. Environmental Chemistry of Soils. New York, NY: Oxford.
- Naylor, S., J. Brisson, M. A. Labelle, A. Drizo, and Y. Comeau. 2003. Treatment of freshwater fish farm effluent using constructed wetlands: the role of plants and substrate. *Water Sci. Technol.* 48 (5): 215-222.
- Pant, H. K., K. R. Reddy, and E. Lemon. 2001. Phosphorus retention capacity of root bed media of sub-surface flow constructed wetlands. *Ecol. Eng.* 17 (4): 345-355.
- Parry, R. 1998. Agricultural phosphorous and water quality: A US environmental protection agency perspective. *J. Environ. Qual.* 27: 258-261.
- Paul, M. J., and J. L. Meyer. 2001. Streams in the urban landscape. *Annu. Rev. Ecol. Syst.* 32: 333-365.
- Prochaska, C. A., and A. I. Zouboulis. 2006. Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate. *Ecol. Eng.* 26 (3): 293-303.
- Redshaw, C. J., C. F. Mason, C. R. Hayes, and R. D. Roberts. 1990. Factors influencing phosphate exchange across the sediment-water interface of eutrophic reservoirs. *Hydrobiologia* 192: 133-245.
- Schueler, T. R. 1996. Irreducible pollutant concentrations discharged from urban BMPs. *Watershed Protection Techniques* 2: 369-372.
- Shilton, A., S. Pratt, A. Drizo, B. Mahmood, S. Banker, L. Billings, S. Glenny, and D. Luo. 2005. 'Active' filters for upgrading phosphorus removal from pond systems. *Water Sci. Technol.* 51: 111-116.

- Smith, S. V., W. H. Renwick, J. D. Bartley, and R. W. Budemeier. 2002. Distribution and significance of small, artificial water bodies across the United States landscape. *Sci. Total Environ.* 299: 21-36.
- Sonzogni, W. C., G. Chesters, D. R. Coote, D. N. Jeffs, J. C. Konrad, R. C. Ostry, and J. B. Robinson. 1980. Pollution from land runoff. *Environ. Sci. Technol.* 14 (2): 148-153.
- Strecker, E. W., M. M. Quigley, B. R. Urbonas, and J. J. Jones. 2001. Determining urban storm water BMP effectiveness. *Journal of Water Resources Planning and Management* 127 (3): 144-149.
- R Development Core Team. 2009. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing.
- USEPA. 1994. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. EPA Method 200.7. Cincinnati, OH: US Environmental Protection Agency, Office of Research and Development.
- USEPA. 2002. Urban Stormwater BMP Performance Monitoring. EPA 821-B-02-001. Washington, DC: US Environmental Protection Agency, Office of Water.
- VDCR. 1999. Virginia Stormwater Management Handbook. Richmond, VA: Department of Conservation and Recreation, Division of Soil and Water Conservation.
- Zeng, L., X. Li, and J. Liu. 2004. Adsorptive removal of phosphate from aqueous solutions using iron-oxide tailings. *Water Res.* 38 (5): 1318-1326.
- Zhu, T., T. Maehlum, P. D. Jenssen, and T. Krogstad. 2003. Phosphorus sorption characteristics of a light-weight aggregate. *Water Sci. Technol.* 48 (5): 93-100.

Facilitated iron reduction as a means of rejuvenating phosphorus removal performance of filtration substrates

S.E. Rosenquist, C.L. Levy, S.T. Sell, W.C. Hession, M.J. Eick, D.H. Vaughan

Abstract

In order to mitigate nutrient pollution in surface runoff more sustainably, design and management efforts must address the finite capacity for phosphorus (P) sequestration in best management practices (BMP) that rely heavily on sorption processes. These BMP include sand filters, bioretention cells, and several types of constructed wetland. This study investigated facilitated, microbial reduction of iron-based filtration substrates to promote controlled release of P previously sequestered by the BMP, P harvest for recycling, and rejuvenation of substrate sorption capacity. Total dissolved phosphorus correlated with total dissolved iron during the reduction process, indicating that microbial iron reduction was capable of releasing previously sequestered P from substrates. Furthermore, results indicated that a sufficient carbon source was necessary, but microbial inoculation was not necessary to facilitate iron reduction. While the process released a large percentage of the previously sequestered P, this release was much slower than initial sequestration of P by adsorption, and further research should seek to develop a more rapid release of P in order to optimize the rejuvenation process for field application.

Introduction

Excess phosphorus (P) has long been associated with eutrophication, which can diminish overall water quality. Algal blooms are typically the most obvious result of excess P loading. The eventual decay of these algal blooms can cause a temporary but significant decrease in dissolved oxygen. As a result, many aquatic species can become oxygen-starved, causing various negative impacts including direct fish kills (Novotny, 2003). Various anthropogenic practices associated with agriculture, urban development, and waste management can contribute to eutrophication (Hogan and Waldbridge, 2007). While point sources of pollution (i.e. wastewater treatment plants) have historically been the largest target for remediation, non-point sources including urban stormwater runoff have recently been receiving increased attention as a significant contributor to excess P loading (Novotny, 2003; Baker et al., 2007).

Water treatment processes found in natural wetlands have been effectively utilized in constructed wetlands (CW), bioretention cells, many other best management practices (BMP) that provide effective, economical, and ecologically sound methods for managing surface-water quality problems (Tenenbaum, 2004). Natural interactions within the water column, vegetation, substrates, and microbial populations function together to alleviate these environmental impacts (Hammer, 1992). However, neither natural nor CW have demonstrated a limitless and non-diminishing capacity for P sequestration (Coveney et al., 2002; Drizo et al., 2002; Kadlec, 2005; Aldous et al., 2007). Since the P cycle has no dominant gas-phase, P removed by BMP will accumulate, mostly in organic or sediment-bound forms (White et al., 2008).

P removal by sorption to substrates has been cited as a major contributor to the sequestration capacity of CW, along with biological uptake by macrophytes and microbes (Lantzke et al., 1998; Keppler and Martin, 2008). While the relative contributions of these mechanisms may differ depending on the specific characteristics of the BMP (Lantzke et al., 1999; Luederitz and Gerlach, 2002), together they generally represent most of the P-sequestration potential. In any case, once equilibrium is reached between adsorbed and dissolved P (Rosenquist et al., 2010), and plant uptake reduces upon sufficient grow-in (Kadlec, 2005), P-sequestration performance can significantly decline. Long-term removal may continue to occur based on accretion of organic sediments, but the percentage of P retained in this way is small, the land requirement large, and the process, while sustainable, is less applicable for high land-value

areas (Hunt and Wossink, 2003; Keppler and Martin, 2008; Kadlec and Wallace, 2009). While some scenarios have been proposed to completely remove previously sequestered P from the BMP, such as biomass harvesting or substrate replacement (Drizo et al., 2002; Kadlec, 2005), these strategies have significant drawbacks such as: 1) the cost of continuously harvesting biomass or physically excavating and replacing sediments; 2) the difficulty of accessing a site once construction is complete and substrates are saturated; and 3) the low efficiency of P removal by biomass harvesting (Vymazal, 2005).

The lifespan for P management by CW is dependent upon many factors both internal (substrate sorption capacity, redox potential, biota) and external (concentration and form of influent P) to the BMP (Aldous et al., 2007). While the amount of particulate P retained in a wetland is influenced by physical processes such as sediment deposition, sequestration of dissolved P requires either plant uptake or sorption to substrates (Aldous et al., 2007). Sorption to sediments can be affected by various geochemical and biological interactions with iron (Fe), aluminum (Al), and calcium (Ca) in CW substrates, while plant uptake of P can be limited by seasonal growth patterns, eventual grow-in, and by the rate of uptake (Kadlec, 2000). Substrates not only provide physical support for macrophytes and microbial biofilms, but also provide sorption capacity with Fe/Al oxyhydroxides. P removal by sorption processes is less seasonally dependent than plant uptake and can sequester dissolved P at a much higher rate (Hammer, 1992; Lantzke et al., 1998; Kadlec, 2005; Keppler and Martin, 2008). P-removal rates tend to be highest in substrates rich in calcium, Fe, and Al due to their high adsorption capacity (Luederitz et al., 2001) with calcium-rich substrates demonstrating more efficacy at higher pH and Fe/Al-rich substrates at lower pH (McBride, 1994).

Sorption reactions include both adsorption and precipitation/coprecipitation processes that can occur between particular ions, in this case P, and the surface of the mineral substrate. Adsorption occurs when P is exchanged between the mineral-substrate/pore-water interface and form complexes on the mineral surface (McBride, 1994). Adsorption can be separated into outer-sphere (weakly bound) and inner-sphere (tightly-bound) complexes, where the latter may also be described as chemisorption or specific adsorption (McBride, 1994) and is of the most interest for stormwater treatment since it is less reversible. P has a strong interaction with sites on Fe/Al oxyhydroxides and as a result many Fe/Al oxyhydroxides minerals have a high P-adsorption capacity (Wilson et al., 2004). Although specific adsorption is favored between P and Fe

oxyhydroxides, this behavior is also strongly affected by the amount of P already adsorbed (Zhang and Huang, 2007) and by the number of available sorption sites in general, since the mineral surface becomes relatively inactive once adsorbents adhere to it (Wilson et al., 2004). The pH of the substrate environment is yet another factor that can influence the rate of specific adsorption of P with Fe oxyhydroxides (Griffioen, 2006; Rosenquist et al., 2010). Variability in sorption capacity can also occur based on physical properties; substrates with a significant amount of clay-sized particles tend to yield a higher sorption capacity due to the high specific surface area present (McGechan and Lewis, 2002). This physical property dependence can create a critical limitation to sorption capacity, especially when designs require higher hydraulic conductivities.

While sorption reactions involving P and Fe are often favored thermodynamically in CW environments, there are limitations and specific circumstances where net desorption has occurred. Weakly-bound P can be released from the reactive sites on sand or gravel by means of anion exchange (Aldous et al., 2007) especially if they are only involved in outer-sphere complexes (McBride, 1994). In addition, further release of more tightly bound P may occur under reducing conditions, common in CW, where low redox potential has correlated with net release of P (Komatsu et al., 2006). In an aerobic environment the association formed between the P and the oxide mineral tends to be relatively insoluble and immobile, but in anaerobic conditions Fe can be reduced from ferric (Fe^{3+}) to ferrous (Fe^{2+}), allowing the P to be removed from the substrate (Brady and Weil, 2002). While this process has been known to occur in CW and can be detrimental to overall treatment performance (Carleton et al., 2000), if the redox potential of the system were more closely controlled, the Fe-reduction process may be useful for rejuvenation of the sorption capacity of the substrate. Since Fe can provide much of the sorption capacity in substrates at neutral pH, Fe-based substrates may be able to release much of their previously sequestered P upon a facilitated iron-reduction cycle.

The primary means of Fe reduction in natural wetlands is through microbial metabolism (Lovely et al., 1991). Fe-reducing microorganisms support their energy needs through an oxidation-reduction process involving an electron donor (organic carbon) and a terminal electron acceptor (Fe oxyhydroxides) (Scheibe et al., 2006). Fe reduction and dissolution by serving as the terminal electron acceptor facilitates the release of P. A study of tropical forest soils showed that with the aid of Fe-reducing microorganisms, Fe^{3+} was reduced to Fe^{2+} , facilitating the

release of P under anoxic conditions in a laboratory incubation experiment (Peretyazhko and Sposito, 2005). While this biotic-reduction/P-release process proceeds much more slowly under natural conditions than P sequestration by adsorption, optimal environmental conditions for microbial metabolism might enhance the kinetics. For example, the reduction process may be accelerated by the presence of humic substances such as polyphenols that serve as an electron shuttle and abiotically reduce Fe (McBride, 1994).

Once Fe reduction has occurred releasing previously sequestered P into solution, complete recycling requires harvesting the released P from the BMP. At least two possibilities exist: 1) removal of the high-P, high-Fe solution for use as a liquid fertilizer; or 2) facilitation of a precipitation reaction, causing a stable Fe-P solid to be formed, which can be flocculated and removed for use as a fertilizer. In either case, P is harvested and recycled to support feedstock production, alleviating some of the need for continued mining of ever-scarcer P-rich mineral sources (Abelson, 1999).

This study is part of a larger project developing a novel BMP, the urban wetland filter (UWF) with renewable P sorption capacity for treating urban stormwater. In urban areas, high land-value and limited availability of large land plots are significant obstacles to the implementation of CW (Hunt and Wossink, 2003). Required hydraulic residence time (HRT) for biological uptake and sedimentary accretion, finite pollutant assimilatory capacity, and hydraulic conductivity (in subsurface-flow wetlands only) are generally the technical limitations that cause large land areas to be required (Kadlec and Wallace, 2009). With a process to rejuvenate finite sorption capacity, the rapid kinetics of P-removal by sorption processes can decrease required BMP space while optimizing removal of dissolved P (DP). The UWF pairs small (<140 m²) wetland cells with an existing retention pond, positioning cells off-line from stormwater flow while they alternate between filtration and rejuvenation cycles. While the pond removes sediment-bound P, the wetland cell design can focus on removing DP.

This study of the rejuvenation process for substrate sorption capacity addressed the following research questions: 1) does a filtration substrate contain enough microbes to reduce Fe without inoculation?, 2) what is the effect of a carbon-source addition toward facilitating Fe reduction in the substrate versus a control without carbon-source addition?, 3) will dissolved-P concentrations positively correlate with dissolved Fe concentrations upon Fe reduction?, 4) what

percentage of previously adsorbed P will be released by the Fe-reduction process?, and 5) how will final concentrations compare to influent concentrations observed during P loading?

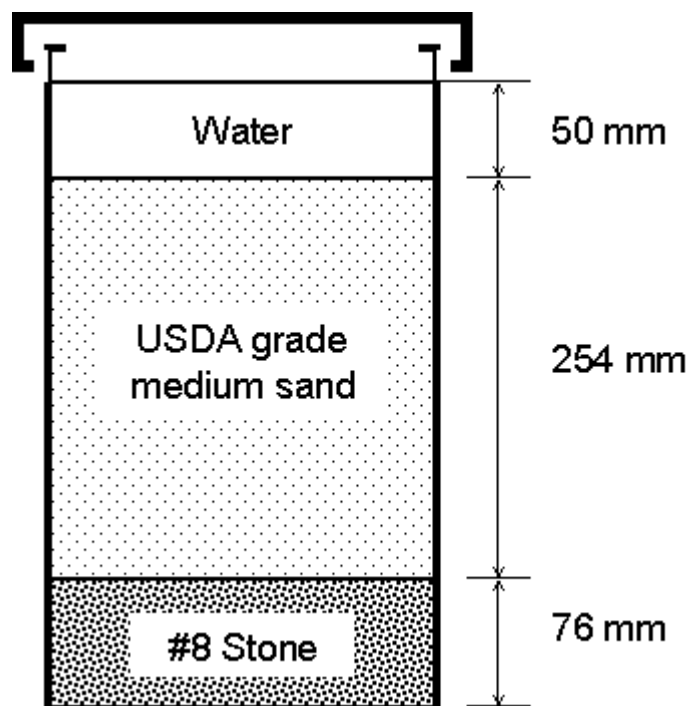
Materials and Methods

This study included two complementary experimental setups. The main portion of the study took place using flow-through wetland cells (FTWC) to investigate the central research questions with conditions approximating field installation. In addition, a set of batch reactor wetland cells (BRWC) were utilized to allow for testing of additional experimental factors, addressing additional research questions, and providing replicates of multiple factors for statistical power.

Flow-through wetland cells (FTWC)

Experimental Setup

The FTWC consisted of six, 20-L cylindrical containers filled with 25 kg of USDA-grade, medium sand media placed above a layer of limestone gravel (fig. 3.1). The sand media, sourced from a pit mine in New Castle, VA, had total Fe content between 0.2% and 0.7% by mass. The P-loading process was the main focus of another study in this research program and is described in detail by Rosenquist et al. (2010). The flow regime during P-loading was from bottom to top through the gravel layer then the sand media. The gravel layer served to distribute flow throughout the sand and promote piston-type flow. The filter media remained saturated throughout the loading process, but flow was intermittent and characterized by a 20-h flow period followed by "antecedent dry periods" of varying duration. Influent concentrations during P-loading were between 0.1 mg/L and 0.6 mg/L. During the reduction-reaction period conducted in this study, cells had opaque lids to minimize evaporation and algal growth.



Rosenquist

Figure 3.1 - FTWC cross section showing layers of gravel, sand, and standing water

Experimental Design

The FTWC included two treatment groups with three replications. For a control group (cells 1-3), no additional carbon-source was added, while the experimental treatment group (cells 4-6) involved exchanging the water in the FTWC with a sucrose solution carbon source by flow-through over a 2-h period. The final concentration of sucrose in the FTWC was between 100 mg/L and 150 mg/L, depending on the extent of the pore-water exchange.

Sampling and Sample Analysis Procedures

Sampling was from the standing water on top of each bucket in 20-mL volumes at the time of carbon addition and initially at one-day intervals. After temporal trends were established, sampling intervals increased to between 3-d and 7-d. Sampling included 306 samples overall from the six FTWC over a 253-d period. Gravimetric settling in the FTWC provided differentiation of dissolved constituents for sample analysis, as this portion of the study did not include sample filtration. All samples were analyzed by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) in accordance with EPA Method 200.7 (USEPA, 1994) to

determine total dissolved phosphorus (TDP) and total dissolved iron (TDI) for each sample. Along with the above sampling schedule, a handheld pH meter (Hanna Instruments, Woonsocket, RI) provided pH measurements and a handheld dissolved oxygen meter (YSI Incorporated, Yellow Spring, OH) provided dissolved oxygen measurements. Dissolved oxygen served as a surrogate for estimating gross changes in redox potential. Periodic calibration of both the pH and dissolved oxygen instruments followed in accordance with the manufacturer's instructions.

Data Analysis

Graphical analysis included the following variables: 1) pH, 2) dissolved oxygen, 3) TDP, 4) TDI, and 5) TDP/TDI correlation. After a distinct break in the TDP/TDI correlation appeared, including two linear regions of differing slope, a least-squares breakpoint analysis determined the threshold concentration between the two linear regions. This procedure preceded a segmented linear regression analysis using a model with an indicator variable for the breakpoint between the two slope regions. This process tested for a correlation between Fe reduction and release of previously adsorbed P into solution, and for differences in the slope observed in the two regions. Lastly, a comparison between the final concentrations in the carbon-treated FTWC and the influent concentrations used to load the FTWC enabled concentration comparison and estimates the percentage of previously adsorbed P released. Statistical analyses were performed with software from the R-project (R Development Core Team, 2009). For data values below the analytical limits of the instrument, the analytical limit served for calculations.

Batch-reactor wetland cells (BRWC)

Experimental Setup

The BRWC consisted of 36, 250-mL NalgeneTM containers containing 100 g of USDA-grade-medium sand of the same type described under the FTWC setup. The addition of 90 mL of distilled water and 10 mL of 350-mg/L stock P solution enabled the saturation of the sand in each BRWC. The BRWC were agitated for 72 h and dewatered by vacuum filtration. After filtration, the glass-fiber filter used became part of the dewatered sample to conserve P in the cell.

Experimental Design

Once saturated with P, the 36 BRWC became four experimental groups based on the carbon source provided. These carbon sources included: 1) distilled water (control), 2) 250 g/L sucrose solution, 3) surface water grab sample from a local retention pond (with slight P-contribution accounted for), and 4) a 50% combination of sucrose solution and surface-water sample. These groups subdivided into one-day, two-day, and three-day reaction times. There were three replications for each carbon-source and reaction-time combination. Each BRWC had 100 mL of the designated carbon source added gravimetrically. Each BRWC received a cap, 30 s of agitation, and storage in a dark, climate-controlled space.

Sampling and Sample Analysis Procedures

After the dewatering process in the BRWC, gravimetric analysis enabled estimation of the extent of dewatering and together with sample taken for TDP analysis provided an estimate of un-sorbed P remaining. After the designated reaction time, a sample taken from each BRWC by pipetting from the standing water on top of the substrate and filtering through 0.45- μ m glass-fiber filter provided for analysis. Additional samples taken in the same manner from three BRWC of each carbon-source type after 20-d and 36-d reaction times provided for extended monitoring. One filtered sample and one filtrate weight was lost in processing resulting in two lost data points from the set. The remaining 59 samples were analyzed by ICP-AES in accordance with EPA Method 200.7 (USEPA, 1994) to determine TPD and TDI for each sample.

Data Analysis

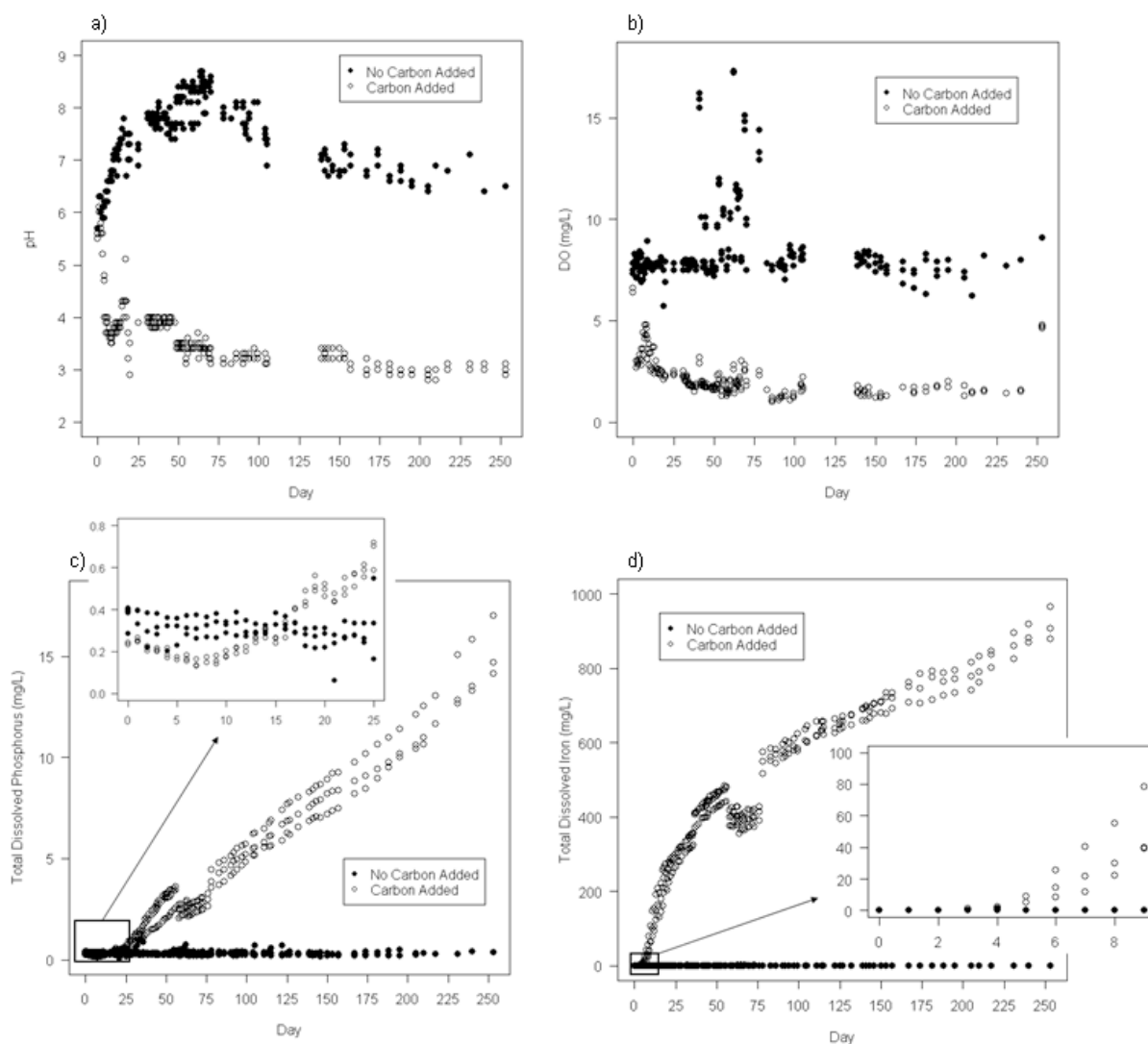
Three calculated values for each of the 36 BRWC provided for further analysis: 1) the mass of P initially adsorbed, 2) the mass of P released at each time interval, and 3) the percentage of initially adsorbed P released at each time interval. For data values below the analytical limits of the instrument, the analytical limit served for calculations. Due to a lack of normality among residuals, a Kruskal non-parametric test applied to the data tested for differences between means with pairwise multiple comparisons with a Bonferroni correction factor to determine which means were different. Statistical analyses were again performed with software from the R-project (R Development Core Team, 2009).

Results and Discussion

Flow-through wetland cells (FTWC)

pH

Both the carbon-treated cells and the control cells initially displayed near-neutral pH; the carbon-treated cell pH dropped significantly and remained low throughout the study, while the control cell pH rose initially and then fell slightly (fig. 3.2a). Although slight fluctuations in pH occurred among cells within the control group and the treatment group, there was a much more noticeable difference between groups. Control cells consistently exhibited higher pH than treatment cells, which may be an indication of redox-processes and microbial activity. The direction of pH change was somewhat unexpected, however, since reduction reactions as a whole tend to increase pH toward 7.0 (McBride, 1994). It is possible that secondary chemical and microbial reactions taking place in the cells were responsible for this decrease in pH. Some possibilities include: 1) H^+ producing precipitation reactions of siderite (McBride, 1994), 2) complex interactions with organic matter creating organically complexed, soluble forms of Fe^{3+} while releasing H^+ , or 3) the production of organic acids through microbial respiration. This observed decrease in pH may explain some of the initial decrease in TDP discussed under TDP results. The loss of dissolved oxygen and pH data for a 3-wk period near the middle of the study explains the gaps seen in figure 3.2a and 3.2b.



Rosenquist, R-Project

Figure 3.2 - Trends in a) pH, b) dissolved oxygen, c) TDP, and d) TDI during the study reveal significant differences between carbon-treated and control cells

Dissolved Oxygen

Dissolved oxygen concentrations can be a good indicator of substrate redox condition since, according to McBride (1994), the dominance of microbial activity transitions from aerobic to anaerobic processes when dissolved oxygen concentrations reach trace levels. Initially, both the control and carbon-treated cells had dissolved oxygen concentrations near 8 mg/L, but the carbon-treated cells reached dissolved oxygen content near 2 mg/L within a few days (fig. 3.2b). Concentrations near 2 mg/L probably do not represent trace levels, but several factors must be

considered: 1) measurements were taken at the top of the reactor and may not be representative of pore-water throughout the FTWC, 2) the instrumentation used in this study for dissolved oxygen is useful for providing gross estimates and comparisons and likely provides better precision than accuracy, and 3) Fe may have been reduced in the presence of some dissolved oxygen by soluble organics (McBride, 1994). The control cells maintained dissolved oxygen concentrations around 8 mg/L throughout the study period, though significant variation did exist within this group. Especially high values seen for control cells (fig 3.2b) were probably due to analytical error. Given these conditions, dissolved oxygen conditions, hence redox potential, did lower as expected with the addition of a carbon source.

Total Dissolved Phosphorus

TDP steadily increased throughout the study period for carbon-treated cells (fig. 3.2c) while TDP concentrations in the control cells remained low. A slight initial decrease in TDP occurred in the treatment cells, seen in the inset of figure 3.2c, is likely due to higher thermodynamic favorability for adsorption at lower pH. A group of data seen in figure 3.2c (day 58 - day 76), corresponding to a particular run on the ICP-AES instrument, has noticeably lower values for TDP than the rest of the data, mostly likely due to analytical error. The rate of P release (> 200 days) in the cells was much slower than the previous P adsorption (< 20 days) (Rosenquist et al., 2010) and was probably limited by the biological Fe-reduction process.

Total Dissolved Iron

TDI remained constant during the study for the control cells; however, a significant increase occurred in the carbon-treated cells suggesting that the microbial reduction process required the addition of a carbon source (fig. 3.2d). The TDI increase in the carbon-treated cells occurs 4-6 days after the addition of carbon (fig 3.2d, insert). A group of data from the same days as for TDP above (day 58-day 76) appear lower in figure 3.2d, again probably due to analytical error. Apart from this, a second-order decrease in the relationship of TDI with time occurred with an inflection point near 500 mg-Fe/L. The change is likely due to the complete reduction of the labile Fe pool and/or some other decrease in bioavailability of Fe as a terminal electron acceptor.

Iron/P Correlation

A graphical analysis of the correlation between TDP and TDI revealed two distinct slope-regions (fig. 3.3). The best fit for the threshold concentration between the two slope-regions in the data was 524 mg-Fe/L, this second-order increase corresponds well to the second-order decrease in TDI (fig. 3.2d). This result may indicate that re-sorption onto remaining bioavailable Fe attenuated P release before a threshold concentration of Fe reduction allowed more rapid P release. Significant positive correlation exists between TDP and TDI in both slope regions, while the difference in the slopes for these regions is significant as well ($p < 0.05$; $R^2=0.96$). For the first region, the estimated slope is 0.007 mg-P/mg-Fe, while for the second region the estimated additional slope is 0.023 mg-P/mg-Fe. These slopes correspond to a 4-fold increase in P released for a given amount Fe reduced, after reaching a threshold amount of Fe reduction.

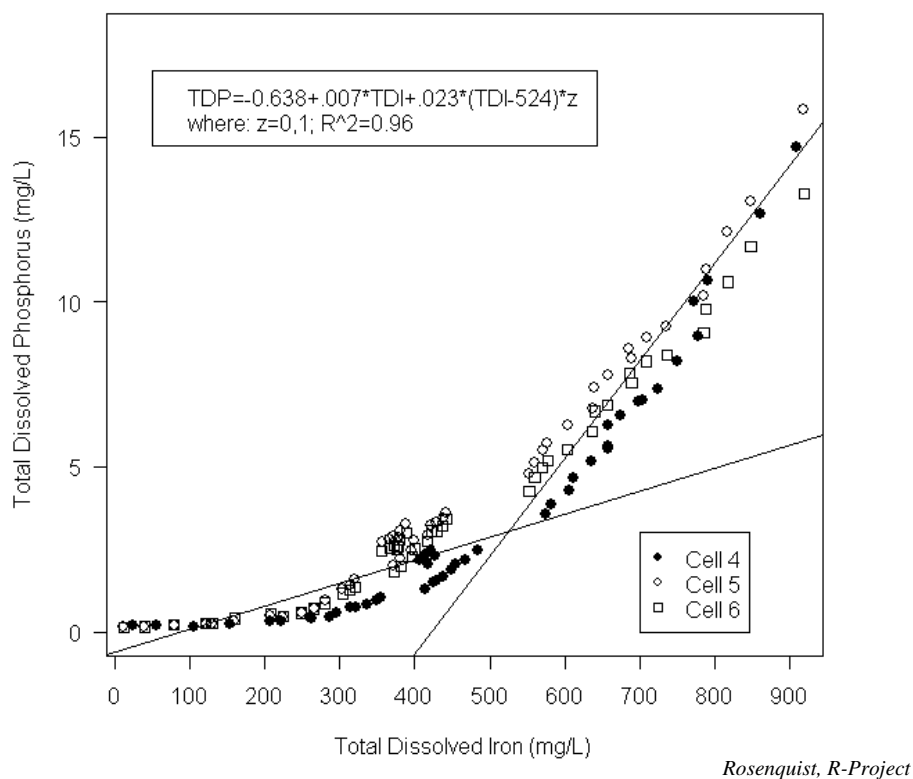


Figure 3.3 - The correlation plot for TDP (mg/L) versus TDI (mg/L) for data after start of Fe reduction contains two distinct slope-regions

Comparison of P-loading and Post-reduction TDP Concentrations

Comparing the TDP concentration in the carbon-treated FTWC for the last sample day (Day 253) to the influent concentrations over the entire P-loading period indicates that Fe reduction in this system is capable of releasing P at concentrations well above those present during adsorption (Table 3.1).

Table 3.1 - Comparison of P concentrations in carbon-treated FTWC

	Mean (mg/L)	Standard Deviation
Influent Concentrations during P Loading	0.25	0.16
Final Concentration after Reduction (253d)	15.3	1.50
95% Confidence Interval on Percent Increase (%)	4080 - 8790	

Comparing the estimates of total mass of P both adsorbed and released provides an estimate of the percent of previously adsorbed P released by the reduction process (Table 3.2). This percentage can also lead to inferences about the amount of time necessary to complete the rejuvenation process.

Table 3.2 - Rejuvenation percentage of carbon-treated FTWC

	Cell 4	Cell 5	Cell 6
Estimate of Previously Adsorbed P (mg)	295	274	198
Estimate of P in solution (mg)	178	149	154
Percent Desorption of Previously Adsorbed P (%)	60.5	54.3	77.9
95% Confidence Interval on Percent Desorption (%)	33.8 - 94.6		

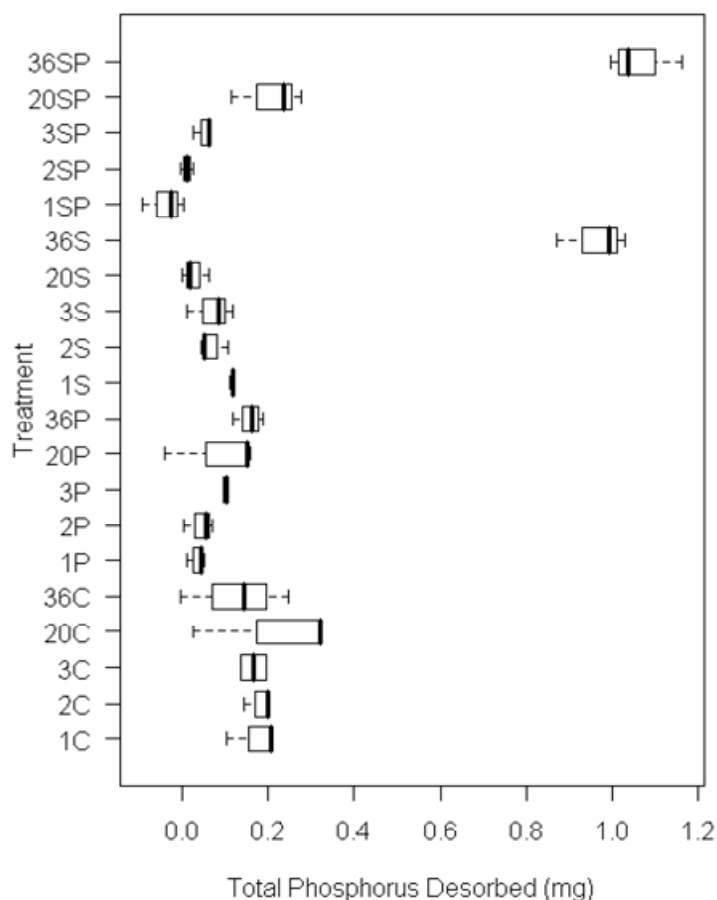
Coloration

Over the sampling period, the color of samples taken from the top of the carbon-treated FTWC became increasingly darker with yellow, then tan, and then increasingly darker brown colors observed.

Batch-reactor wetland cells (BRWC)

Total Dissolved Phosphorus

There was also a statistical difference in the means of P desorption in the treatment groups from the BRWC (p -value=0.002; Kruskal test). Pairwise multiple comparisons of all groups revealed that the 36-d sugar-solution and 36-d sugar-solution/surface-water treatments were significantly different from all other treatments (fig. 3.4), indicating that a carbon-source addition in excess of that available from the surface water sample was necessary to drive Fe reduction. P desorption in these two treatments was not statistically different, indicating that any microbial inoculation gained from a surface runoff sample was not necessary to achieve P release.



Rosenquist, R-Project

Figure 3.4 - Total desorbed P for the various BRWC treatments (C-Control; S-Sugar; P-Pond; SP=Sugar/Pond) and retention times in days (plot depicts: $Q_1-1.5*IQR$; Q_1 ; Median; Q_3 ; $Q_3+1.5*IQR$)

Total Dissolved Iron

An analysis of TDI in all groups provides another significant difference between treatments (p -value=4.33E-5; Kruskal test), with pairwise multiple comparisons indicating that again the 36-d sugar-solution and 36-d sugar-solution/surface-water treatments were significantly different from all other treatments (fig. 3.5). Unlike the results for TDP, TDI in the 36-d sugar-solution treatment was significantly higher than TDI in the 36-d sugar-solution/surface-water treatment. A possible explanation for this result is a higher sugar concentration, providing more carbon for additional growth and metabolism of Fe-reducing microorganisms.

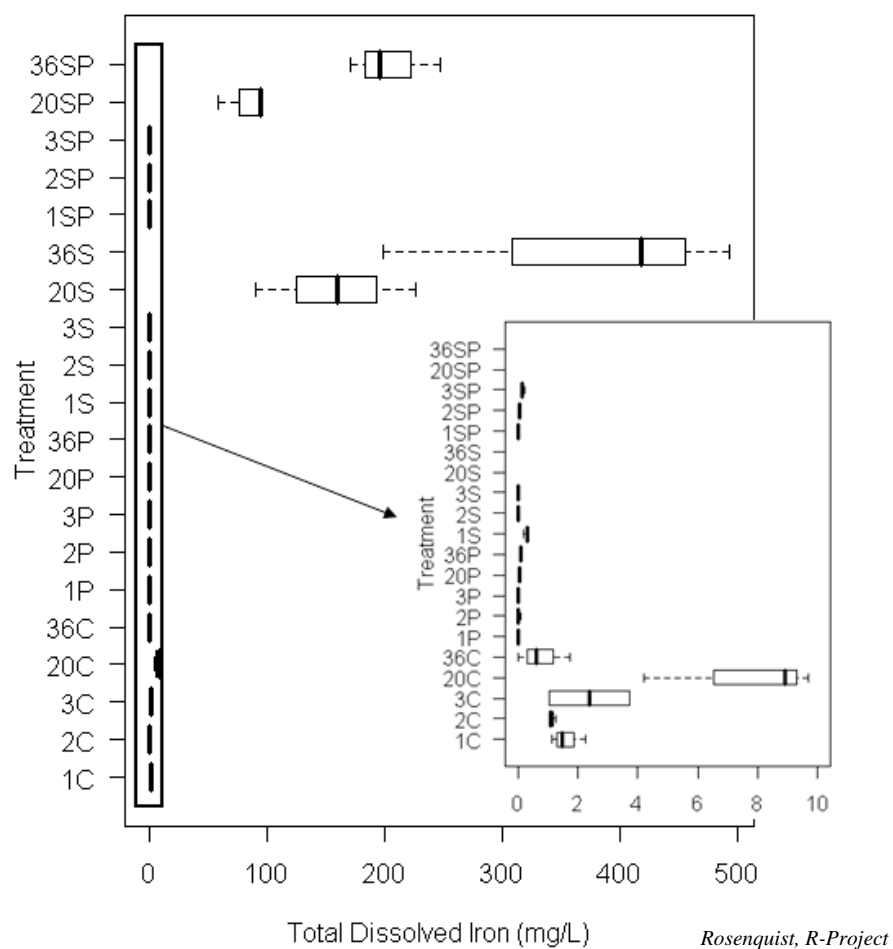


Figure 3.5 - TDI for the various BRWC treatments (C-Control; S-Sugar; P-Pond; SP=Sugar/Pond) and retention times in days (plot depicts: $Q_1-1.5*IQR$; Q_1 ; Median; Q_3 ; $Q_3+1.5*IQR$)

No statistical difference in initial P adsorption between treatment groups was observed (p -value=0.907; Kruskal test; fig. 3.6). The time before significant Fe-reduction/P-desorption took place ($20\text{-d} < t < 36\text{-d}$) agrees with the results from the FTWC. Percent desorption for the 36-d treatments with sugar-solution and sugar-solution/surface-water had a mean of 32.7% with a standard deviation of 4.42%.

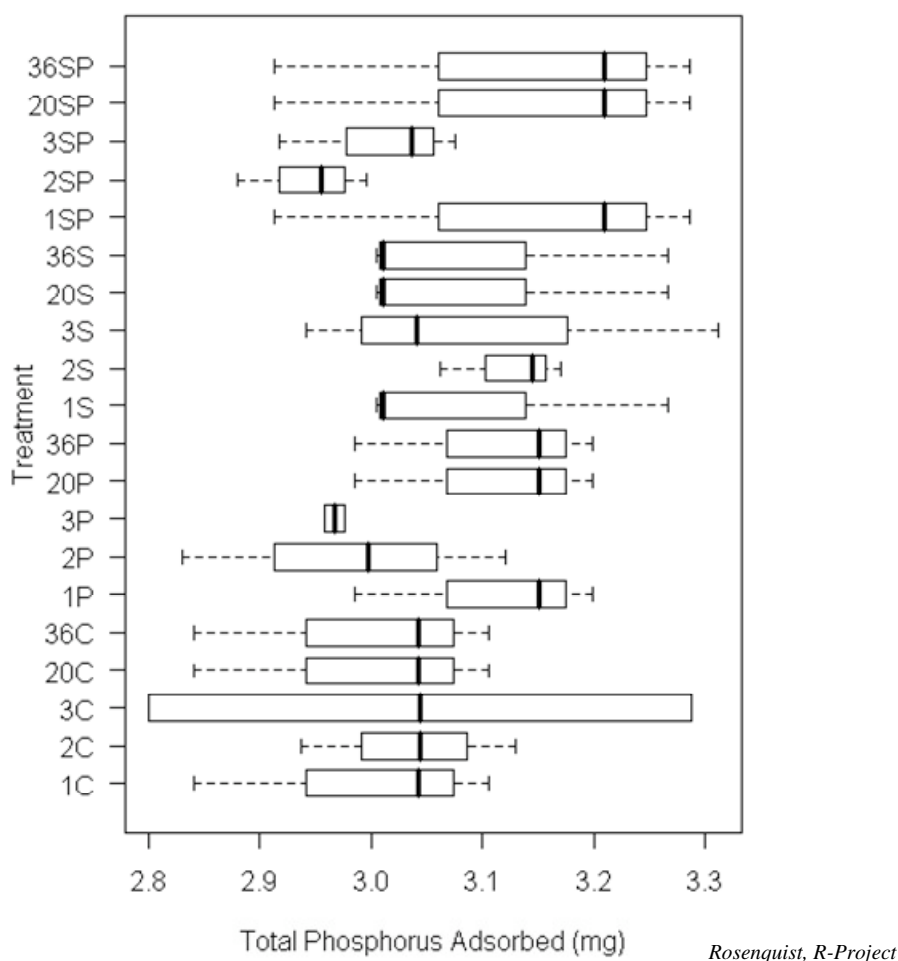


Figure 3.6 - Total initially adsorbed P for the various BRWC treatments (C-Control; S-Sugar; P-Pond; SP=Sugar/Pond) and retention times in days (plot depicts: $Q_1-1.5*IQR$; Q_1 ; Median; Q_3 ; $Q_3+1.5*IQR$)

Summary of FTWC and BRWC Results

The results from the FTWC indicate that a facilitated Fe-reduction process can release a large percentage of P adsorbed to substrates during filtration of water with typical stormwater concentrations of P. Results from the BRWC further indicate that the addition of a carbon source

in excess of that available in a surface-water sample was necessary, but that inclusion of the surface water to provide microbial seeding was not necessary to initiate Fe reduction.

Conclusions

Results obtained from both FTWC and BRWC indicate a significant ability to release previously sequestered P within substrates by microbial reduction of Fe. The following conclusions can be made based on the above results: 1) Fe-reducing microorganisms are naturally present in the sand media and inclusion of the surface-water sample did not significantly increase the amount of Fe reduced or P released; 2) addition of a carbon source was necessary to promote microbial reduction of Fe; 3) dissolved P was positively correlated with dissolved Fe indicating that release of previously-sequestered P in substrates accompanies Fe reduction; 4) the two-region relationship between P release and Fe reduction indicates that P release is attenuated below a threshold of Fe dissolution, possibly due to a availability for re-adsorption while some Fe³⁺ coatings remain on substrate surfaces; 5) A high percentage of previously adsorbed P can be released as a result of microbial Fe reduction, though the process is slower by orders of magnitude than adsorption for the same P load; and 6) P concentration in rejuvenating cells can increase by orders of magnitude over the influent, P-loading concentrations .

While the dissolution of Fe and subsequent release of P in the FTWC continued to increase throughout the study period, TDP concentrations will reach a maximum (at least upon complete release of all available P). Given the results, it is feasible that this method can release the majority of previously adsorbed P in substrates. However, to achieve efficient cycling between rejuvenation and filtration cycles the rejuvenation time must be decreased, necessitating further research to facilitate faster Fe reduction. Once P is desorbed, there are two additional challenges, which present opportunities for further research. First, the development of a process that will either remove a high-concentration, dissolved-P solution or precipitate a solid for harvest. Then, recoating the sand media with Fe is necessary to prepare the substrate for continued adsorption of P. This study has provided, in the context of the larger research project, further indication that a BMP based upon the rejuvenation of substrate sorption capacity by microbial reduction is a practical method to improve nutrient management in urban areas and reduce the environmental and economic impacts of eutrophication.

Acknowledgements

The authors would like to thank the National Science Foundation for providing support for students who worked on this project as a part of the NSF Research Experiences for Undergraduates grant. In addition, the authors would like to specifically acknowledge assistance from exceptional faculty (Dr. Tess Wynn and Dr. Daniel Gallagher), staff (Laura Teany and Athena Tilley), and students (Molly Julian, Gina Hayes, Yemi Ojumu, Cody Newbill, Sarah Brahman, Jonathan Pennington, and Alyse Egner) who were all critical to the success of this study.

References

- Abelson, P. H. 1999. A potential phosphate crisis. *Science* 283 (5410): 2015.
- Aldous, A. R., C. B. Craft, S. J. Carla, M. J. Barry, and B. B. Leslie. 2007. Soil phosphorus release from a restoration wetland, Upper Klamath Lake, Oregon. *Wetlands* 27 (4): 1025–1035.
- Baker, B. J., K. W. King, and H. A. Torbert. 2007. Runoff losses of dissolved reactive phosphorus from organic fertilizer applied to sod. *Trans. ASABE* 50 (2): 449-454.
- Brady, N. C., and R. R. Weil. 2002. *The Nature and Properties of Soils*. Upper Saddle River, N.J.: Prentice Hall.
- Carleton, J. N., T. J. Grizzard, A. N. Godrej, H. E. Post, L. Lampe, and P. P. Kenel. 2000. Performance of a constructed wetlands in treating urban stormwater runoff. *Water Environ. Res.* 72 (3): 295-304.
- Coveney, M. F., D. L. Stites, E. F. Lowe, and R. C. Battoe. 2002. Nutrient removal from eutrophic lake water by wetland filtration. *Ecol. Eng.* 19: 141–159.
- Drizo, A., Y. Comeau, C. Forget, and R. P. Chapuis. 2002. Phosphorus saturation potential: A parameter for estimating the longevity of constructed wetland systems. *Environ. Sci. Technol.* 36 (21): 4642-4648.
- Griffioen, J. 2006. Extent of immobilization of phosphate during aeration of nutrient-rich, anoxic groundwater. *Journal of Hydrology* 320 (3/4): 359-369.
- Hammer, D. 1992. Designing constructed wetlands systems to treat agricultural nonpoint source pollution. *Ecol. Eng.* 1 (1/2): 49-82.
- Hogan, D. M., and M. R. Waldbridge. 2007. Best management practices for nutrient and sediment retention in urban stormwater runoff. *J. Environ. Qual.* 36: 386-395.

- Hunt, W. F., and A. Wossink. 2003. The Economics of Structural Stormwater BMPs in North Carolina. UNC-WRRI-2003-344. Raleigh, NC: UNC-WRRI.
- Kadlec, R. H. 2000. The inadequacy of first-order treatment wetland models. *Ecol. Eng.* 15: 105-119.
- Kadlec, R. H. 2005. Phosphorus removal in emergent free surface wetlands. *J. Environ. Sci. Health, Pt. A: Environ. Sci. Eng. Toxic Hazard. Subst. Control* 40 (6): 1293-1306.
- Kadlec, R. H., and S. D. Wallace. 2009. *Treatment Wetlands*. Boca Raton, FL: CRC Press.
- Keppler, A. M., and J. F. Martin. 2008. Investigating the performance of a laboratory-scale ecological system to treat dairy wastewater. *Trans. ASABE* 51 (5): 1837-1846.
- Komatsu, E., T. Fukushima, and H. Shiraishi. 2006. Modeling of P-dynamics and algal growth in a stratified reservoir - mechanisms of P-cycle in water and interaction between overlying water and sediment. *Ecol. Model.* 197 (3/4): 331-349.
- Lantzke, I. R., A. D. Heritage, G. Pistillo, and D. S. Mitchell. 1998. Phosphorus removal rates in bucket size planted wetlands with a vertical hydraulic flow. *Water Res.* 32 (4): 1280-1286.
- Lantzke, I. R., D. S. Mitchell, A. D. Heritage, and K. P. Sharma. 1999. A model of factors controlling orthophosphate removal in planted vertical flow wetlands. *Ecol. Eng.* 12 (1): 93-105.
- Lovely, D. R., E. J. P. Phillips, and D. J. Lonergan. 1991. Enzymatic versus nonenzymatic mechanisms for Fe(III) reduction in aquatic sediments. *Environ. Sci. Technol.* 25 (6): 1062-1067.
- Luederitz, V., E. Eckert, M. Lange-Weber, A. Lange, and R. M. Gersberg. 2001. Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. *Ecol. Eng.* 18: 157-171.
- Luederitz, V., and F. Gerlach. 2002. Phosphorous removal in different constructed wetlands. *Acta Biotechnology* 22 (1/2): 91-99.
- McBride, M. B. 1994. *Environmental Chemistry of Soils*. New York, NY: Oxford.
- McGechan, M. B., and D. R. Lewis. 2002. Sorption of phosphorus by soil, part 1: Principles, equations, and models. *Biosys. Eng.* 82 (1): 1-24.
- Novotny, V. 2003. *Water Quality*. Hoboken, NJ: John Wiley and Sons, Inc.
- Peretyazhko, T., and G. Sposito. 2005. Iron(III) reduction and phosphorous solubilization in humid tropical forest soils. *Geochemica et Cosmochimica Acta* 69 (14): 3643-3652.

- Rosenquist, S. E., W. C. Hession, M. J. Eick, and D. H. Vaughan. 2010. Variability in adsorptive phosphorus removal by structural stormwater best management practices. *Ecol. Eng.*: In Press. <http://dx.doi.org/10.1016/j.ecoleng.2009.12.008>.
- Scheibe, T. D., Y. Fang, C. J. Murray, E. E. Roden, and J. Chen. 2006. Transport and biogeochemical reaction of metals in a physically and chemically heterogeneous aquifer. *Geosphere* 2 (4): 220-235.
- R Development Core Team. 2009. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing.
- Tenenbaum, D. J. 2004. Constructed wetlands: Borrowing a concept from nature. *Environ. Health Perspect.* 112 (1): 44-48.
- USEPA. 1994. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. EPA Method 200.7. Cincinnati, OH: US Environmental Protection Agency, Office of Research and Development.
- Vymazal, J. 2005. Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. *Ecol. Eng.* 25 (5): 478-490.
- White, J. R., L. M. Gardner, M. Sees, and R. Corstanje. 2008. The short-term effects of prescribed burning on biomass removal and the release of nitrogen and phosphorus in a treatment wetland. *J. Environ. Qual.* 37: 2387-2391.
- Wilson, G. V., F. E. Rhoton, and H. M. Selim. 2004. Modeling the impact of ferrihydrite on adsorption-desorption of soil phosphorus. *Soil Science* 169 (4): 271-281.
- Zhang, J., and X. Huang. 2007. Relative importance of solid-phase phosphorus and iron on the sorption behavior of sediments. *Environ. Sci. Technol.* 41 (8): 2789-2795.

Urban wetland filter: field results in the development of a renewable practice for managing phosphorus in stormwater runoff from high land-value areas

S. E. Rosenquist, W.C. Hession, M.J. Eick, D.H. Vaughan

Abstract

Degradation of surface water quality caused by excess nutrient loads in stormwater runoff is a major environmental and economic problem in the U.S. Phosphorus (P) is typically the limiting nutrient for the harmful algal growth seen in freshwater bodies and the best target to prevent eutrophication, the biological process associated with this degradation. Constructed wetlands (CW) and other stormwater filtration practices that include P removal by sorption processes (SP) in substrates can provide economical treatment of stormwater, but they have certain obstacles and limitations. Over the past three years, a multi-study research program has focused on understanding the key variables that influence P removal by SP in substrates and developing the urban wetland filter (UWF), a unique management practice for P in stormwater. The UWF minimizes required CW size for use in high land-value areas, allows for periodic rejuvenation of P sequestration potential in the CW substrates, and enables harvesting of P for recycling as a fertilizer. This study, the first to test the UWF in the field, involved six vertical flow wetland cells which contained a substrate of either sand or a combination of sand and cast-iron filings and filtered water from a eutrophic retention pond. Results support the following conclusions: 1) P removal is likely dependent on multiple factors, including influent P concentration, previous substrate/solution equilibrium, pH, and time; 2) the rejuvenation cycle is capable of releasing P removed during stormwater filtration; 3) inclusion of cast-iron filings in the sand substrate promotes additional P removal over sand alone and enables further removal after rejuvenation; but 4) inclusion of cast-iron filings may limit the release of P during rejuvenation.

Introduction

Nutrient pollution in runoff has been directly linked to harmful algal blooms in many US water bodies (Boesch et al., 2001). The impact of harmful algal blooms is a general decrease in the ecological service that these water bodies can provide and may also include declines in commercial and recreational fish populations (Boesch et al., 2001), taste and odor problems for drinking water reservoirs, and losses in the aesthetic appeal of these valuable and beautiful natural resources (Camargo and Alonso, 2006). Phosphorus (P) is the limiting nutrient for the harmful algal growth seen in most freshwater and even some saltwater systems (Fisher et al., 1992) and is likely the best target to prevent eutrophication, the biological process associated with these algal blooms.

While remediation efforts have been successful in reducing point sources of P, non-point or diffuse sources of P continue contribute significantly to surface water bodies (Boesch et al., 2001). In Virginia, particularly in the Chesapeake Bay watershed, non-point sources of pollution are being targeted for new regulations that are intended to decrease the nutrient stress on the Bay (Dowling, 2009). These regulations aim at regulating the allowable export of phosphorus (P) from stormwater, especially in newly developed and redeveloped urban areas. Various management practices presented to the land owner or developer provide options to decrease nutrient exports from a particular drainage area including constructed wetlands (CW), bioretention areas, and other practices that include P removal by sorption processes (SP).

Static nutrient removal performance is a typical assumption for assessing the efficacy of various stormwater management practices and can be accurate under certain conditions and over a limited amount of time. However, performance of these management practices can vary significantly due to a range of circumstances, or just a sufficiently long period of time (Drizo et al., 2002; Kadlec, 2005). Variation over time is especially relevant if appropriate maintenance is not performed (Hunt and Lord, 2006). Many of these management practices rely heavily on SP in either captured sediment or filtration substrates to provide the P removal capacity desired (Arias and Brix, 2005; Shilton et al., 2005). While SP can be an effective and efficient means of sequestering P from stormwater, it is a dynamic process (Kadlec, 2005), reliant on many factors to determine both the possible reductions in P concentration, and the length of time that these reduction can be sustained. One factor proposed to explain variation in removal by sorption is the available concentration gradient based on both the current influent concentration and the

previous equilibrium condition between substrate adsorbed P and solution P. Without a positive concentration gradient remaining between substrate and solution, removal by sorption is drastically reduced (Lantzke et al., 1998; Rosenquist et al., 2010).

This study is part of a multi-study research program that has focused on understanding the key variables that influence P removal by SP in substrates and developing the urban wetland filter (UWF). The UWF is a unique application of CW for managing P in stormwater, specifically tailored to the unique demands of a high land-value setting. The UWF minimizes required CW size for use in high land-value areas, allows for periodic rejuvenation of P-sequestration potential in the CW substrates, and enables harvesting of P for recycling as a fertilizer. The specific objectives of this study were: 1) to quantify the benefit of the addition of cast-iron filings to P removal performance in a CW; 2) to verify the efficacy of the rejuvenation process with cells filtering in the field; 3) to investigate the effects of cast-iron filing addition on the rejuvenation process; 4) to determine if the addition of cast-iron filings would enable continued adsorption of P after rejuvenation; and 5) to test the concentration-gradient model on P removal performance of filters in the field.

Weiss et al. (2007) reported in a study comparing the cost and effectiveness six different stormwater management practices that "constructed wetlands have been the least expensive to construct and maintain if appropriate land is available." The study goes on to say that despite the high effectiveness of CW in removing pollutants, including P, the land availability assumption can be a major obstacle for CW implementation. This study is the first to field test the UWF concept, which was first described Rosenquist et al. (2010). In addition, the ability to harvest P from the wetland provides a source for recycling P as a fertilizer, and a tangible product for nutrient trading. With estimates placing the value of P removed from stormwater with current technology between \$24 and \$1,346 per kg depending on the influent and effluent concentrations (Sano et al., 2005), the costs of installation and maintenance for the UWF could be quickly offset by either nutrient trading credits or direct use of harvested P to offset fertilizer costs. The key feature of the UWF that enables P recycling is a rejuvenation cycle based on the microbial reduction of iron (Fe) in the filtration substrate. Oxidized forms of Fe demonstrate large P sorption capacities (Shilton et al., 2005) but once they are reduced, much of the adsorbed P is released (Peretyazhko and Sposito, 2005; Rosenquist et al., In Review). This process has

demonstrated the capacity to release P that was sequestered in the wetland during filtration (Rosenquist et al., In Review).

After the rejuvenation cycle is complete, it becomes necessary to replace the oxidized-Fe (Fe^{3+}) coatings on the substrate in order to achieve further sorption of P. This replacement process is the role of the cast-iron filings investigated in this study. Several previous studies have investigated the possibility of adding zero-valent Fe (Fe^0), often in the form of cast-iron filings, to filtration substrates in order to increase their sorption capacity, and extend their useful lifetime (Luederitz and Gerlach, 2002; Kaplan, 2004; Drizo et al., 2006; Erickson et al., 2007). Fe^0 is also of interest due to its stable oxidation state under reduced conditions. When Fe^0 particles oxidize, they can form a coating of Fe^{3+} that has a high sorption capacity for P. When the environment becomes anaerobic, microbes reduce this oxidized coating from Fe^{3+} to a much more soluble Fe^{2+} , releasing the adsorbed P. However, the underlying Fe^0 is indisposed to further reduction and remains stable until the system becomes aerobic again. When the system returns to an aerobic state, Fe^{3+} coatings can again form on the surface of the Fe^0 particles while as an additional benefit the redox-cycling process may promote Fe^{3+} coating in the bulk substrate as well (Kaplan, 2004).

Methods and Materials

Study Site

A siphon system fed stormwater simultaneously to two wetland cells from a stormwater retention pond located on the Virginia Tech campus (fig. 4.1). A section of slotted well screen (slot width of 0.5 mm) pre-filtered the water to exclude trash and detritus. The retention pond used in this study drains several areas that are likely contributors of P through runoff including a dairy farm, a recently active construction area with associated erosion of high-P sediments, and heavily fertilized turf areas.

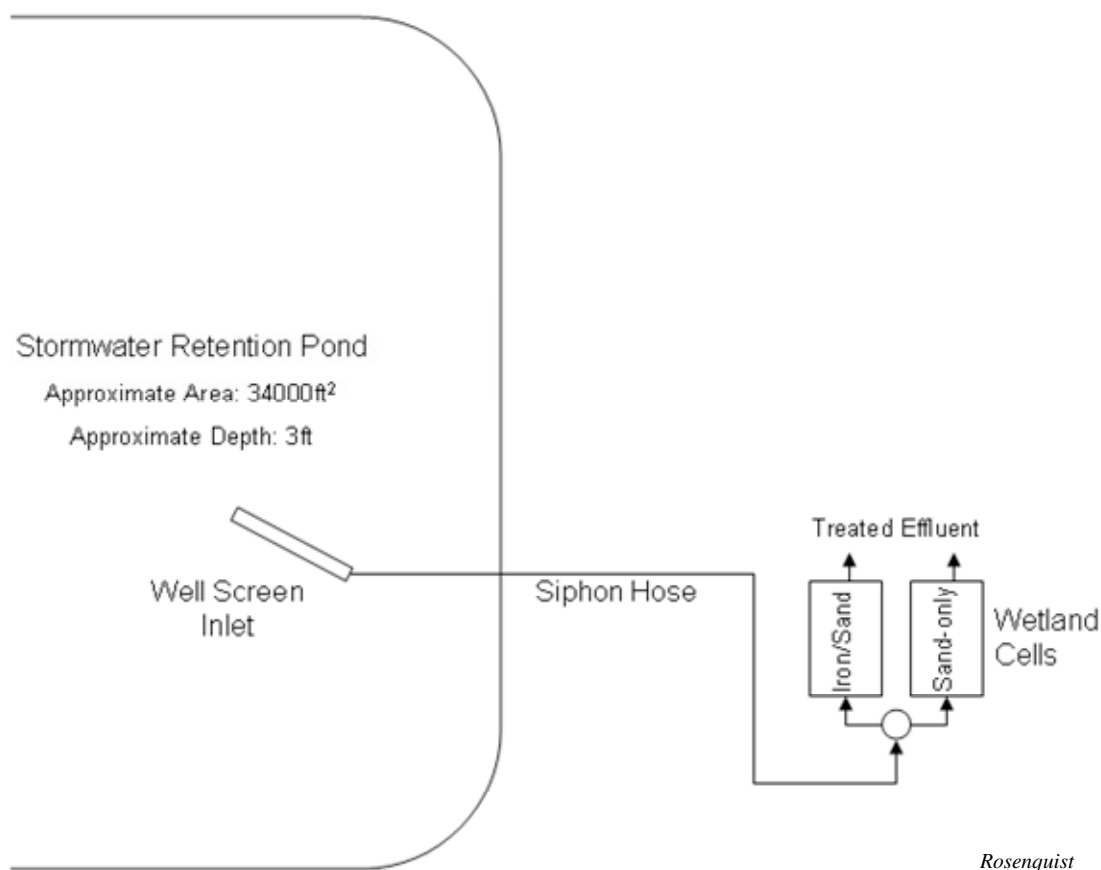


Figure 4.1 - Experimental setup of field-scale wetland cells at a Virginia Tech stormwater retention pond

Wetland Cell Construction

Six, rectangular, plastic containers (38 cm tall x 46 cm L x 33 cm W) contained the wetland cells (fig. 4.2). Cell construction began with 8 cm of limestone gravel containing a slotted section of plastic pipe. This pipe connected to a bulkhead fitting on one end of the container to function as the water outlet for the cell. Above the gravel, 8.5 L of substrate including USDA grade medium sand (0.2% - 0.7% Fe by mass) sourced from Newcastle, VA and in some cases a cast-iron filing waste product sourced from a local machining operation. The water inlet and flow control structure was located above the wetland substrate and connected through another bulkhead fitting in the opposite end of the container from the outlet. Cells were set up with downward, vertical flow. Between 5 cm and 6 cm of head remained above the substrate due to a constant-head float valve (Hudson Valve Company, Bakersville, CA) that restricted flow to a single direction.

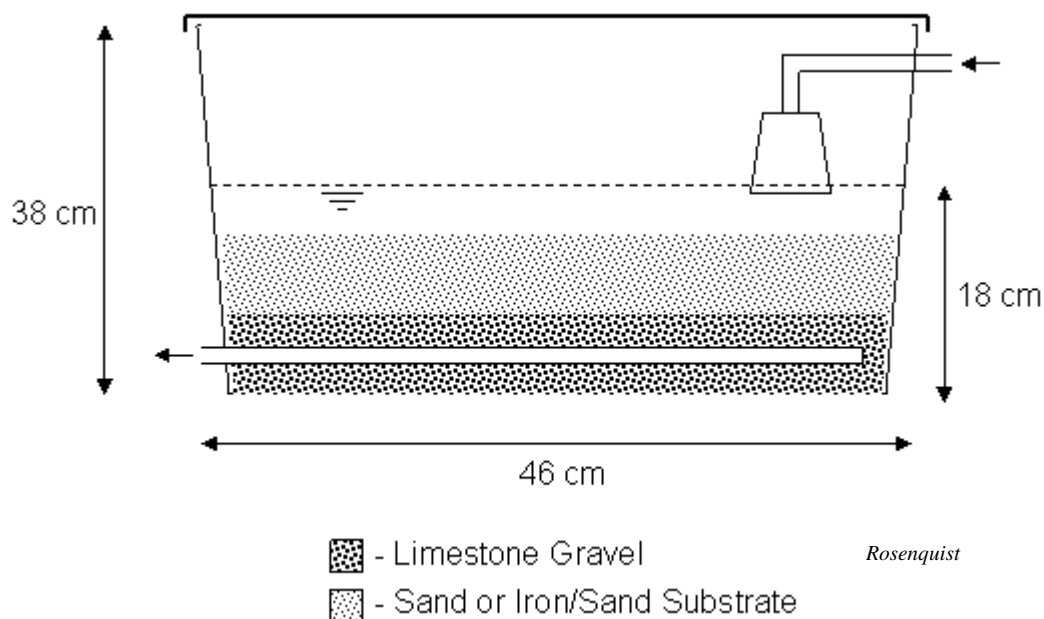


Figure 4.2 - Construction of the field-scale wetland cells

Experimental Design

This study had two experimental factors, sand-only versus iron/sand substrates and pre-rejuvenation versus post-rejuvenation runs of the wetland cells. The iron/sand cells, included sand thoroughly mixed with cast-iron filings at a 2:1 volumetric ratio, which corresponded roughly to a 1:1 mass ratio. There were three replicates of each type of cell, but only six cells in total since a given cell provided both a pre- and post-rejuvenation filtration run (fig. 4.3). The rejuvenation cycle consisted of adding 1000 g of sucrose sugar to each of the cells while saturated without flow to initiate Fe-reduction, then storing them for 50 days to promote the release of adsorbed P. Cells were stored in a climate-controlled space maintained between 18° C and 26° C. Each 48-h filtration run included one sand-only cell and one iron/sand cell run simultaneously. Three of these runs occurred before and three occurred after the rejuvenation cycle.

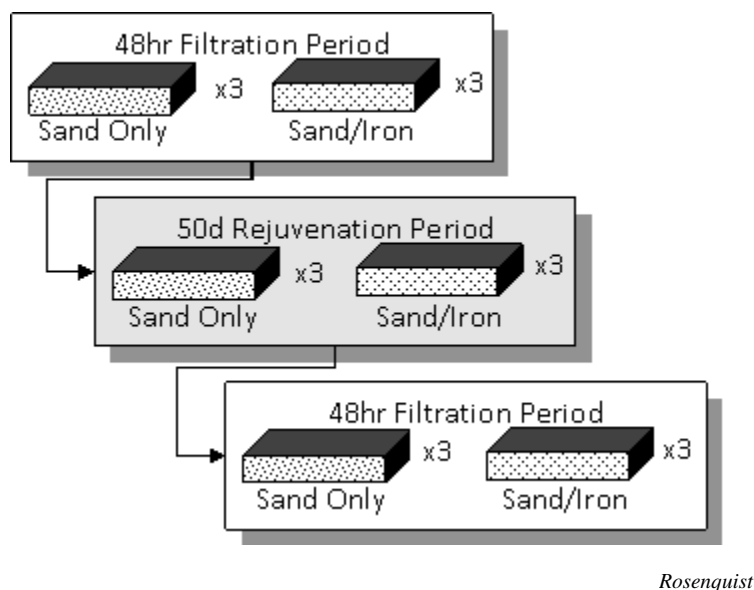


Figure 4.3 - Each of the six, wetland cells ran through three cycles including a pre-rejuvenation filter cycle, the rejuvenation cycle, and a post-rejuvenation filter cycle

Sampling and Sample Analysis

Water sampling during each run involved three automated samplers (ISCO 3700, Lincoln, NE), one located at the inlet to both cells and one located at each outlet. During each filtration run, the automated sampler gathered 24 multiplexed samples consisting of four, 200-mL samples taken at 30-minute intervals combined to form each composited sample. During one of the six runs, specifically the second post-rejuvenation run, automated sampler failure resulted in 12 missing inlet samples. An estimate of the inlet concentration during this period came from interpolation between a triplicate grab sample taken at the end of the run and the last sample taken by the automated sampler. A pH measurement taken from each of the 24 sample bottles after the run by a handheld pH meter (Hanna Instruments, Woonsocket, RI) tracked any changes in pH during the run. An additional sample bottle positioned at each outlet received effluent from the cells and held 1000 mL of continuously overflowing effluent for collection by two of the automated samplers. The third automated sampler collected influent samples from the inlet structure behind the float valves. Volumetric capture with a graduated cylinder and stopwatch provided flow rate measurements for the beginning and the end of each filtration run (Table 4.1). Interpolation of these two values provided flow rate estimates for each sampling time during a particular run.

Table 4.1 - Flow rates (L/min) observed before and after filtration runs

Run	Sand-only	Iron/Sand
	Before/After	Before/After
Pre-Rejuvenation, Cells 1	0.52/0.59	0.48/0.63
Pre-Rejuvenation, Cells 2	0.60/0.53	0.58/0.30
Pre-Rejuvenation, Cells 3	0.72/0.68	0.74/0.50
Post-Rejuvenation, Cells 1	0.71/0.57	0.50/0.54
Post-Rejuvenation, Cells 2	0.55/0.45	0.51/0.25
Post-Rejuvenation, Cells 3	0.53/0.43	0.39/0.35

Grab samples, taken from the top of the cells at day 0, day 33, and day 50 captured the changes occurring during the rejuvenation cycle. Sampling on day 50 included a composite sample in addition to the grab sample and a pH measurement. A volume measurement of the water resident in the cells when they were gravity drained allowed for mass calculations. The rejuvenation cycle did not include any cell rinsing prior to the post-rejuvenation filtration runs.

Sample preparation involved digestion of all samples by the ascorbic acid method (Virginia Tech Department of Biology, 2008). A colorimetric autoanalyzer (SEAL Analytical, Mequon, WI) used in accordance with standard operating procedures (Virginia Tech Department of Biology, 2008) provided analysis for total phosphorus (TP) from the six filtration runs. Based on concerns of color interference, inductively coupled plasma atomic emission spectroscopy (ICP-AES) conducted according to EPA method 200.7 (USEPA, 1994) provided analysis of TP and total iron (TI) for samples from the rejuvenation cycle.

Data Analysis

Filtration Runs

Visual analysis included graphing observed TP and pH trends for all filtration runs. For each 2-hr period in the filtration runs, a P-mass removal rate (mg/h) calculation drew on the associated influent concentration, effluent concentration, and flow-rate data. Because of a lack of normality among residuals (Shapiro-Wilkes Test, $p < 2.2E-16$) and the overall likelihood of non-normality in environmental sampling, the Kruskal-Wallis Test was used to test for any differences between treatment types including all cells as well as within treatment groups between replicate cells. Pairwise analysis with a Bonferroni correction factor to adjust p-values (p) followed the initial test to determine which groups were different from each other. A

bootstrap method (Chernick, 1999) with 10^6 iterations provided confidence intervals for P-mass removal rates and P-mass in solution during rejuvenation. Software from R-project (R Development Core Team, 2009) was utilized for all statistical analyses in this study.

Rejuvenation Process

A linear regression model using an indicator variable for substrate type was used to test the relationship between Fe and P in solution for the rejuvenation data. A significant relationship ($p \leq 0.05$) between these two variables supported the Fe-reduction process as a means to release adsorbed P from CW substrate. Pairwise analysis with a Bonferroni correction factor, using P-mass in solution as an estimate of the amount of P released through rejuvenation of the substrate, enabled comparisons between substrate types and sampling times during rejuvenation. Confidence intervals gathered by the bootstrap method cited above, provided additional comparison between substrate types and sampling time as well as between estimated rejuvenation totals and estimated filtration totals. Pairwise analysis with a Bonferroni correction factor also provided testing for significant differences in pH between rejuvenation and filtration.

Modeling Variability in Removal

Multivariate linear regression with backward selection was applied to the removal rate data to test for correlations with relevant variables including time, effluent pH, influent concentration, and the maximum previous effluent concentration at each point during the run (since this concentration should represent the existing substrate/solution equilibrium point). Effluent pH data were only included for analysis of pre-rejuvenation runs since the relationship between pH and removal was confounded in post-rejuvenation runs by carryover from the rejuvenation process. A Bonferroni correction factor provided adjustment to p to account for model application to subsets of the data.

Quality Control

Use of the pH meter in this study included periodic calibration in accordance with manufacturer specifications. Because TP (not TDP) was used to measure differences in P removal (due to sample collection and preservation requirements), measurements of total suspended solids (TSS) ensured that any differences in removal between cells could not be attributed to differences in physical removal processes. Measurements of TSS included a randomly selected group of five inlet, five sand-only effluent, and five iron/sand effluent

samples. Mean TSS removals for the cells were 3.44 mg/L (sand-only) and 1.76 mg/L (iron/sand). Analysis indicated no significant difference between mean TSS removal in the two substrate types ($p = 0.15$), thereby supporting the assumption of similar physical removal properties in the two substrate types. In addition, visual analysis of the filtered solids indicated that some of the solid mass filtered from the iron/sand effluent might have been Fe exported from the cells. Another quality control measure was the inclusion of a known standard to compare results for TP between the two analytical instrument types. Means for the standard analyzed in three separate runs on each instrument were 0.77 mg/L (ICP-AES) and 0.75 mg/L (colorimetric autoanalyzer). Analysis indicated no significant difference between these means ($p = 0.16$). A test of the sampling bottles ensured that variations in sample holding time were not affecting measured concentrations. This test revealed no significant correlation between time and TP in samples including influent, sand-only effluent, and iron/sand effluent held in bottles up to 9 days (all $p \geq 0.26$). To eliminate interference caused by carryover from the rejuvenation process, data management included omission of the first two data points for all post-rejuvenation cells from the removal-rate comparison between treatment groups and the multivariate regression analysis for variability in removal rate.

Results and Discussion

Filtration Runs

Experimental results indicated variation in P removal between both the substrate type and between pre- and post-rejuvenation runs (fig. 4.4). Effluent concentrations in general were lower for iron/sand cells than for sand-only cells, suggesting that the addition of cast-iron filings increases the P removal rate. As anticipated, iron/sand cells appeared to retain more sorption capacity after rejuvenation than sand-only cells. Sand-only cells acted as net-P sources in post-rejuvenation runs, likely because cells were not rinsed after rejuvenation and the sand-only cells had little or no sorption capacity left to re-adsorb P. Lower initial concentrations in the post-rejuvenation iron/sand cells indicate that P-sorption capacity was available in these cells by the time filtration began. Scale adjustment included omission of the initial concentrations in post-rejuvenation sand-only cells (0.39, 0.56, and 0.88, respectively) from Figure 4.4 because displaying these extreme points restricts visual analysis of the rest of the data. Graphically, results indicate variation between replicate runs.

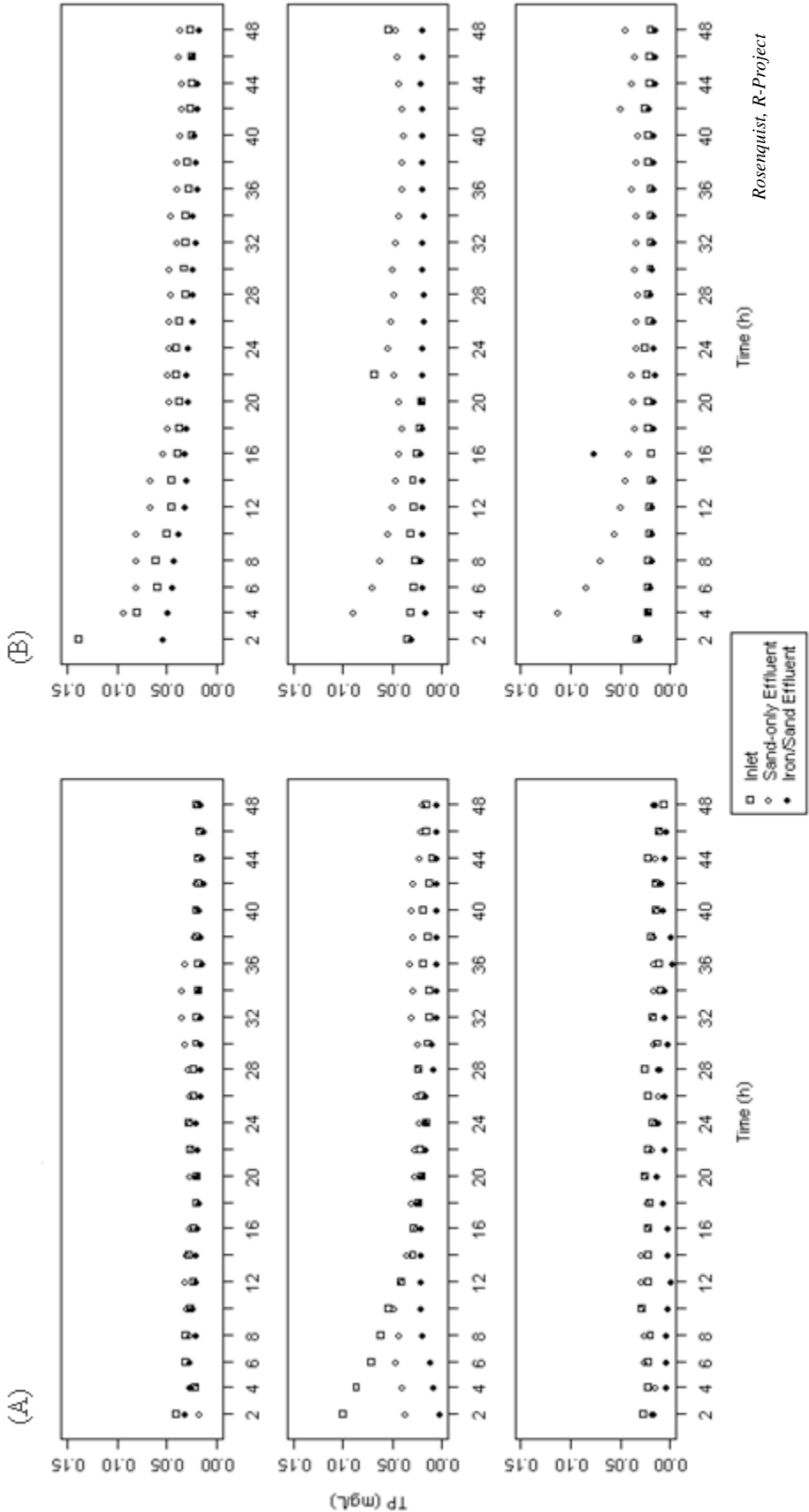


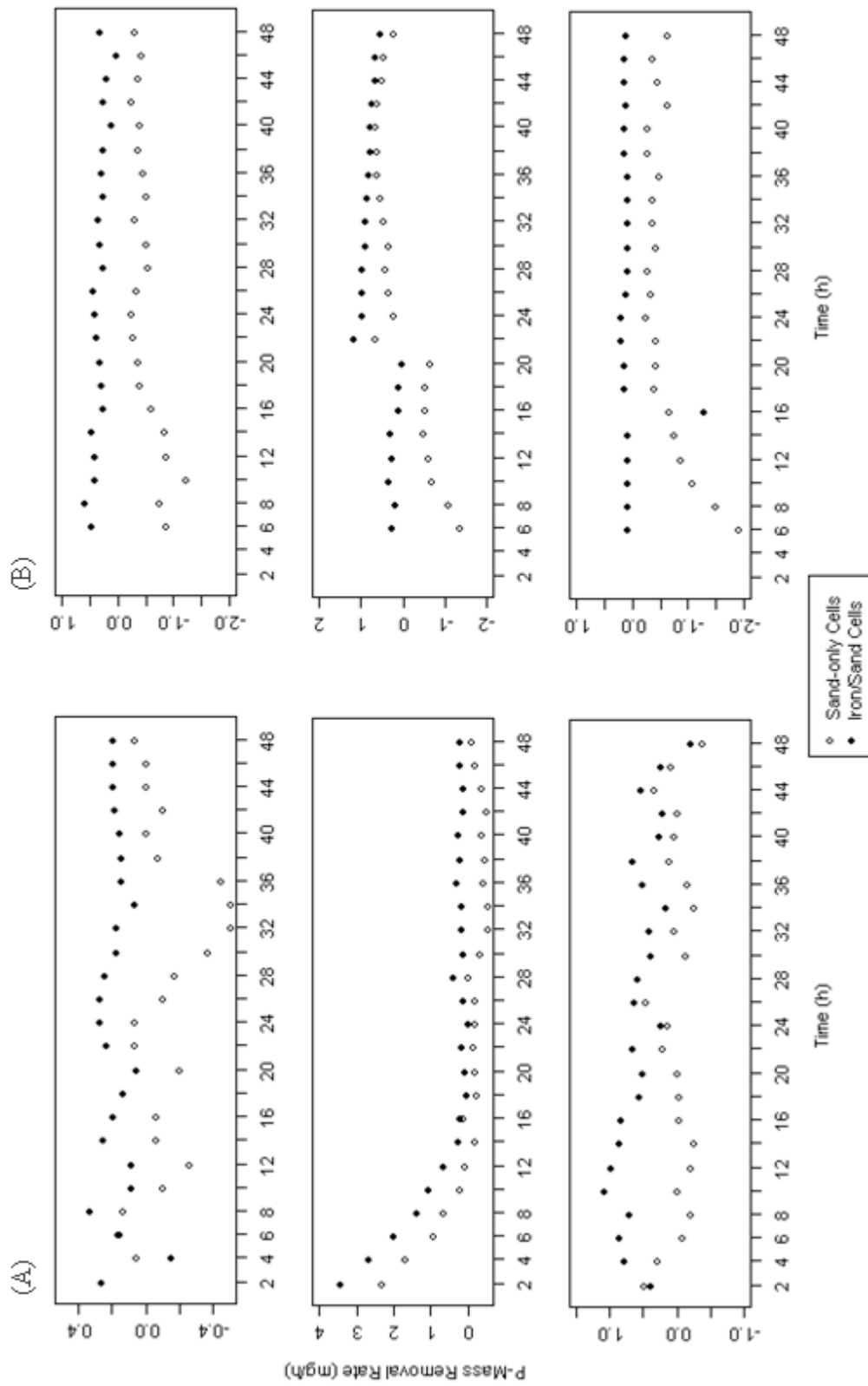
Figure 4.4 - Total phosphorus (TP) trends observed during filtration runs for (A) pre-rejuvenation runs and (B) post-rejuvenation runs

Rosenquist, R-Project

P-mass removal rates in the iron/sand cells maintained positive removal rates longer than sand-only cells in all but one pre-rejuvenation run (fig. 4.5). The one special case, seen in a pre-rejuvenation run (fig. 4.5, top left), is arguably not representative of a true cessation in P removal capacity. In all post-rejuvenation runs, iron/sand cells attained positive removal rates earlier and maintained positive removal rates longer than sand-only cells. These factors indicate that the addition of cast-iron filings may also increase the lifetime of P removal as reported by Erikson et al. (2007).

While relatively little variation in pH occurred in pre-rejuvenation runs, larger pH fluctuation did occur during post-rejuvenation runs and is probably a lingering effect of the rejuvenation process. There could also be changes in the pH properties of post-rejuvenation substrate since effluent pH continues to be lower than influent pH throughout the post-rejuvenation runs (fig. 4.6).

Comparison between treatments groups with replicate cells considered together showed that all treatment groups were statistically different except pre-rejuvenation iron/sand and post-rejuvenation iron/sand (fig. 4.7; $p \leq 0.05$). Pre- and post-rejuvenation iron/sand cells had the highest mean removal rates followed by pre-rejuvenation sand-only cells and lastly post-rejuvenation sand-only cells. Only three significant differences occurred between replicate cells of the same type including post-rejuvenation sand-only cells one and two, post-rejuvenation sand-only cells two and three, and post-rejuvenation iron/sand cells two and three. All of these comparisons involved the second post-rejuvenation run with estimated input concentrations during the second half of the run. The confidence intervals shown in Table 4.2 summarize the filter performance of different treatment groups during filtration runs.



Rosenquist, R-Project

Figure 4.5 - P-mass removal rate trends observed during filtration runs for (A) pre-rejuvenation runs and (B) post-rejuvenation runs

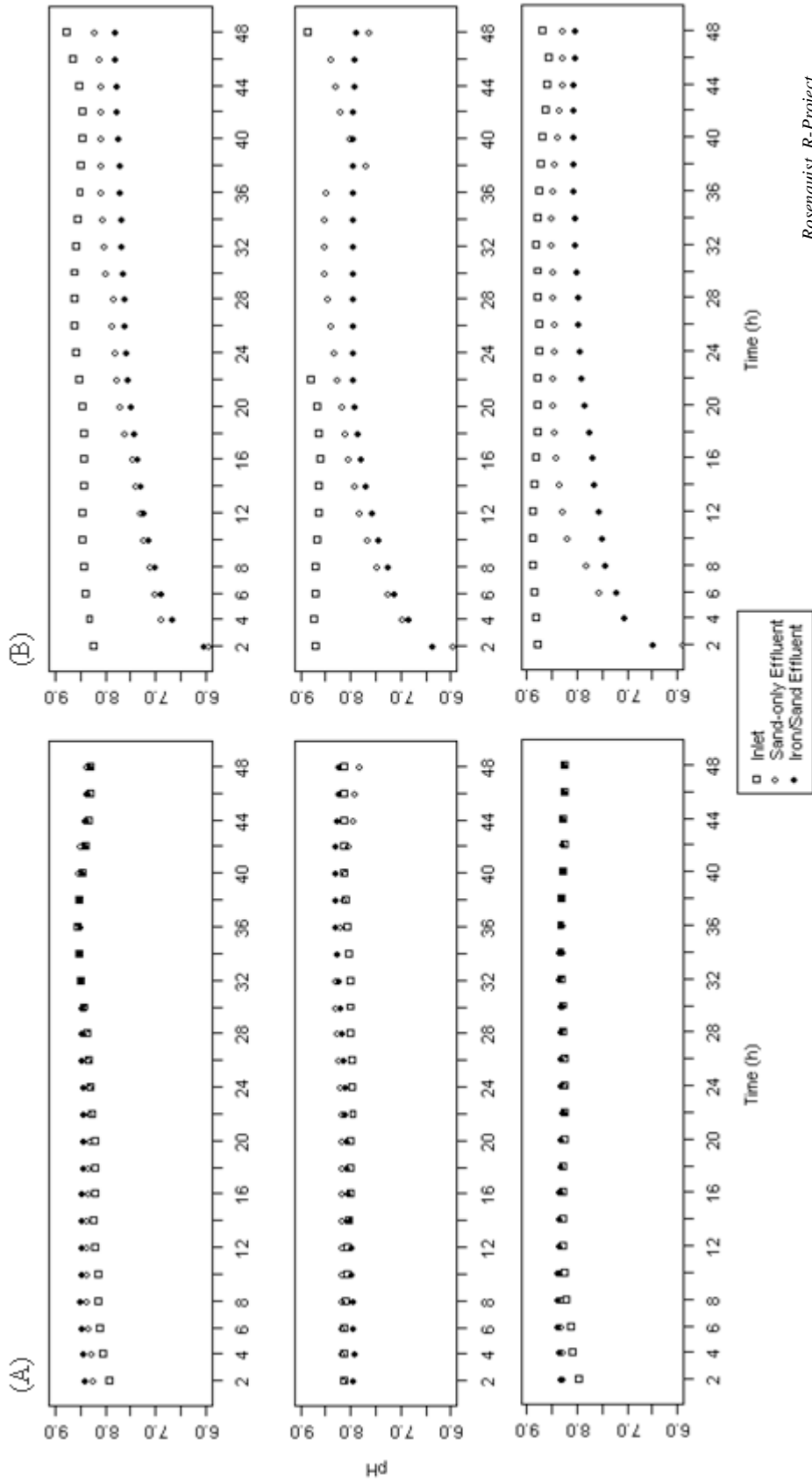
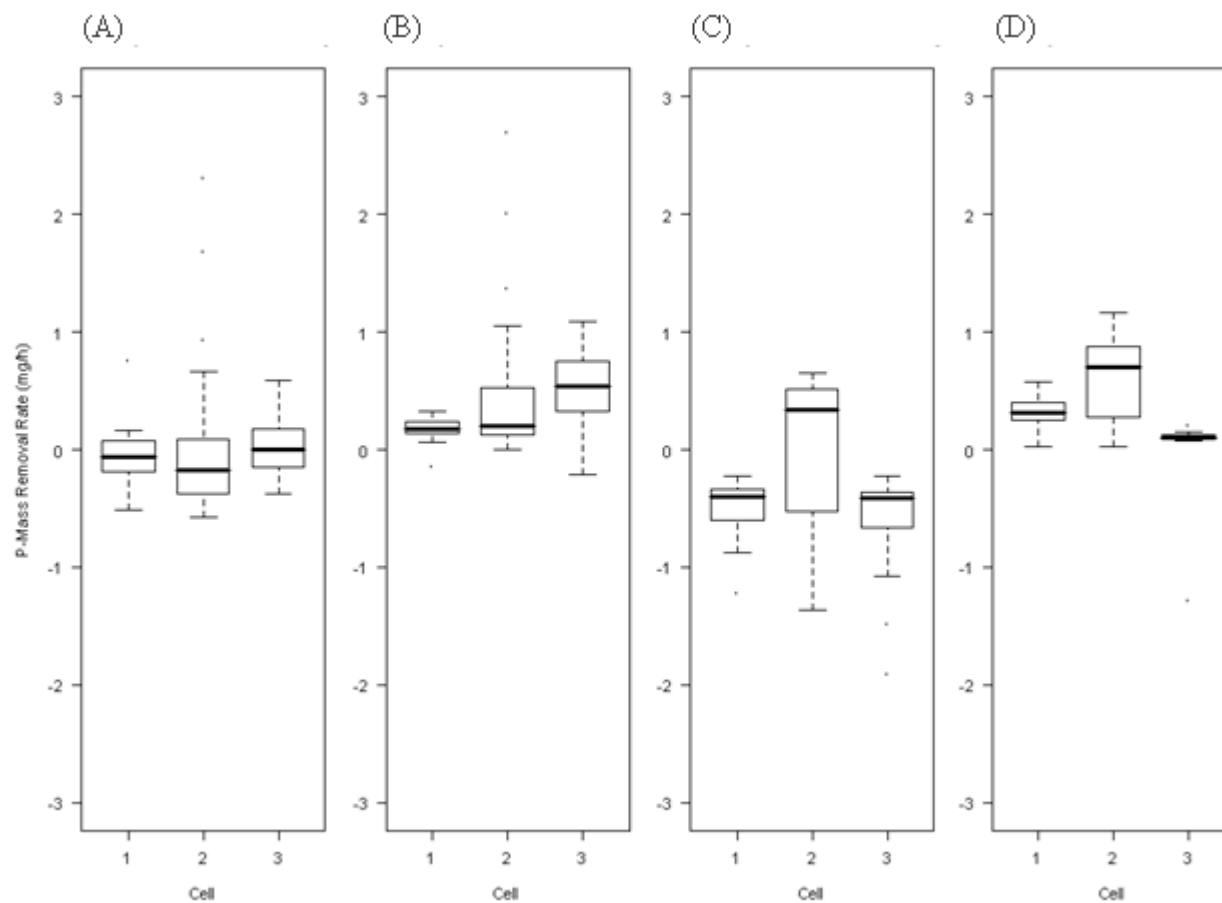


Figure 4.6 - pH trends observed during filtration runs for (A) pre-rejuvenation runs and (B) post-rejuvenation runs

Table 4.2 - 95% confidence intervals for mean P-mass removal rates (mg/h)

Treatment Group	Lower Limit	Upper Limit
Pre-Rejuvenation Sand-only	-0.09	0.12
Pre-Rejuvenation Iron/Sand	0.31	0.57
Post-Rejuvenation Sand-only	-0.48	-0.22
Post-Rejuvenation Iron/Sand	0.24	0.41



Rosenquist, R-Project

Figure 4.7 - P-Mass Removal Rates (mg/h) between treatments and cells for (A) pre-rejuvenation sand-only cells, (B) pre-rejuvenation iron/sand cells, (C) post-rejuvenation sand-only cells, and (D) post-rejuvenation iron/sand cells

Rejuvenation Process

Regression analysis of data from the rejuvenation cycle showed a strong positive relationship between Fe and P (fig. 4.8). Substrate type made a significant difference in the slope of this model, but not the intercept, with iron/sand cells releasing less P for a given amount of Fe

dissolved. The coefficients were lower than in bench-scale trials (Rosenquist et al., In Review), possibly due to lower influent concentrations, therefore less P adsorbed. The same study predicted that below a certain threshold of Fe^{3+} dissolution from sand substrate, re-adsorption onto remaining Fe^{3+} might have attenuated the rate of increase in P concentration. The higher total mass of Fe in the iron/sand cells could be increasing the threshold required to avoid re-adsorption and delaying further release of P into solution. This theory may explain the significant difference in slope between the two substrate types, with the sand-only cells being in the higher post-threshold slope region while the iron/sand cells are still in the lower pre-threshold slope region. Alternatively, this effect could be due to experimental methods as precipitation of Fe-P solids during or immediately following the digestion process could have excluded some of the P in the samples from ICP-AES analysis.

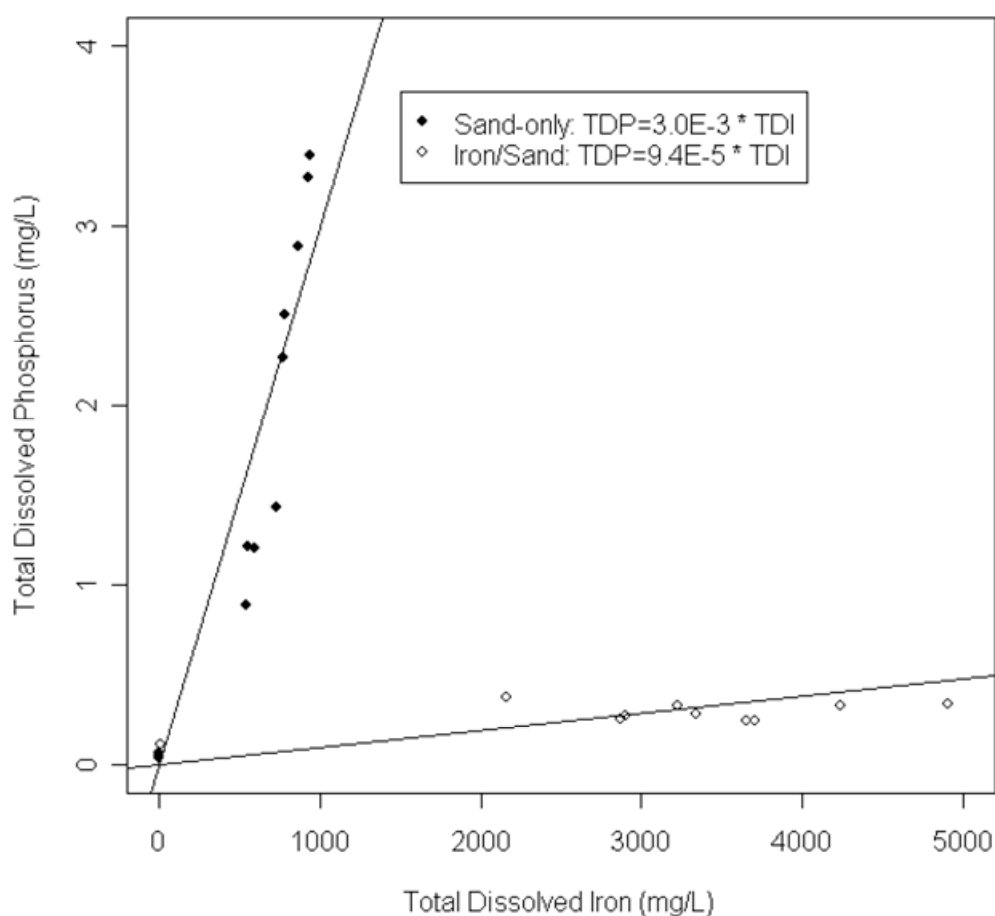


Figure 4.8 - Correlation of TI to TP in solution during rejuvenation ($R^2=0.90$)

Rosenquist, R-Project

Mean pH of the water resident in both cell types was significantly decreased by the end of the 50-day rejuvenation cycle compared to when it entered during filtration (Table 4.3; $p \leq 0.05$). In addition, mean pH of the sand-only cells at the end of the rejuvenation cycle was significantly lower than mean pH of the iron/sand cells ($p \leq 0.05$). There was no significant difference between substrate types when it entered during filtration ($p > 0.05$).

Table 4.3 - Rejuvenation process effects on pH in wetland cells

Time	Sand-only pH	Iron/Sand pH
Final Pre-Rejuvenation Effluent Samples	8.15	8.27
End of Rejuvenation Cycle	4.17	5.82

Comparison of P release between substrate types/times during rejuvenation showed a significant difference only between sand-only, 50-days and all other substrate type/time combinations ($p \leq 0.05$). The lack of a significant difference between other means was probably due to both the low number of replicates available for the test, and the conservative nature of the Bonferroni correction method. A less rigorous comparison based on the bootstrap-derived confidence intervals (Table 4.4) indicated no difference in initial concentration for the two substrate types, an increase in concentration for the sand-only substrate between both time intervals, and an increase in concentration for the iron/sand substrate during the first, but not the second time interval.

Table 4.4 - 95% confidence intervals for mean of TP in solution (mg)

Cell Type/Time Combination	Lower Limit	Upper Limit
Sand-only 0-days Rejuvenation	0.47	0.67
Sand-only 33-days Rejuvenation	11	15
Sand-only 50-days Rejuvenation	24	37
Iron/Sand 0-days Rejuvenation	0.41	1.3
Iron/Sand 33-days Rejuvenation	3.0	5.9
Iron/Sand 50-days Rejuvenation	3.2	4.2

Referencing the estimates of P released during rejuvenation (Table 4.4) to the amount sequestered during filtration (Table 4.5) showed that sand-only cells released more P than was sequestered during the pre-rejuvenation run. This surplus P is probably attributable to the pre-

study substrate either by previous adsorption of P to the substrate (quantified in Appendix A) or possibly organic-P associated with the substrate. The amount of P released by iron/sand cells during rejuvenation is less than the amount of P sequestered in both pre- and post-rejuvenation runs. This finding indicates either that additional sorption capacity was created by the rejuvenation process as proposed by Maynard et al. (2009) and also by Zhang et al. (2010) or that additional sorption capacity was available at the end of the pre-rejuvenation run and carried through the rejuvenation process. Either way, these results indicate that the iron/sand substrate, unlike the sand-only substrate was capable of maintaining sorption capacity after the Fe-reducing rejuvenation cycle.

Comparison of the rate of Fe reduction in this study to the first 50 d of a previous bench-scale study (Rosenquist et al., In Review) reveals significant differences (fig. 4.9a; $R^2=0.97$) with field-scale, sand-only cells displaying higher reduction rates than bench-scale sand-only cells. These higher reduction rates might be explained by the presence of humic acids from the surface water filtered in the cells in this study which may act as a electron shuttle and facilitate iron-reduction (Lovley et al., 1998). Iron/Sand cells displayed even higher reduction rates, probably due to the presence of more bioavailable iron. This finding may indicate that bioavailability of the terminal electron acceptor is a limiting factor for rate of rejuvenation. Comparison of the rate of P release (fig. 4.9b) reveals no clear differences; however, the starting concentrations for the field-scale cells in this study were noticeably lower.

Table 4.5 - 95% confidence intervals for P-mass removed by filtration (mg)

Treatment Group	Lower Limit	Upper Limit
Pre-Rejuvenation Sand-only	-4.3	5.8
Pre-Rejuvenation Iron/Sand	15	27
Post-Rejuvenation Sand-only	-23	-11
Post-Rejuvenation Iron/Sand	12	20

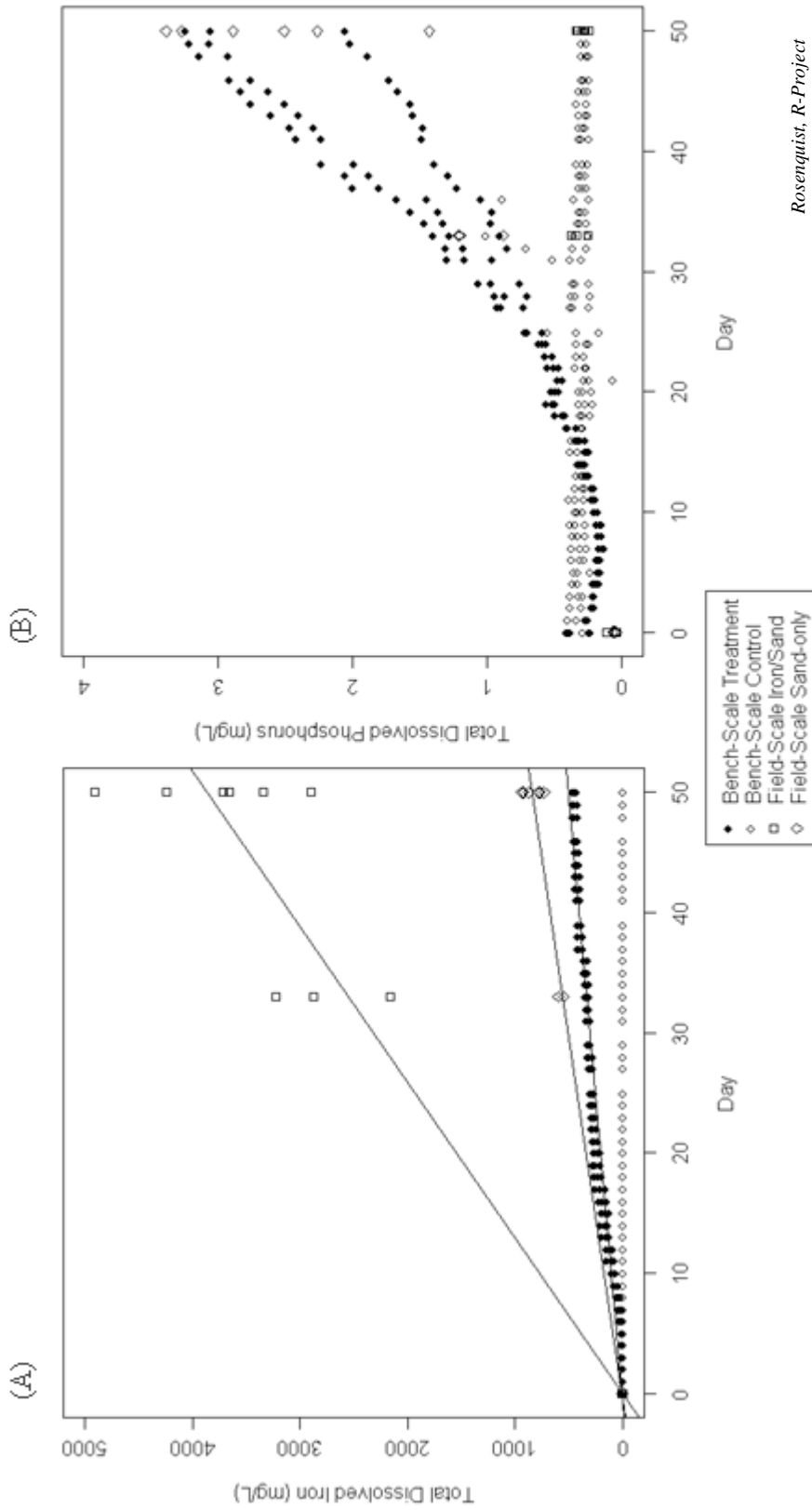


Figure 4.9 - Comparison of rates of (A) Fe reduction and (B) P release between bench-scale and field-scale cells

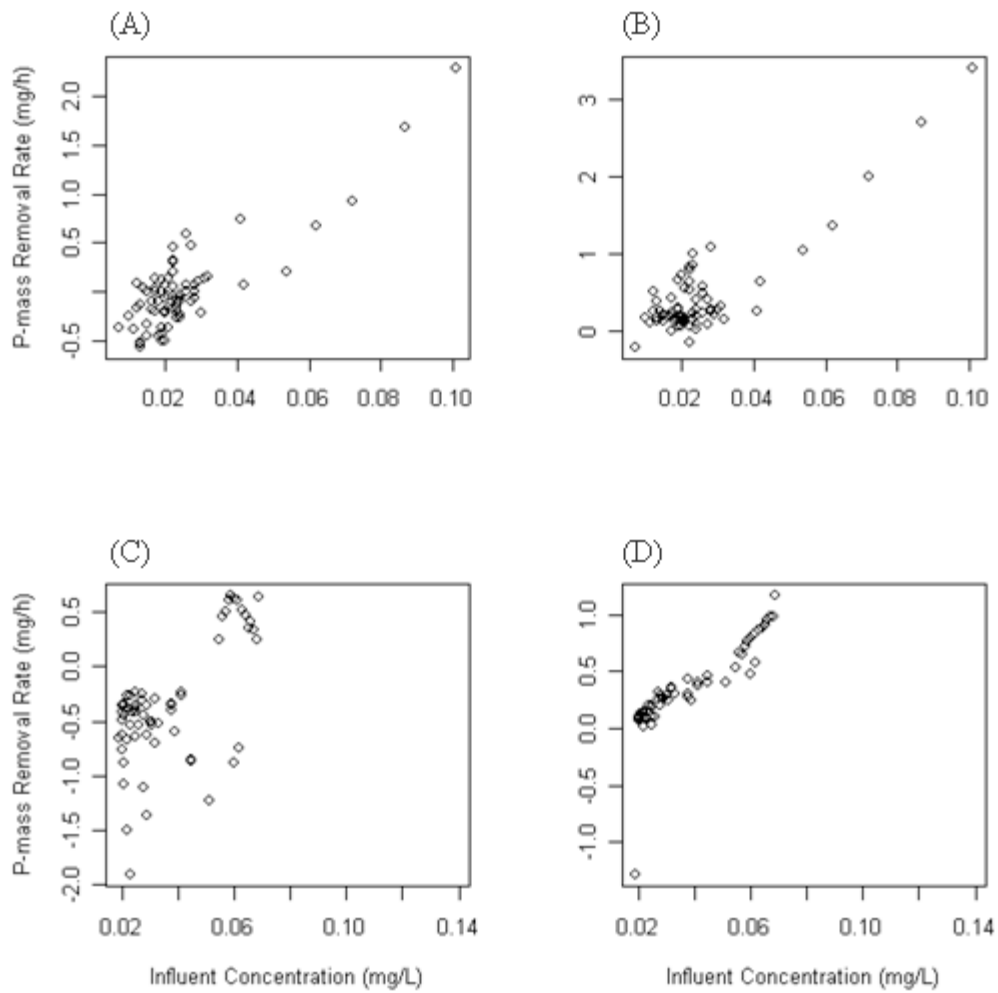
Modeling Variability in Removal

At least one of the proposed regression variables was significant in every treatment group of the filtration runs (Table 4.6). Influent concentration (IC) was the only variable significantly correlated to P-mass removal rate (MRR) for all treatment groups (fig. 4.10). This dependence on IC is in agreement with several of the first-order models reviewed by Rouseau et al. (2004). The maximum previous effluent concentration (MPEC) was significant for both pre-rejuvenation groups indicating, in agreement with bench-scale study by Rosenquist et al. (2010), that a substrate/solution equilibrium at a higher previous concentration may decrease performance of the filter at subsequent lower concentrations due to the lack of a concentration gradient (fig. 4.11).

Table 4.6 - Correlation coefficients for each treatment group

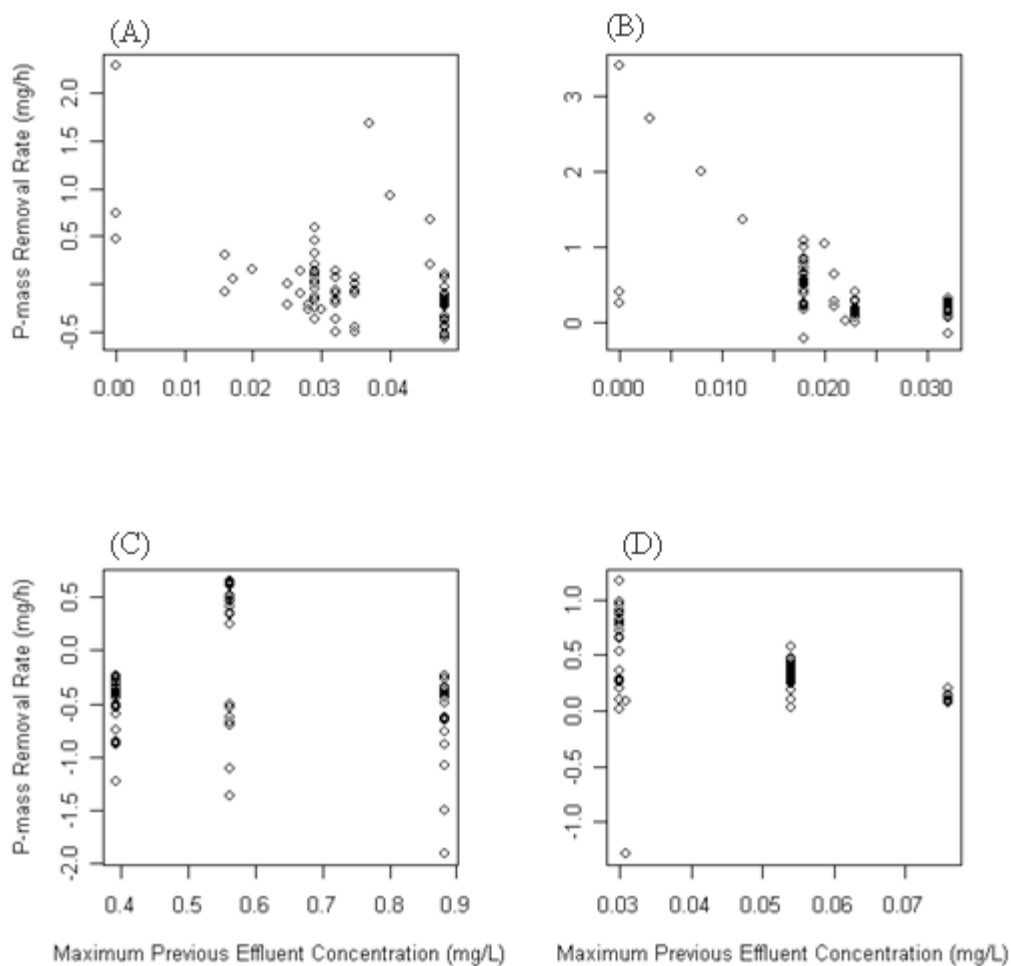
Treatment Group	R ²	Explanatory Variables			
		Influent Concentration	MPEC	pH	Time
Pre-Rejuvenation Sand-only	0.87	25	-18	-0.59	0.01
Pre-Rejuvenation Iron/Sand	0.80	26	-20	*	*
Post-Rejuvenation Sand-only	0.72	20	*	N/A	0.02
Post-Rejuvenation Iron/Sand	0.72	18	*	N/A	*

*Variable was not significant at $\alpha = 0.05$



Rosenquist, R-Project

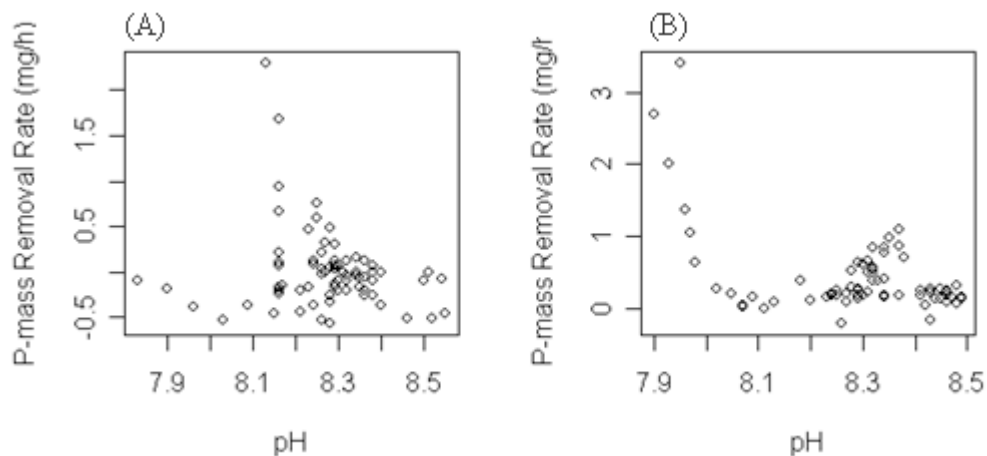
Figure 4.10 - Correlation of P-mass removal rate with influent concentration for (A) pre-rejuvenation sand-only cells, (B) pre-rejuvenation iron/sand cells, (C) post-rejuvenation sand-only cells, and (D) post-rejuvenation iron/sand cells



Rosenquist, R-Project

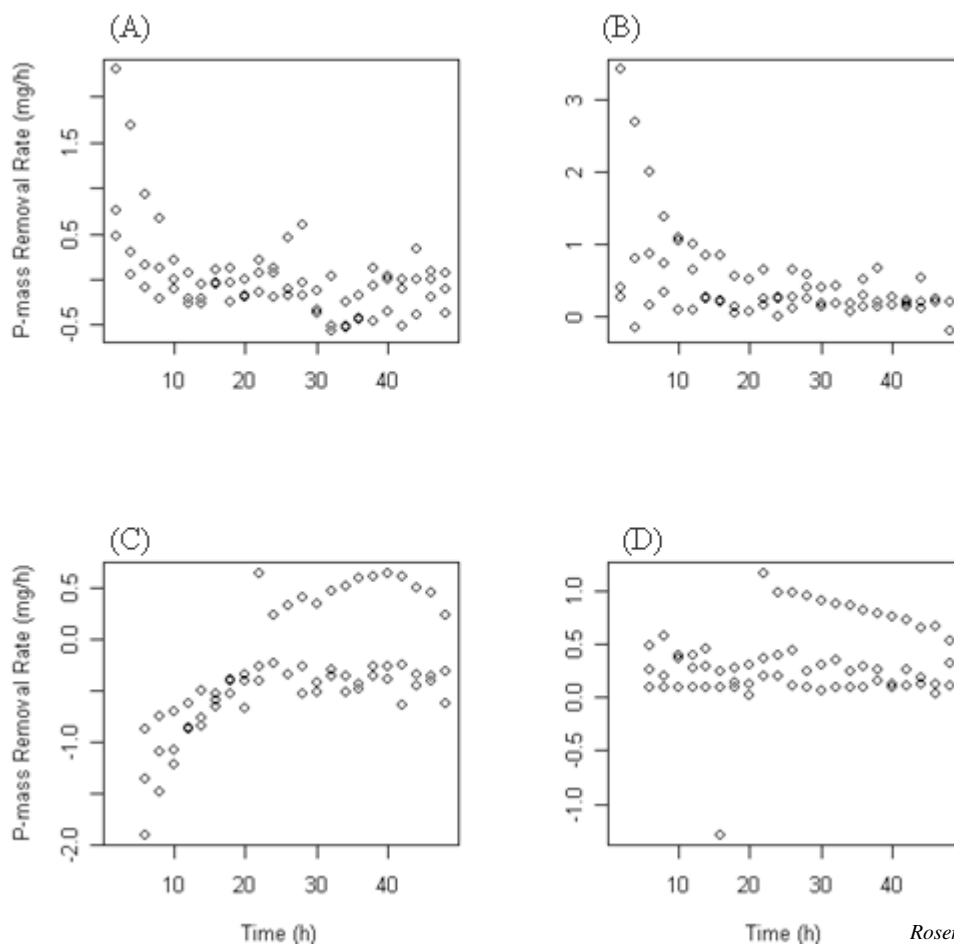
Figure 4.11 - Correlation of P-mass removal rate with the maximum previous effluent concentration for (A) pre-rejuvenation sand-only cells, (B) pre-rejuvenation iron/sand cells, (C) post-rejuvenation sand-only cells, and (D) post-rejuvenation iron/sand cells

Effluent pH displayed a significant, negative correlation with MRR in one treatment group (fig. 4.12), again consistent with previous studies (Zeng et al., 2004; Rosenquist et al., 2010). While time was negatively associated with IC across the entire study, time was also significant and positively correlated with MRR for two treatment groups, but provided very little additional explanation of variability with IC also included (fig. 4.13). One possible explanation for this trend is the occurrence of slow diffusion of P into micropores of the material, slowly generating further concentration gradient after a previous maximum. In general, IC had the most explanatory power in the model, followed by MPEC and pH, and then followed by Time.



Rosenquist, R-Project

Figure 4.12 - Correlation of P-mass removal rate with effluent pH for (A) pre-rejuvenation sand-only cells and (B) pre-rejuvenation iron/sand cells



Rosenquist, R-Project

Figure 4.13 - Correlation of P-mass removal rate with time for (A) pre-rejuvenation sand-only cells, (B) pre-rejuvenation iron/sand cells, (C) post-rejuvenation sand-only cells, and (D) post-rejuvenation iron/sand cells

Conclusions

Field-scale study of the UWF concept has provided support and verification for some of the results and conclusions from previous bench-scale studies. In addition, new information about the role of cast-iron filings in the substrate provides promise for its contribution to providing renewable adsorption capacity in CW without substrate replacement. The following conclusions can be drawn from this study regarding field verification of previous bench-scale studies: 1) a continuously-loaded, subsurface-flow CW with a sand substrate is capable of removing P from water filtered from a stormwater retention pond; 2) the rate of P removal by SP is subject to variability from multiple sources and is not completely described by a first-order model; 3) probable sources of variability include influent concentration (the typical first-order model), but also the previous substrate/solution equilibrium condition, pH, and time (likely based on diffusion); 4) a rejuvenation process for sorption capacity, based on the facilitated reduction of Fe^{3+} in CW substrates, is capable of removing a significant amount of adsorbed P for removal and recycling without substrate replacement; and 5) the rate of Fe reduction under field conditions is higher than under bench-scale conditions.

It is important to consider, in any attempt at using the results of this study to predict removal in a similarly designed CW that in addition the variables mentioned above there may be dependence on the filter volume and flow rate as well. The filter volume/flow rate ratio probably influences at least the lifetime of P removal in the filter and possibly the P removal rate as well. This mechanism may explain the performance differences observed by Line et al. (2008) for stormwater wetlands with different surface area/drainage area ratios. Removal lifetime would likely increase as the ratio increased while removal rate may decrease if the ratio was too large causing a retention time too long to maintain aerobic conditions. Also, the rate of mass removal would likely increase proportionally to the flow rate and volume if their ratio stayed the same. In regards to operation of the vertical-flow wetland cells, the downward-flow cells in this study were preferred over the upward-flow cells in previous studies of the UWF project due to simpler setup and no tendency to fluidize like the upward flow cells, allowing higher flow rates. Steps to overcoming potential limitations of the downward-flow cells compared to upward-flow cells (clogging and reduced mixing) include a pre-filter to exclude large particles/debris and by promoting mixing through a standing water layer, a gravel layer, and a well-distributed outlet structures.

The following additional conclusions can be made regarding the addition of cast-iron filings to the CW substrate: 1) the addition of cast-iron filings to a sand substrate can increase the rate of P removal and probably the P removal lifetime of a continuously-loaded, subsurface flow CW; 2) the addition of the cast-iron filings may have adversely affected the rejuvenation process by increasing the threshold of Fe-reduction necessary to obtain a higher rate of P release; 3) the addition of cast-iron filings can provide a means of maintaining sorption capacity after the rejuvenation cycle; and 4) the rejuvenation process may function in conjunction with the Fe^0 to increase sorption sites in the bulk material.

Based on these conclusions it is reasonable to recommend further investigation and pilot studies regarding the addition of cast-iron filings to CW substrate to improve P removal rates, improve P removal lifetime, and enable rejuvenation of sorption capacity through facilitated Fe-reduction. Also recommended, based on the lack of P release during rejuvenation in iron/sand cells, is a decrease in the ratio of cast-iron filings to sand in order to maintain the benefits to P-removal performance, while minimizing any cost to the rejuvenation process. Future research can benefit the UWF concept by finding ways to increase the rate of microbial Fe-reduction, possibly based on the addition of humic acids, and by developing a Fe-P precipitation reaction in the rejuvenated cells so that the P released might be more easily recycled as a solid rather than as a more cumbersome, high-concentration solution.

Acknowledgements

The authors would like to thank the National Science Foundation for providing support for students who provided assistance on this project as a part of the NSF Research Experiences for Undergraduates grant. In addition, the authors would specifically like to acknowledge assistance from exceptional faculty (Dr. Durelle Scott), staff (Laura Teany and Amy Egan), and students (Sarah Walker, Jonathan Pennington, and Alyse Egner) who were all critical to the success of this study.

References

- Arias, C. A., and H. Brix. 2005. Phosphorus removal in constructed wetlands: can suitable alternative media be identified? *Water Sci. Technol.* 51 (9): 267-273.
- Boesch, D. F., R. B. Brinsfield, and R. E. Magnien. 2001. Chesapeake bay eutrophication: scientific understanding, ecosystem restoration, and challenges for agriculture. *J. Environ. Qual.* 30: 303-320.
- Camargo, J. A., and A. Alonso. 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. *Environ. Int.* 32: 831-849.
- Chernick, M. R. 1999. *Bootstrap Methods: A Practitioners Guide*. New York, N.Y.: Wiley-Interscience.
- Dowling, D. C. 2009. Virginia Stormwater Management Program (VSMP) Permit Regulations. 4VAC50-60. Richmond, VA: Virginia Soil and Water Conservation Board, Virginia Code Commission.
- Drizo, A., Y. Comeau, C. Forget, and R. P. Chapuis. 2002. Phosphorus saturation potential: A parameter for estimating the longevity of constructed wetland systems. *Environ. Sci. Technol.* 36 (21): 4642-4648.
- Drizo, A., C. Forget, R. P. Chapuis, and Y. Comeau. 2006. Phosphorus removal by electric arc furnace steel slag and serpentinite. *Water Res.* 40 (8): 1547-1554.
- Erickson, A. J., J. S. Gulliver, and P. T. Weiss. 2007. Enhanced sand filtration for stormwater phosphorus removal. *J. Environ. Eng.* 133 (5): 485-497.
- Fisher, T. R., E. R. Peele, J. W. Ammerman, and L. W. Harding. 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Mar. Ecol. Prog. Ser.* 82 (1): 51-63.
- Hunt, W. F., and B. Lord. 2006. *Maintenance of Stormwater Wetlands and Wet Ponds*. Raleigh, NC: North Carolina Cooperative Extension Service.
- Kadlec, R. H. 2005. Phosphorus removal in emergent free surface wetlands. *J. Environ. Sci. Health, Pt. A: Environ. Sci. Eng. Toxic Hazard. Subst. Control* 40 (6): 1293-1306.
- Kaplan, D. 2004. Enhanced contaminant desorption induced by phosphate mineral additions to sediment. *Environ. Sci. Technol.* 38 (11): 31-53.
- Lantzke, I. R., A. D. Heritage, G. Pistillo, and D. S. Mitchell. 1998. Phosphorus removal rates in bucket size planted wetlands with a vertical hydraulic flow. *Water Res.* 32 (4): 1280-1286.

- Line, D. E., G. D. Jennings, M. B. Shaffer, J. Calabria, and W. F. Hunt. 2008. Evaluating the effectiveness of two stormwater wetlands in North Carolina. *Trans. ASABE* 51 (2): 521-528.
- Lovley, D. R., J. L. Fraga, E. L. Blunt-Harris, L. A. Hayes, E. J. P. Phillips, and J. D. Coates. 1998. Humic Substances as a Mediator for Microbially Catalyzed Metal Reduction. *Acta Hydrochim. Hydrobiol.* 26: 152-157.
- Luederitz, V., and F. Gerlach. 2002. Phosphorous removal in different constructed wetlands. *Acta Biotechnology* 22 (1/2): 91-99.
- Maynard, J. J., A. T. O'Geen, and R. A. Dahlgren. 2009. Spatial relationships of phosphorus sorption in a seasonally saturated constructed wetland soil. *Soil Sci. Soc. Am. J.* 73 (5): 1741-1753.
- Peretyazhko, T., and G. Sposito. 2005. Iron(III) reduction and phosphorous solubilization in humid tropical forest soils. *Geochemica et Cosmochimica Acta* 69 (14): 3643–3652.
- Rosenquist, S. E., W. C. Hession, M. J. Eick, and D. H. Vaughan. 2010. Variability in adsorptive phosphorus removal by structural stormwater best management practices. *Ecol. Eng.*: In Press. <http://dx.doi.org/10.1016/j.ecoleng.2009.12.008>.
- Rosenquist, S. E., C. L. Levy, S. T. Sell, W. C. Hession, M. J. Eick, and D. H. Vaughan. In Review. Facilitated iron reduction as a means of rejuvenating phosphorus removal performance of filtration substrate. *Trans. ASABE*:
- Rousseau, D. P. L., P. A. Vanrolleghem, and N. De Pauw. 2004. Model-based design of horizontal subsurface flow constructed treatment wetlands: a review. *Water Res.* 38 (6): 1484–1493.
- Sano, D., A. Hodges, and R. Degner. 2005. Economic Analysis of Water Treatments for Phosphorus Removal in Florida. Gainesville, FL: Florida Cooperative Extension Service.
- Shilton, A., S. Pratt, A. Drizo, B. Mahmood, S. Banker, L. Billings, S. Glenn, and D. Luo. 2005. 'Active' filters for upgrading phosphorus removal from pond systems. *Water Sci. Technol.* 51: 111-116.
- Virginia Tech Department of Biology. 2008. Simultaneous Persulfate Digestion for Total Nitrogen and Total Phosphorous in Water. Standard Operating Procedure. Blacksburg, VA: Virginia Polytechnic Institute and State University.
- R Development Core Team. 2009. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing.

- USEPA. 1994. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. EPA Method 200.7. Cincinnati, OH: US Environmental Protection Agency, Office of Research and Development.
- Weiss, P. T., J. S. Gulliver, and A. J. Erickson. 2007. Cost and pollutant removal of stormwater treatment practices. *Journal of Water Resources Planning and Management* 133 (3): 218-229.
- Zeng, L., X. Li, and J. Liu. 2004. Adsorptive removal of phosphate from aqueous solutions using iron-oxide tailings. *Water Res.* 38 (5): 1318-1326.
- Zhang, W., J. W. Faulkner, S. K. Giri, L. D. Geohring, and T. S. Steenhuis. 2010. Effect of soil reduction on phosphorus sorption of an organic-rich silt loam. *Soil Sci. Soc. Am. J.* 74 (1): 240-249.

Overall Conclusions and Recommendations

The cumulative results of this research program are promising for the effectiveness and practicality of the UWF concept as a P management practice for stormwater in high land-value areas. This management practice represents a low-cost and easily implemented strategy to enable municipalities to retrofit existing stormwater infrastructure to meet new NPS pollutant requirements. With such an expansive network of retention ponds currently available, the opportunities for implementation are vast. Upon such widespread use, the UWF could enable significant improvement in the contribution that urban areas make to large-scale eutrophication such as that seen in the Chesapeake Bay. In addition, based on the ability to harvest phosphorus for recycling, the UWF concept presents a great opportunity for nutrient trading since nutrient credits will be very easy to justify and quantify.

Sorption Modeling

Bench-scale results indicated that P removal by SP depends strongly on the relative equilibrium between solution P and adsorbed P in the substrate. The iron-oxide sand filtration substrate was capable of removing a significant amount of dissolved P from filtered water. The following conclusions derive from modeling SP in the wetland cells: 1) filter "age" based on percent of theoretical sorption capacity is a poor predictor of the lifetime of P removal in the CW; 2) P removal may not occur even with theoretical sorption sites remaining as predicted by isotherm testing if no concentration gradient exists; 3) overall sorption potential based on batch-experiment-derived isotherm curves and maximum influent concentrations may under-predict sorption in a flow-through situation; 4) P removal is negatively correlated with pH; 5) P removal is positively correlated to the concentration gradient present between solution and adsorbed P; 6) substrates will likely gain additional concentration gradient slowly as P diffuses into micropores; and 7) concentration gradient may also be driven by influent concentration increase, addition of more sorption sites, or by harvesting P from the substrate;

Field-scale results verified that a continuously-loaded, subsurface-flow CW with a sand substrate is capable of removing P from water filtered from a stormwater retention pond. The following field-scale conclusions support the bench-scale model for SP: 1) the rate of P removal by SP is subject to variability from multiple sources and is not completely described by a first-

order model and 2) probable sources of variability include influent concentration (the typical first-order model), but also the previous substrate/solution equilibrium condition, pH, and time (likely based on diffusion).

With an experimental run considered analogous to a storm event, P removal by SP during a given event is likely dependent on historical loadings to the BMP (mass and concentration from previous events). As a general trend, effluent concentrations will likely converge with influent concentrations over time, assuming that no additional concentration gradient is established. This convergence may help explain the "irreducible concentrations" seen in field studies of stormwater BMP and may explain any variation in the level of this concentration between sites due to different loading histories.

Rejuvenation

Results obtained from both batch and flow-through studies indicate a significant ability to release previously-sequestered P within substrates by microbial reduction of Fe. The following conclusions are supported by these studies: 1) Fe-reducing microorganisms are naturally present in the sand media and inclusion of the surface-water sample did not significantly increase the amount of Fe reduced or P released; 2) addition of a carbon source was necessary to promote effective microbial reduction of Fe; 3) dissolved P was positively correlated with dissolved Fe, indicating that release of previously-sequestered P in substrates accompanies Fe reduction; 4) a high percentage of the previously-adsorbed P can be released by Fe reduction; 5) however, the process was slower by orders of magnitude than adsorption for the same P load; 6) a two-region relationship between P release and Fe reduction indicates that P release is attenuated below a threshold of Fe dissolution, possibly due to a availability for re-sorption while some Fe³⁺ coatings remained on substrate surfaces; and 7) P concentration in rejuvenating cells can increase by orders of magnitude over the influent, P-loading concentrations. Field study of the rejuvenation process verified its capability for releasing a significant amount of the P adsorbed during filtration of water retained in a stormwater pond. Furthermore, field study showed that the rate of Fe reduction under field conditions is higher than under bench-scale conditions.

While the dissolution of Fe and subsequent release of P in the FTWC continued to increase throughout the study period for all studies, P release will certainly reach a maximum, probably with a diminishing release rate at some point.

Design Considerations

Potential design considerations from modeling include the following: 1) for the same BMP design, less P removal by SP may occur for a lower influent concentration than for a higher influent concentration; 2) for the same influent concentration, P removal in a BMP with less available sorption sites (less total volume or less sorption site density) will be less and will likely decrease and/or become negligible more quickly; 3) if influent concentration decreases significantly from a sustained higher level, P removal by SP will become negligible or even reverse; 4) P removal during a given loading is positively correlated to the time since the last loading; 5) spatial gradients of P in substrate may be a better indicator of remaining sorption potential than isotherm-derived maximums; 6) designs that maximize aerobic conditions during filtration may improve retention of adsorbed P; and 7) inclusion of pH buffering materials designed to maintain neutral pH may promote additional sorption capacity.

Furthermore, any estimates of future effluent concentrations or load reductions from SP should include information about historical concentration maxima, sorption capacity of the media, and the amount of P currently adsorbed. It is also important to consider, in any attempt at using the results of study to predict removal in a similarly designed CW that, in addition to the variables mentioned above, there may be dependence on the substrate volume and flow rate as well. The substrate-volume/flow-rate ratio probably influences at least the lifetime of P removal in the filter and possibly the P removal rate as well. This mechanism may explain the performance differences observed for stormwater wetlands with different surface area/drainage area ratios. Removal lifetime would likely increase as the ratio increased while removal rate may decrease if the ratio was too large causing a retention time that is too long to maintain aerobic conditions. Also, the rate of mass removal would likely increase proportionally to the flow rate and volume if their ratio stayed the same. In regards to operation of the vertical-flow wetland cells, the downward-flow cells were preferred over the upward-flow cells due to simpler setup and no tendency to fluidize like the upward flow cells, allowing higher flow rates. Potential limitations of the downward-flow cells compared to upward-flow cells (clogging and reduced mixing) can be overcome by including a pre-filter to exclude sediment/debris and by promoting mixing by including a standing water layer, a gravel layer, and a well-distributed outlet structure.

The following design considerations relate to the addition of cast-iron filings to CW substrate: 1) addition of cast-iron filings to a sand substrate increases the rate of P removal and probably the P removal lifetime of a continuously-loaded, subsurface-flow CW; 2) addition of cast-iron filings may adversely affect the rejuvenation process by increasing the threshold of Fe-reduction necessary to obtain a higher rate of P release; 3) the addition of cast-iron filings can provide a means of maintaining sorption capacity after intentional or unintentional Fe reduction; and 4) the rejuvenation process may function in conjunction with the Fe^0 to increase sorption sites in the bulk material. Based on the decreased P release during rejuvenation in iron/sand cells, future designs should have a lower ratio of cast-iron filings to sand to maintain the benefits of to P-removal performance, while minimizing any cost to the rejuvenation process.

Recommendations for Future Study

Two significant challenges remain in the development of the UWF including 1) the acceleration of the rejuvenation process, possibly by inclusion of humic acid, in order to decrease the cycle time and by extension the number of cells required for continuous operation and 2) the development of a precipitation process to harvest released P as a solid rather than as a more cumbersome, high-concentration solution. In addition, the promising results in these studies support further investigation and pilot studies regarding the addition of cast-iron filings to CW substrate to improve P removal rates, improve P removal lifetime, and enable rejuvenation of sorption capacity through facilitated Fe-reduction.

Appendix A: Supplementary Research Studies

Field-scale study of phosphorus removal by sorption: comparison of substrates and residence times

S.E. Rosenquist, S. Braman, C. Newbill, W.C. Hession, D.H. Vaughan

Abstract

Stormwater ponds with permanent pools present a unique opportunity to provide additional water quality treatment. Constructed wetlands (CW) have demonstrated great potential for water quality treatment, including treatment of excess phosphorus (P). A CW designed to complement water quality treatment in the stormwater pond could decrease nutrient loads from urban runoff, while making use of existing infrastructure and minimizing cost. This study evaluated three constructed wetland substrates and two hydraulic retention times (HRTs) in field-scale cells to develop a CW optimized for this application. Results indicated no significant differences in P removal performance for the three substrates tested, but did indicate a significant difference in P removal between HRTs with the lower HRT displaying better P removal. This study also provided many insights toward improved research methods for evaluating wetland substrate filtration through future studies.

Introduction

Urban stormwater management has historically focused on peak flow attenuation, often with stormwater ponds, but has largely ignored water quality, including excess nutrients. The prevalence of these stormwater ponds provides an underutilized opportunity for additional treatment of retained stormwater. Constructed wetlands (CW) are capable of removing phosphorus (P) from stormwater through physical, chemical, or biological processes (Kadlec and Wallace, 2009) and could provide a means of additional treatment to stormwater retained in stormwater ponds.

Stormwater ponds with permanent pools are capable of some P removal by sedimentation (Comings et al., 2000), so P removal to complement stormwater ponds should focus on removing dissolved phosphorus (DP). Both biological uptake by plants and chemical sorption are capable of removing DP, but due to the large land requirements for biological uptake (Kadlec and Wallace, 2009), chemical sorption may be most applicable for urban areas where space adjacent to stormwater ponds is limited (Hunt and Wossink, 2003). Crucial factors to DP removal by

chemical sorption include properties of the substrate, and the properties of stormwater flow through the substrate (Farahbakhshazad and Morrison, 2003; Maynard et al., 2009).

Properties of the Substrate

Previous studies have evaluated a range of substrates for their P removal performance. These options are organized and discussed here according to origin.

Natural Materials

Natural materials range in composition with the most predominate P-sorption constituents being calcium, iron, and aluminum (McBride, 1994; Namasivayam et al., 2005). Wollastonite is a calcium metasilicate and removed 45% of P in field studies, but resulted in effluents with high pH. Bauxite, mainly aluminum and iron oxides, has limited field data, but shows good P sorption properties. Laterite is an aluminum and iron rich sand found in the tropics and Ireland that has demonstrated 80-90% P removal in laboratory studies but data on field performance is limited (Westholm, 2006).

Significant data is available for calcareous materials such as limestone and dolomite sand mixtures. Dolomite sand mixtures removed 30-50% of P in field studies and 45% in laboratory studies while maintaining effluents below a pH of eight (Prochaska and Zouboulis, 2006; Westholm, 2006). Few studies have used pure limestone as a sorption material because of the significant increase in pH (Westholm, 2006). One study evaluated a wetland with a calcite filter, and found up to 62% removal before saturation at 3 months (Arias et al., 2003). Evaluations of marine sediments such as maerl, demonstrate up to 98% removal of P, likely due to high porosity and specific surface area. Again, limited field data is available. Various types of shells and shell sands show promise because they are rich in calcium and magnesium. There is little available data for these types of substrates and a lack geographic availability may further limit their use (Westholm, 2006).

Substrate size is an important property for chemical sorption, especially for natural substrates, as small grain sizes accompanied by an increased surface area can substantially increase the potential for removal by chemical sorption (Zhu et al., 2003; Maynard et al., 2009). However, a balance is important in order to maintain between maintaining a sufficient hydraulic conductivity to prevent clogging (Prochaska and Zouboulis, 2006) while maximizing surface

area. Natural substances may be desirable for P removal in stormwater because they are readily available, reasonably efficient at P removal, and provide little risk of contamination with the possible exception of pH in calcareous materials.

Industrial Byproducts

Slag is the residue of ores processed at metal purification plants. Westholm (2006) reviewed both blast furnace slag and electric arc slag, which demonstrated 30-60% P removal, although field studies were limited. Removal performance of the iron slag improved with increased pH and temperature (Shilton et al., 2005). While these potential substrates do remove P efficiently, they can harm water quality in the process. As a result, some studies investigated combining slag with limestone gravel and peat to mitigate these effects. However, pH was too high and became detrimental to plant growth (Naylor et al., 2003).

Another byproduct considered was burnt oil shale because it is rich in aluminum. Burnt oil shale is the solid waste of a process similar to the burning of fossil fuels, using sedimentary rock that has not fossilized. Unfortunately, research has revealed rather poor P-adsorption capacity for this material (Drizo et al., 1999; Westholm, 2006). Ochre has a high ferrous iron content and therefore a potential high sorption capacity for P. Unfortunately, ochre also has a high toxic metal content (Ni, Cu, Cd, Cr, Pb, Zn) making it unadvisable for water treatment (Heal et al., 2005). Fly and bottom ash are coal combustion byproducts known to be rich in silicate, aluminum and iron and are abundant in the Appalachian region. A significant shortcoming of fly and bottom ash is their significant and exponential decrease in hydraulic conductivity (Westholm, 2006).

Industrial byproduct display desirable properties for P removal, especially their high quantities of iron, calcium, and aluminum, but they are severely limited by the risk of adverse water quality effects including changes to pH and release of toxic metals.

Manufactured Materials

Lightweight aggregates (LWA) are essentially natural materials heated to extremely high temperatures, yielding low density, high porosity material. A study investigating at a variety of LWAs showed that P-removal performance varied amongst LWA type by two orders of

magnitude but all resulted in elevated pH. The study included iron-rich sand, which outperformed half of the LWAs in P removal (Zhu et al., 1997).

Filtralite is a Norwegian-manufactured LWA with P removal rates up 95% in laboratory but just 34% in the field (Zhu et al., 1997; Westholm, 2006). Further investigation indicated that calcium and aluminum in Filtralite contributed the most to P removal (Zhu et al., 2003). Another common brand of manufactured substrate is LECA, a Swedish-made LWA. LECA is rich in aluminum and iron and displayed good short-term P-adsorption properties (Drizo et al., 1999).

Lightweight aggregates are very favorable due ability for P sorption combined with and adequate hydraulic conductivity, but like some other materials are often limited by pH effects. Additionally, the process to create LWAs is expensive and energy intensive, creating a high cost for implementation and less attractive environmental impact if life-cycle analysis is included.

In summary of available substrate options, care in selecting a CW substrate is necessary to ensure that it will perform well at removing P, perform hydraulically and that it will not deteriorate other aspects of water quality such as changing pH or introducing heavy metals. For the application in this study, natural materials (especially those high in iron, calcium, and aluminum) are preferable due to their low cost, availability, and low environmental impact combined with sufficient P-removal performance. Iron-based materials are especially attractive due to their theoretical and experimentally verified capacity for efficient P removal through sorption, even at neutral pH.

Properties of Stormwater Flow through the Substrate

Hydraulic retention time, involving the relationship between flow rate and wetland size, is also important to CW design. While increased residence time theoretically allows for additional interactions with sediments and increases the probability for sorption, lower residence times may effectively promote sustained aerobic conditions. Aerobic conditions are more favorable for P removal by iron in substrates, as anaerobic conditions can lead to the release of P with the reduction of associated iron (Komatsu et al., 2006).

Previous research indicates P-removal performance can increase with higher hydraulic residence times (Shilton et al., 2005). In another study, hydraulic residence times of 5 days and 10 days had associated P removal of 37% and 69% removal, respectively (Chick and Mitchell,

1995). Conversely, yet another study showed that P-removal increased with higher flow rates, implying lower retention times for the same filtration volume; however, this increase was at least partially due to higher loads of P being filtered (Farahbakhshazad and Morrison, 2003).

Flow regime may also affect P removal. Flow regime refers to the basic hydraulic structure of a CW design. The first classification for flow regime in a CW is whether the flow is primarily through the substrate (subsurface-flow wetlands) or primarily through vegetation above the substrate (surface-flow wetlands). The first waste water treatment wetlands were horizontal subsurface-flow wetlands (Vymazal, 2005). Further classification for subsurface-flow wetlands is whether the primary flow direction is horizontal or vertical (Kadlec and Wallace, 2009). Vertical, subsurface flow wetlands branch further by either upward or downward flow.

Some flow regimes may be more suitable for promoting chemical sorption of DP. Subsurface-flow wetlands provide more interaction with the substrate, which is the primary mechanism of phosphorus removal by sorption processes; however, there is also a greater potential for clogging if suspended solids are present in influent. Vertical subsurface-flow wetlands with upward flow may help prevent clogging and may also promote additional mixing within substrate (Farahbakhshazad and Morrison, 2003).

Research Objectives

The purpose of this research was to develop and test a CW for optimal DP removal from stormwater ponds. Objectives include evaluation of substrate types and flow rates with regard to P removal and the experiential development research methods for testing CW substrate filtration. This study will specifically test the following hypotheses:

1. calcium-based and iron-based sands will remove more phosphorus than the control sand;
and
2. wetland cells with longer hydraulic residence times will remove a higher percentage of P than cells with shorter retention times.

Methods and Materials

Experimental Setup

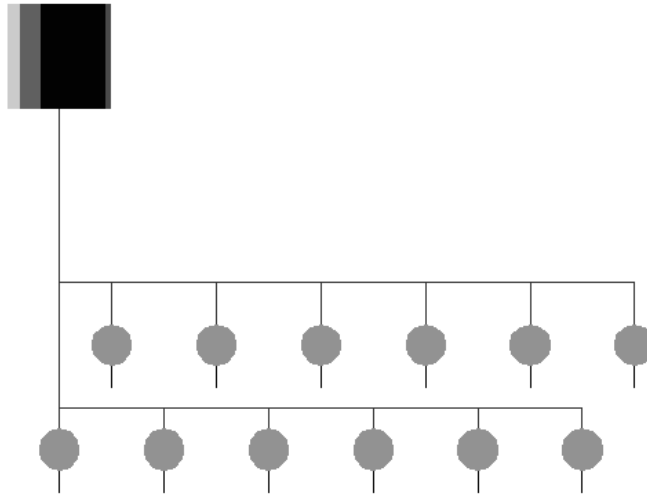
Water for this study came from a 1,000,000 L pond located at Prices Fork Research Center near Blacksburg, Virginia. The primary source of water for the pond was not surface runoff but an underground limestone aquifer pumped into the pond from a nearby well. However, the pond's primary use is for research studies and, at the time of this study, another project was in process and involved circulating water from the pond through a vegetated flume containing large amounts of nutrients. The pond had significant algal growth, indicating appropriate nutrient levels for this study. A 1230-L, plastic tank provided a constant head for the experimental wetland cells, located in a level area just below the pond (fig. A.1).



Rosenquist

Figure A.1 - The tank is located in the top left while the pond is contained just behind the earthen embankment seen across the center of the photograph

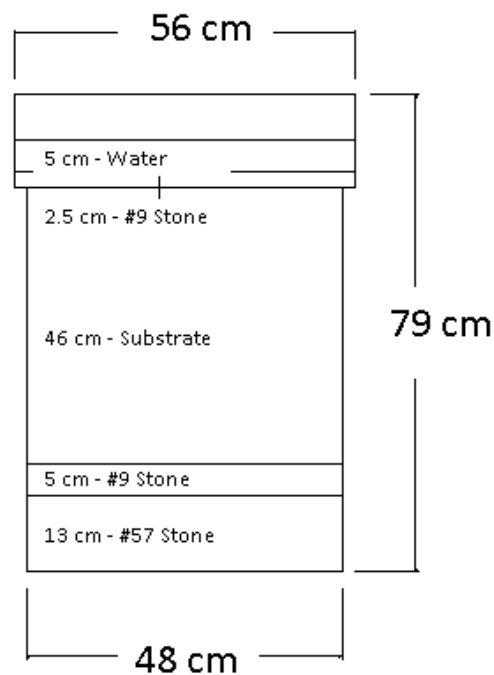
At the tank, a small water pump and 12-volt, deep-cycle battery, contained in small wooden housing ran constantly with overflow going back the pond to keep the tank full and provide a constant head. Twelve 167-L plastic containers approximately 79 cm tall and averaging 50 cm in diameter contained the experimental wetlands (fig. A.2). These cells had a vertical, subsurface, upward flow.



Braman and Newbill

Figure A.2 - Arrangement of field-scale wetland cells

The twelve cells were identical apart from the substrate used within the cell. The cells consisted of three materials including #57 stone (1.25 cm-1.9 cm in diameter), #9 stone (0.32 cm to 0.64 cm in diameter) and one of three filtration substrates (all approximately USDA sand in size). The cells had horizontal layers of these three materials (fig. A.3).



Rosenquist

Figure A.3 – Field-scale experimental wetland cell

The inlet and outlet were in the top (5 cm above last gravel layer) and bottom (within bottom gravel layer) of each cell, respectively, and fitted with bulkhead fittings to allow connection with polyvinylchloride (PVC) piping. The cell inlet structure was a 41-cm PVC pipe with slits every 5 cm. A network of PVC pipes connected each cell to the tank.

Experimental Design

The two experimental factors in this experiment were substrate type (two experimental types with a control) and hydraulic residence time (two levels). The three substrate-types included an iron-based substrate, a calcium-based substrate, and a low-iron, low calcium control substrate (fig. A.4, A.5). Each substrate had four replications.

LABORATORY RESULTS																				
Sample ID	Lab ID	pH	EpH	ppm in soil (mg/kg)										%						ppm SS
				P	K	Ca	Mg	Zn	Mn	Cu	Fe	B	mg/kg Est. CEC	Acidity	Base Sat	Ca Sat	Mg Sat	K Sat	OM	
ACCA	29732	8.89	N/A	2	10	2909	1780	0.2	1.5	0.1	11.6	0.1	29.2	N/A	100.0	49.7	50.2	0.1		
ACFE	29734	6.85	6.52	12	69	1174	606	1.2	23.1	0.3	77.9	0.2	11.0	0.3	99.7	53.0	45.1	1.6		
ACYS	29733	7.53	N/A	2	4	125	55	0.3	2.5	0.2	5.5	0.1	1.1	N/A	100.0	57.5	41.7	0.8		

VT Soil Test Laboratory, fair use

Figure A.4 - Chemical properties for each substrate before filtration; ACCA is the calcium-based substrate, ACFE is the iron-based substrate, and ACYS is the control substrate

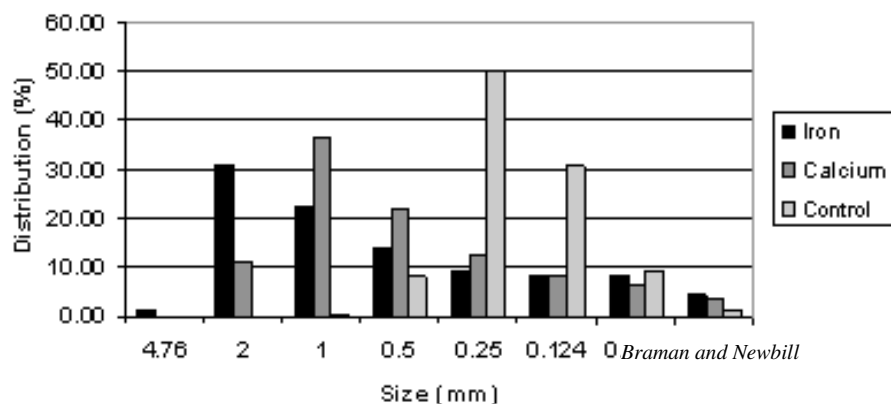


Figure A.5 - Particle size distribution for each substrate

The two target hydraulic residence times were 19.3 min and 28.6 min, which corresponded with target, flow rates of 0.7 L/min and 0.35 L/min. Each HRT had six replications. A manometer (demarcated plastic tubing attached to a wooden stick) installed between the ball valves and the inlet structure allowed for daily flow rate monitoring and

adjustments. Equations 1-3 provided the target flows and anticipated head requirements from the target hydraulic residence times.

Bernoulli's Equation

$$v_1^2/2g + z_1 + p_1/\gamma = v_2^2/2g + z_2 + p_2/\gamma + h_L \quad (1)$$

where

v = velocity

z = elevation

p = pressure

γ = specific weight of water

h_L = friction loss

Darcy's Law

$$Q = K \cdot H \cdot A / L \quad (2)$$

where

Q = flow rate

K = hydraulic conductivity (Table A.1)

H = the elevation head

A = cross sectional area

L = column height.

$$HRT = \rho \cdot V / Q \quad (3)$$

where

ρ = porosity (originally published values, revised with experimental values; Table A.2)

V = volume

Q = flow rate

Table A.1 - Experimentally determined hydraulic conductivities for each substrate

Substrate Type	Average Value (cm/s)
Iron-based Sand	0.026
Calcium-based Sand	0.012
Control Sand	0.019

Values obtained according to standard soil test methods

Table A.2 - Experimentally determined porosity for each substrate

Substrate Type	Average Value (cm/s)
Iron-based Sand	0.44
Calcium-based Sand	0.38
Control Sand	0.46

Values obtained according to standard soil test methods

Sampling and Sample Analysis

Grab samples were taken from the tank outlet and from the top of each of the 12 wetland cells every other day starting July 12, 2007 and ending July 21, 2007. Sample analysis included total phosphorus (TP) and dissolved reactive phosphorus (DRP) (EPA Methods 365.3 and 365.2). Readings for pH were from days 1 and 7 with a handheld pH instrument (Hanna Instruments, Woonsocket, RI).

Data Analysis

In order to evaluate P removal, we converted P concentrations to P load (mg) by including the respective flow rate and time between sampling. Consequently, cells with the higher flow rates had twice the influent P-load. For equitable performance evaluation, we converted load removal to percent P-load removal with respect to the influent P-load. A cumulative P-load from data combined across the entire length of the study served as an overall performance metric for each cell. Pairwise comparison methods tested for differences in performance between substrate types and for changes in pH, while Student's t-test tested for differences between flow rates and for positive cumulative P-load removal. A bonferroni correction factor adjusted p-values for multiple comparisons were where applicable and p-values < 0.05 indicated significance.

Results and Discussion

Total Phosphorus

P-removal performance measured by TP varied drastically during the study (fig. A.6). While we observed no clear increase or decrease, some of the fluctuations seem to occur at the same time in several substrate/HRT combinations, indicating that something other than the substrate and HRT is causing variation. Cumulative P-load removal percentages (fig. A.7)

indicate a possible difference in performance between HRTs, but the difference is not significant. Testing revealed no significant differences in cumulative P-load removal performance between substrates or between HRTs. Furthermore, no treatment group displayed a significant, positive removal percentage overall. Higher P level associated with the iron-based substrate as sourced (fig. A.4) might explain the negative removal rates seen in the long-HRT, iron-based cells (fig. A.7).

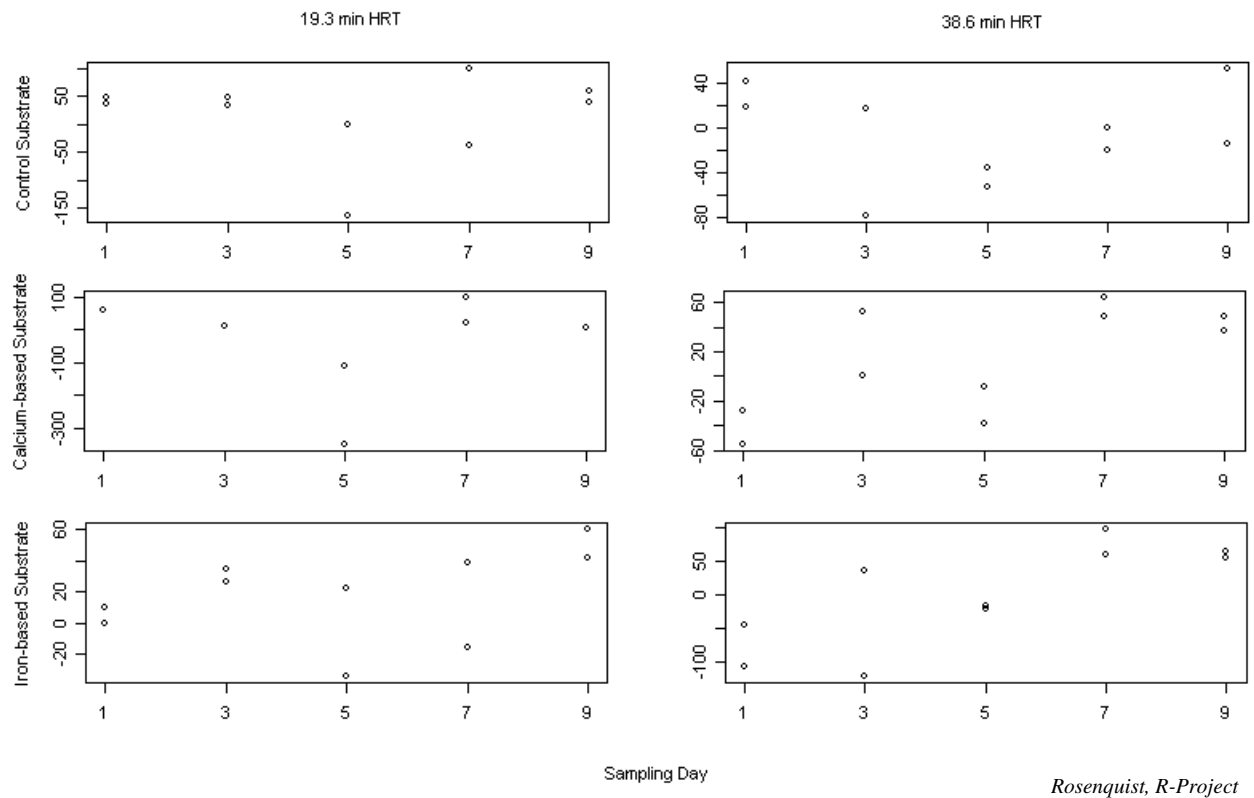


Figure A.6 - P-load (TP) removal percent data trends for each substrates/HRT combination

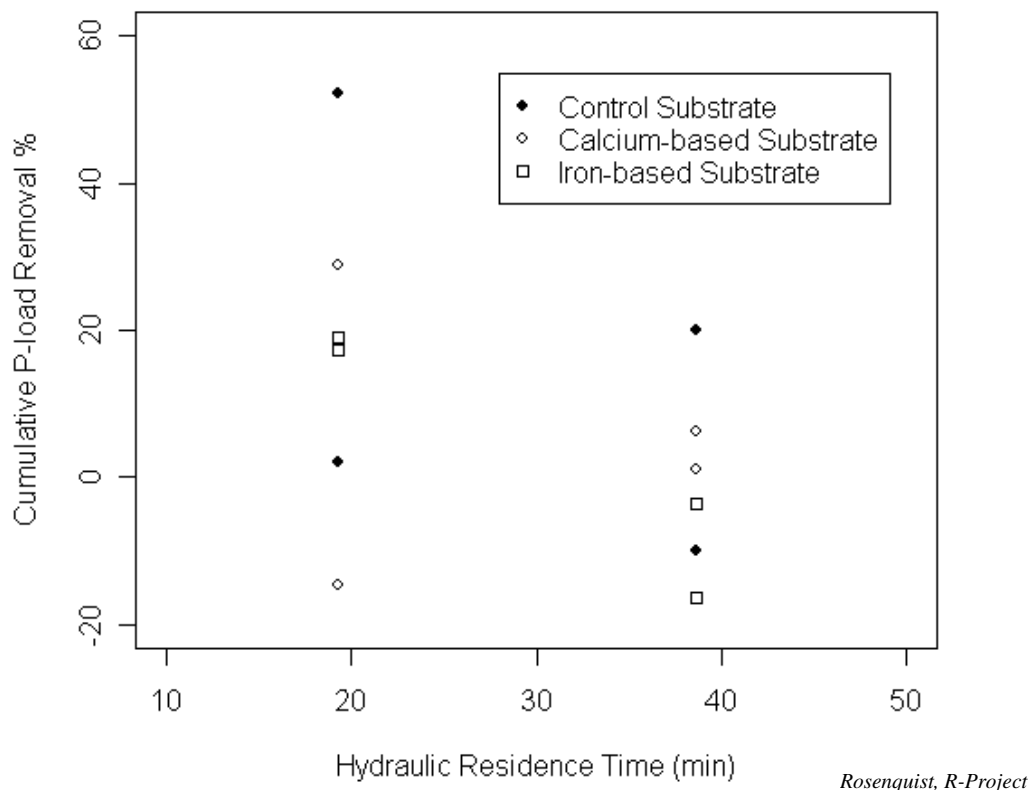


Figure A.7 - Cumulative P-load (TP) removal percentages for the entire study period

Dissolved Reactive Phosphorus

P-removal performance measured by DRP also varied drastically during the study (fig. A.8). Again, there is no clear increase or decrease but some of the fluctuations seem to occur at the same time in several substrate/HRT combinations, especially within the same HRT. Cumulative P-load removal percentages (fig. A.9) reveal a difference in performance between HRTs and for DRP this difference is significant. The lower HRT had a higher mean P-removal percentage, opposite of the trend anticipated. Short-circuiting at the edge of the container due to low head and low pressure is a possible explanation for this trend. Further testing revealed no significant differences in cumulative P-load removal performance between substrates. Only the low HRT group together displayed a significant, positive removal percentage overall.

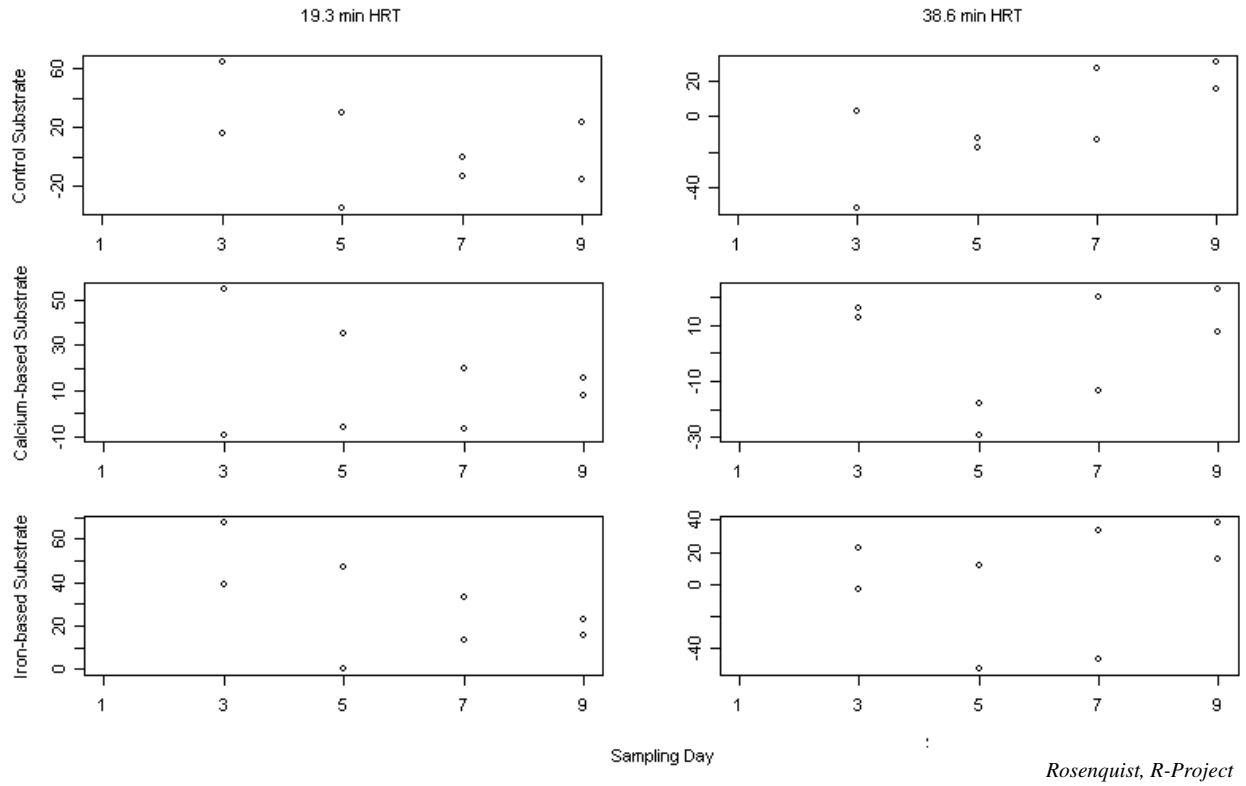


Figure A.8 - P-load (TP) removal percent data trends for each substrates/HRT combination

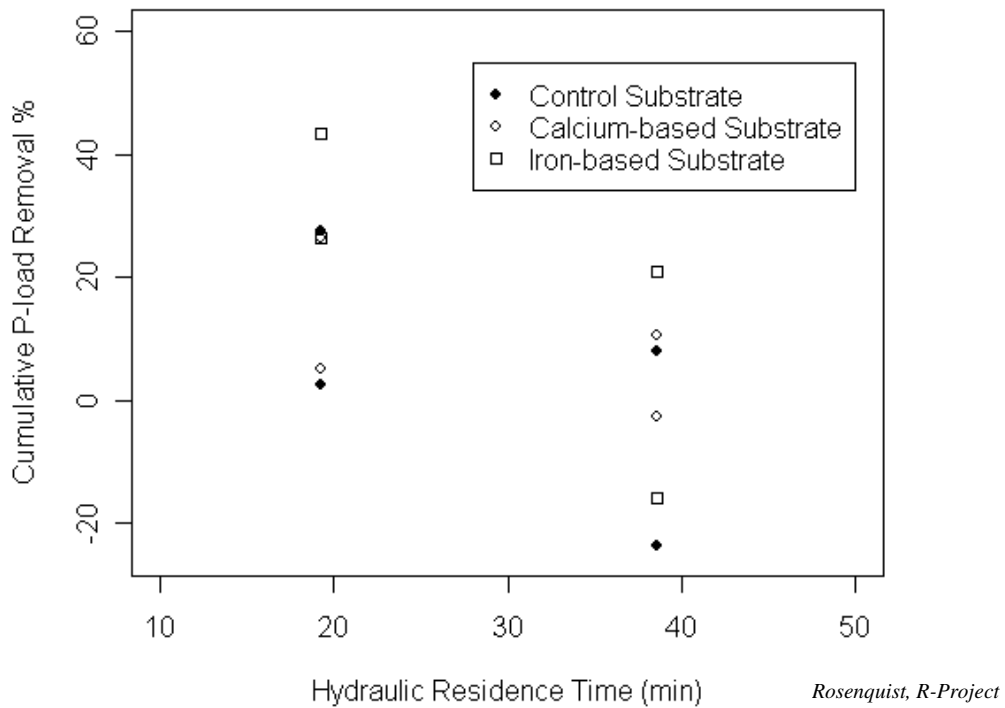


Figure A.9 - Cumulative P-load (TP) removal percentages for the entire study period

pH

Cell pH during the study remained near neutral (7.0 - 8.5) for all influent and effluent values; however, a significant decrease in pH from influent to effluent occurred in iron-based cells, but not for the other two substrates (fig A.10). This decrease was only slight as the average influent concentration was 8.0 and the average effluent concentration from cells with iron-based substrate was 7.7. Overall, none of these materials displayed problems regarding changes in pH between influent and effluent.

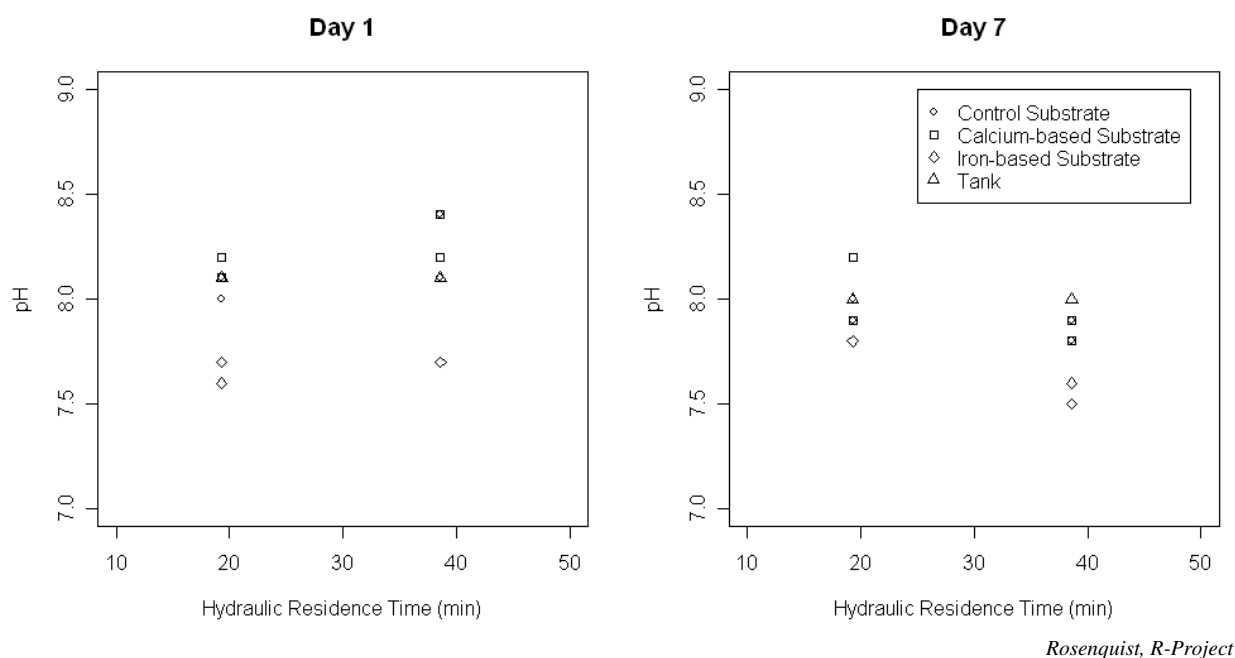


Figure A.10 - Cell pH at the beginning (a, left) and towards the end (b, right) of the study period

Potential Sources of Variability and Lessons Learned

There are several factors suspected that may explain variability in the data and the general lack of significant results. Some of the factors also represent lessons learned that might improve research methods for similar studies.

Sampling Strategy

Due to the possibility of long-term trends in performance, a longer sampling period may provide results that are more useful. In addition, the possibility of performance fluctuations on a time-scale less than 1 d may necessitate more frequent sampling. Natural systems are quite

dynamic, especially during the initial stages, and time-dependent factors such as substrate settling and bio-fouling could contribute to performance variability. Substrates settled during the study by several centimeters. Filling the containers with substrate while they are full of water might prevent such settling.

Treatment Variables

Another factor was a lack of precision in flow control. Cell recalibration occurred daily to maintain the appropriate flow rates, which were only accurate to the target value by plus or minus 10% at best. Settling was most likely central to this problem as the head required to achieve the target flow rate varied widely. In addition, fine control of the head was difficult with the ball valve arrangement.

This study based substrate selection primarily on availability. The substrates were chosen according to their basic composition, but their exact properties were only determined during the study. For example, the "Iron-based" substrate may have contained relatively little iron compared to possible iron-based substrate options. Future research should specify iron or calcium content on a mass basis in advance instead of assuming the substrate to be representative of a particular constituent based only on dominant constituents.

Replication

Another contributing factor could be the lack of replication. Future studies should include at least three replications of each treatment combination.

Equipment and Laboratory Space

The laboratory used to analyze the samples in this study also hosted studies involving dairy manure. The manure tests utilized some of the same equipment, specifically filtration apparatus used for DRP analysis. Analysis of filtration blanks revealed the contamination (fig. A.11). Although sufficient sample was available to re-process data different filters, the associated time delay placed the second analysis outside of the EPA recommended procedure for storage and analysis for DRP. Also based on the mixed use of the laboratory, sample bottles used on 7/13 and 7/15 were subject to a different cleaning process (heat treatment but not acid bath).

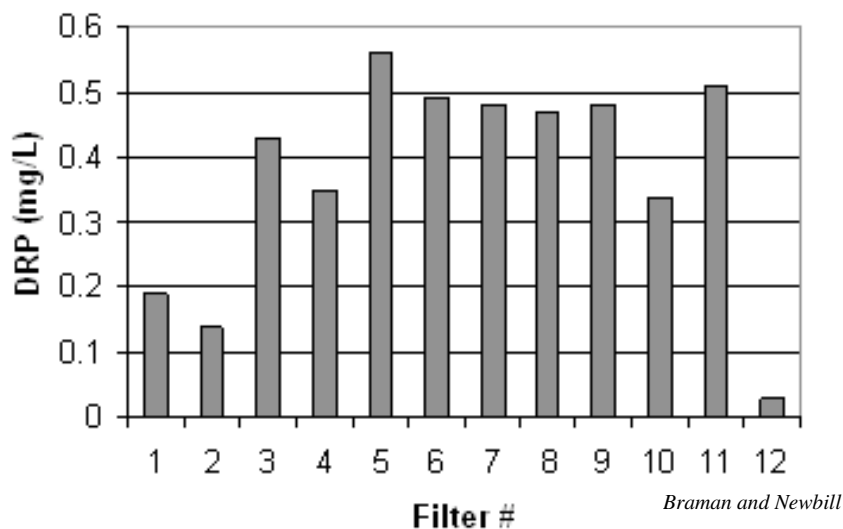


Figure A.11 - DRP observed in quality control filtration blanks

Unspecified or Unmeasured Variables

Particle size distribution and the P already on substrates before filtration may have affected P removal and neither were consistent between substrates. The control sand had a smaller and more uniform particle size distribution, resulting in a larger surface area and potentially providing more reactive area available for P removal. Higher P associated with the iron-based substrate versus the other two substrates (fig. A.4) could decrease P-removal capacity for this substrate. In addition, rust colored deposits on the tubing and bulkhead fittings of the iron-based substrate cells may indicate mobility of iron during the study and a need to measure and track iron concentrations in water.

Short Circuiting

A lack of plug-type flow, short circuiting, probably occurred in at least some cells. Three possible explanations are proposed. First, because the ends of the PVC pipe on the inlet structure were open, the majority of the flow probably entered the gravel through the end of the pipe at the edge of the container. Future setups should plug this opening, forcing distribution through the slits along the pipe. Second, a combination of low head and low flows could have caused short circuiting, allowing the majority of the flow to pass in the less flow-resistant boundary area between the substrate and the smooth walls of the container. If insufficient head was available to force flow through the substrate, minimal contact would occur for sorption. Increasing roughness

on the interior of the container to promote flow through the substrate may correct this problem. Third, both localized and generalized fluidization of the substrate occurred with sufficiently high head, resulting in pipe flow through the substrate. This fluidization may present a serious limitation to the use of vertical subsurface-flow wetlands with upward flow regime and non-cohesive substrates.

Conclusions

The results of this study indicate that none of the designs tested were optimal for P-removal from stormwater ponds; however, the study provided many useful insights for the development of improved research methods in future work. Regarding the specific hypotheses: 1) neither the calcium-based nor iron-based substrates had statistically different P removal than P removal in the control substrate; and 2) cells with longer hydraulic residence times removed a lower percentage of P than cells with shorter retention times, the opposite of the hypothesized relationship.

Acknowledgements

The authors would like to thank the National Science Foundation for providing support for students who participated in this study as a part of the NSF Research Experiences for Undergraduates grant. In addition, the authors would like to acknowledge assistance from exceptional faculty (Dr. Matthew Eick and Dr. Saied Mostaghimi), staff (Laura Teany and Julie Jordan), and students (2007 NSF Fellows and VT-BSE Graduate Students).

Field-scale study of phosphorus removal by sorption: substrate and residence time study follow-up

S.E. Rosenquist, W.C. Hession, D.H. Vaughan

Abstract

A previous study by the authors on phosphorus (P) sorption to wetland substrates provided limited results based, at least in part, on the methods used. This study followed up on objectives of the previous study while incorporating the lessons learned. Specific changes included a different regulation system for hydraulic residence time (HRT), more replications for statistical power, improved specifications and analysis of substrate properties, and different time scales for sampling. Results indicated that both short-term and long-term variation exists with long-term variation being larger than short term. Differences in HRT did appear to affect P removal performance with shorter HRT possibly providing increased removal. Another interesting result was higher than expected P removal in gravel substrates in comparison to the iron-based sand substrate.

Introduction

A previous study by the authors, "Field-Scale Study of Phosphorus Removal by Sorption: Comparison of Substrates and Residence Times" included several key recommendations to improve the quality of the study and the results. The purpose of this study was to follow-up on the previous study, refining the results and conclusions through improved methods. One issue raised in the previous study was the effect of diurnal variations in system properties on performance monitoring. Previous studies have indicated a phosphorus (P) removal dependence on pH (Shang et al., 1992) and redox potential (Carleton et al., 2000). Eutrophic ponds can sometimes demonstrate large diurnal variations in pH and dissolved oxygen (DO) (Correll, 1998) indicating that sampling time may be critical to an accurate quantification of system performance over time. For this reason, this study includes both long-term and diurnal analysis to determine performance. Another addition to this study in follow-up from the previous study was the monitoring of substrate properties in addition to water properties. Iron-based substrate showed the most promise for the purposes of this design based on the efficacy of P removal by sorption at neutral pH (McBride, 1994), equivalent performance with other substrates in the previous

study, and the redox activity of iron as part of a future rejuvenation strategy for sorption capacity. Previous research suggests that substrate size has a large effect on sorption capacity (Zhu et al., 2003) and would predict very little removal for large gravel, making it a good theoretical control substrate. Substrate specific properties in addition to the general specifications used in the previous study have indicated influence on P removal performance, and a more accurate analysis should provide a better understanding of P removal in the system by sorption processes. The objectives for this study are to re-evaluate the affect of substrate type and hydraulic residence time (HRT) on P removal by sorption processes in wetland cells designed to complement the stormwater treatment already present in stormwater ponds. Specific hypotheses in this study were: 1) that an iron-based sand substrate will achieve more P removal than a gravel substrate; 2) that longer HRT will increase P removal in the wetland cells; and 3) that daily sampling time has an impact on P removal performance monitoring.

Materials and Methods

Experimental Setup

The experimental setup in this study was the same as he previous except for several key differences. The first difference was moving the head tank down from the top of the earthen embankment that contained the pond and the experimental cells placed on concrete blocks. Moving the tank enabled the setup of a siphon system and the elimination of the pumping requirement. The siphon enabled a long-term study without the need for continuous power requirement. Laser survey verified correct placement of the concrete blocks that held the cells to the heights for the desired levels of head, theoretically eliminating the need for the ball valve and manometer setup to control head. Cells were located in two offset rows of six cells with 5-ft spacing between each cell. The iron-based substrate used in this study different from the one used in the previous study. The iron-based sand substrate came from a local quarry in New Castle, VA, and contains Fe at a concentration of 0.2 % - 0.7 % by mass. The gravel substrate was the same #9 stone from the previous study and both cells had a 13-cm bottom layer of the #57 stone (fig. A.3). This study did not include the top layer of gravel to allow for periodic substrate sampling. In order to correct for possible short-circuiting around the edges seen in a previous study, a commercially available surfacing roughening product designed for lining the

bed of pick-up trucks was applied to the inside surface of the containers throughout the area where the substrate is located.

Experimental Design

The experimental factors in this study were HRT (low, medium, and high) and substrate type (gravel and iron-based sand). The HRT levels corresponded to three levels of head (7.6 cm, 15.2 cm, and 22.9 cm) produced by the surveyed concrete block locations. Of twelve total experimental cells, nine contained the iron-based sand substrate at different HRT, and three contained the gravel substrate at the lowest HRT.

Sampling and Sample Analysis

Flow started in cells in June 2008 and continued to Dec 2008. Sampling included both a short-term sampling set (every 2 h over a 10-h period) to test for diurnal variations and a long-term set (0 d, 15 d, 22 d, 29 d, 37 d, 45 d, 50 d, 59 d, 65 d, 72 d, 93 d, 121 d) to test for long-term variations. Water sampling in both of these sets included pH (Hanna Instruments, Woonsocket, RI), Temperature (Air and Water), DO (YSI Incorporated, Yellow Spring, OH), and grab samples from the water at the top of the cells and the tank outlet. Sampling for total iron (TI) and total phosphorus (TP) consisted of digestion of grab samples by the K-persulfate method (Clesceri et al., 1999) with 2:1 volumetric concentration followed by analysis by Inductively Coupled Plasma Atomic Adsorption Spectroscopy (ICP-AES). Substrate sampling as part of the long-term set occurred monthly and included Melich-1 extractable Fe and P, pH, and organic matter (OM) by the loss-on-ignition method.

Data Analysis

The primary performance metric used in this study was P-mass removal rate (mg/day) instead of removal percentage as used in the previous study. The authors prefer this method since it is the ultimate goal of stormwater treatment, even if it means a lower removal percentage with a higher flow rate. The EPA has also moved away from removal percentages citing multiple reasons (USEPA, 2002). P-mass removal rate calculations included the flow rate and the difference between influent and effluent concentrations at each sampling time. Either pairwise comparison or the student's t-test enabled statistical comparison, depending on the number of comparisons. Multiple regression provided analysis for the effect of various measured variables in the long-term data set. P-values > 0.05 represented significant results.

Results and Discussion

Diurnal Variations

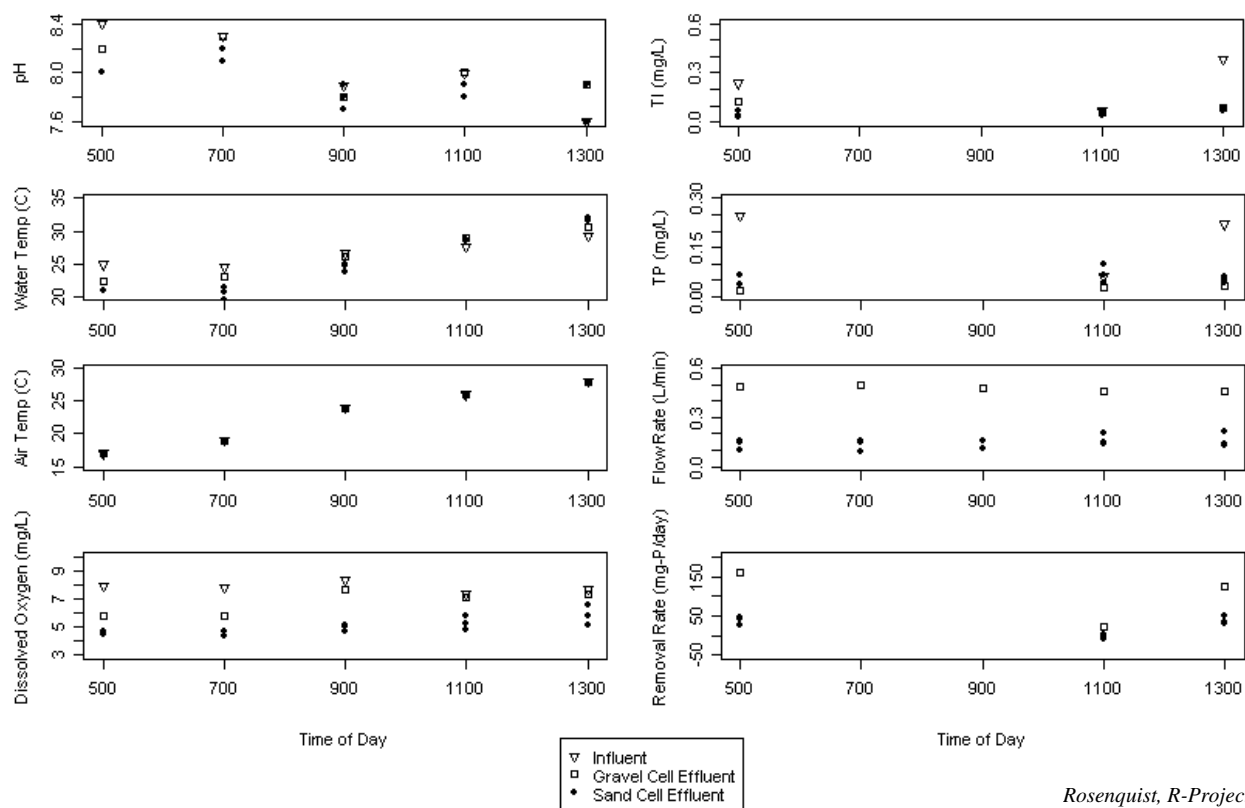


Figure A.12 - Diurnal variation in key properties

The loss of two data points for TP and TI due to label confusion limited the results of this portion of the study (fig. A.12). Results for pH and temperatures do indicate diurnal fluctuations, while DO or flow rate indicate no clear trends. Some variation in P removal occurred, possibly due to pH trends, though no clear trends in this variation were obvious. Another interesting trend, though not statistically verifiable with this data set, is the positive correlation between TI and TP, especially in influent. This correlation may be explained by Fe reduction resulting in P release in the pond (Redshaw et al., 1990).

Long Term Variations – Water Testing

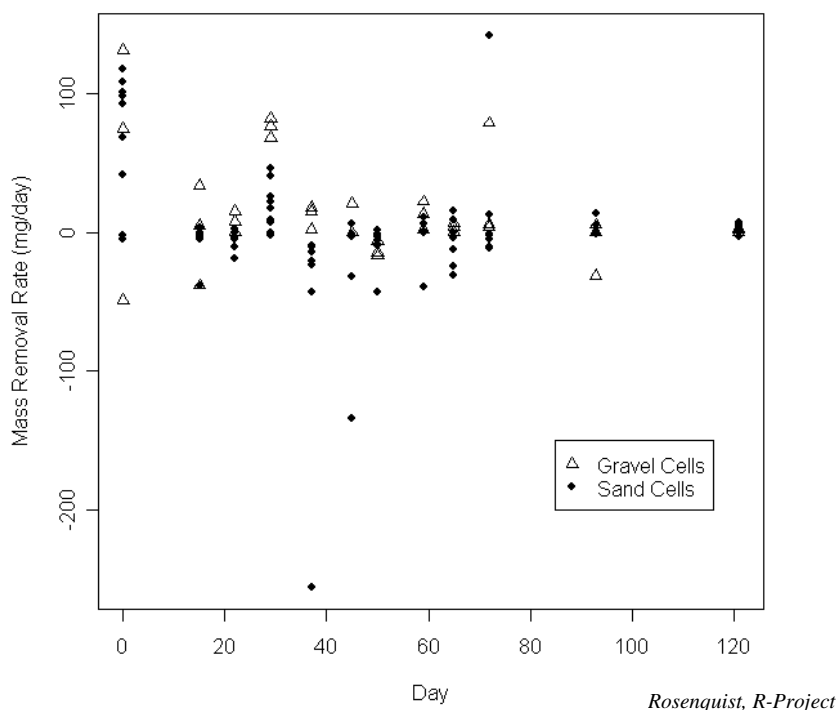
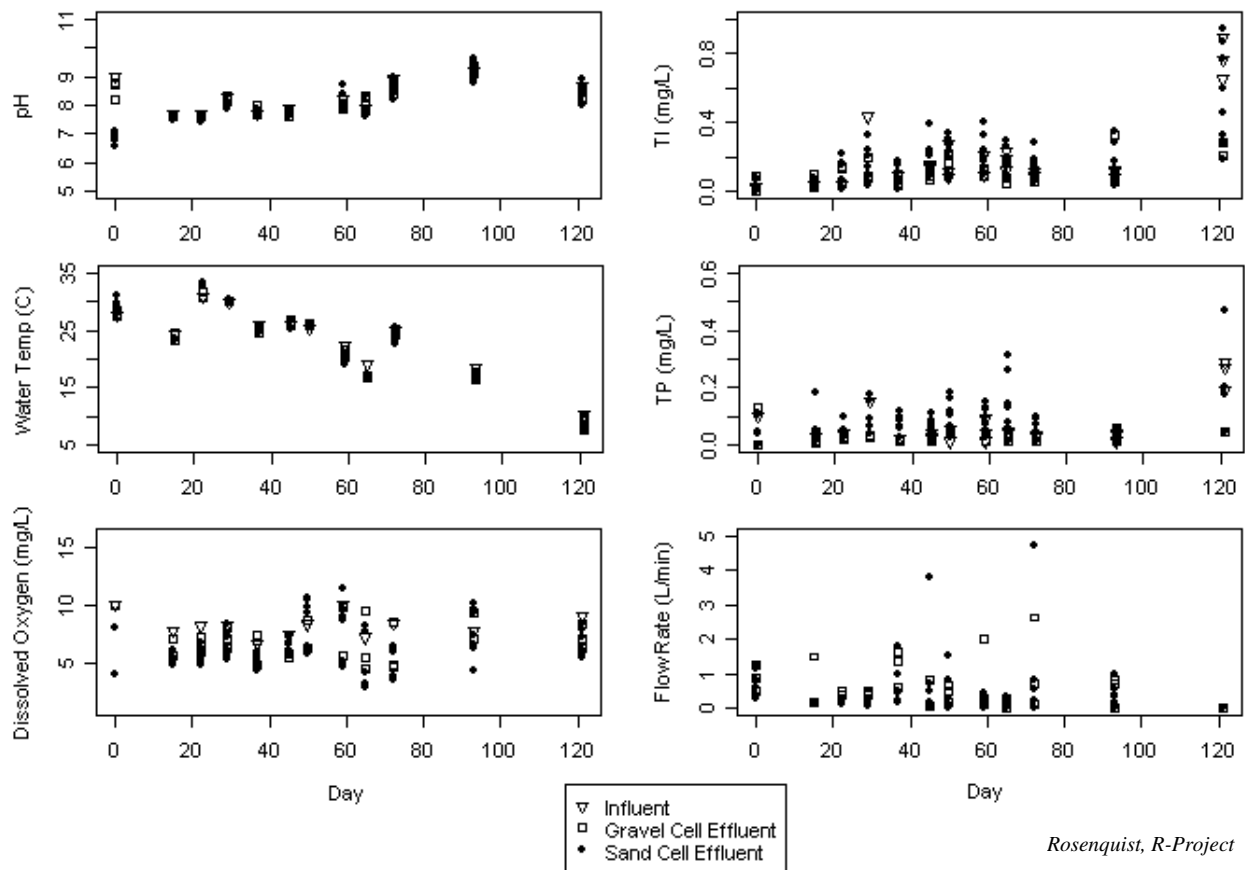


Figure A.13 - Long-term variation in P removal performance for field-scale wetland cells

Results for the long-term data set reveal a general reduction in performance over time with very little P removal taking place after day 40 (fig. A.13); however, several low P removal rates occurred before day 40 as well. Surprisingly, P removal rates in the gravel substrate tended to be higher than the sand substrate throughout the study. The gravel cells probably had higher removal rates than the sand cells (p -value = 0.06), and the HRT for the gravel cells was significantly shorter than the sand cells.

The HRT groups based on head did not function as intended as only the high HRT group was significantly different from the other two. Analysis of P removal revealed no differences between these groups. Using measured flow rates to predict P removal performance (fig. A.15) results revealed a very weak relationship by visual analysis. Regression analysis found no reliable results for any of the measured variables as predictors of P removal rate. In addition, some fluidization occurred in this study even with efforts to prevent short-circuiting and more closely regulate head.

Trends in key variables throughout the long-term data set indicated larger variations outside of diurnal trends (fig. A.14). Only pH and temperature indicate clear trends by visual analysis. None of these variables provided explanation for the variability in P-removal rate.



Rosenquist, R-Project

Figure A.14 - Measured variables from the long-term data set

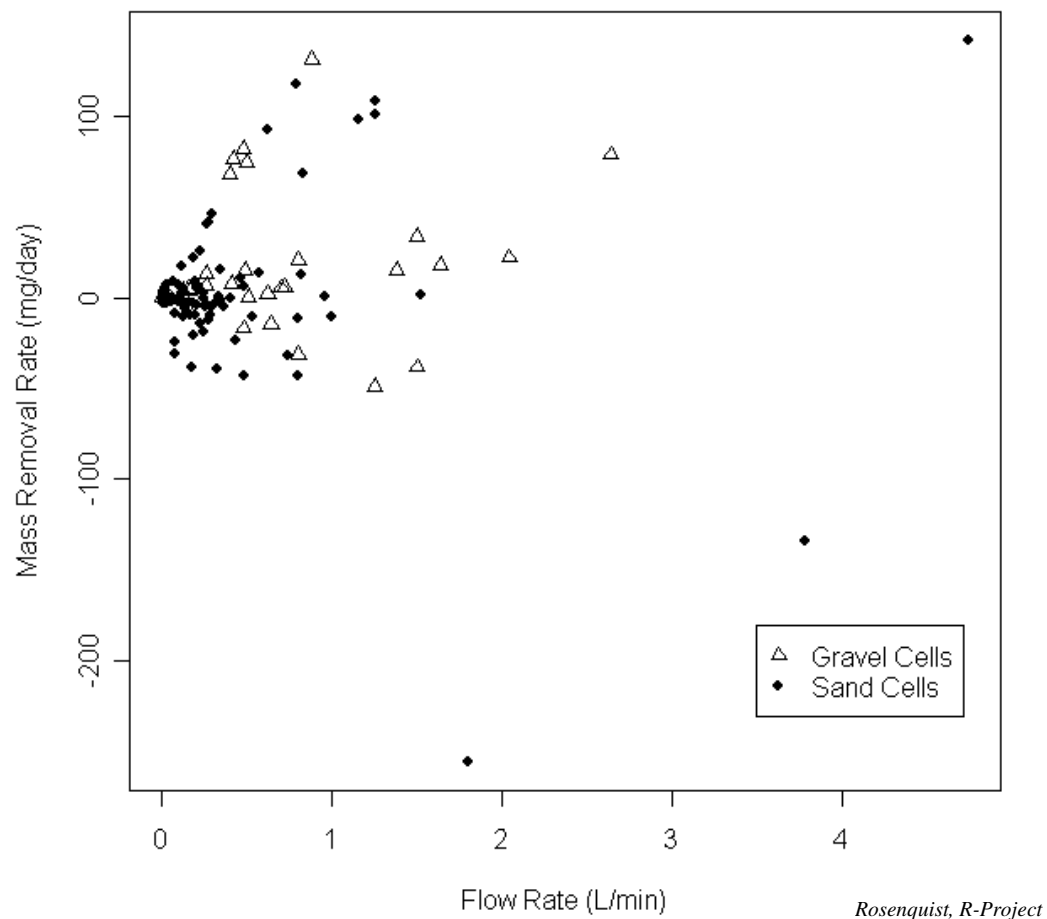


Figure A.15 - Variability in P removal performance across flow rates

Long-term Variations – Substrate Testing

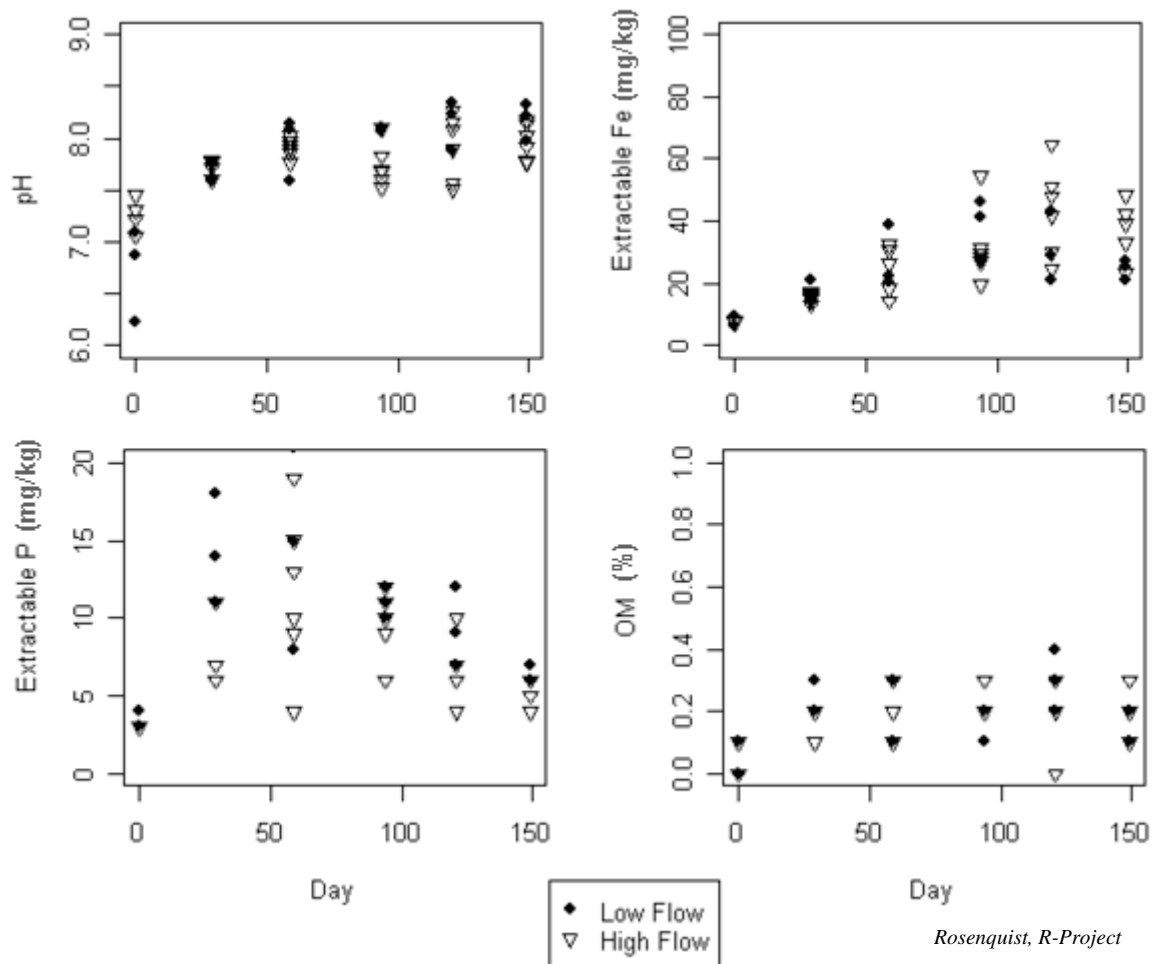


Figure A.16 - Trends in four substrate constituents

Trends from the substrate analysis indicated trends by visual analysis in pH, OM, and extractable Fe and P (fig. A.16). Increases in pH and extractable P appeared to stop at about the same time (day 40 – day 50) as removal rates became negligible in the water analysis. These two results together suggest that P removal by sorption processes reached a capacity at about 40 d with this loading regime and cell size. OM concentrations appeared to stabilize earlier than pH and extractable P, while extractable Fe appeared to increase throughout the study. This increase in extractable Fe in the sand samples may explain the removal performance seen in the gravel, since this substrate should have had little sorption capacity.

Conclusions

The results of this study support a few valuable conclusions pertaining to the experimental factors and pertaining to the changes made in this study from the previous one. Diurnal variation was present in the short-term data set suggesting that the use of one sample to represent even daily performance will make investigation into sources of variability difficult. Results for the gravel substrate suggest either that the original sorption capacity for larger substrates was equivalent for some reason, that the constituents of influent water, specifically Fe, can affect the sorption capacity, or that flow rate has an overriding effect on P removal performance. The relationship of all cells with flow rate suggests that this factor may explain at least some of this difference in P removal. Long-term trends in removal rate suggest that removal capacity for these substrates and loading regime decreased significantly after approximately a month. Both water and substrate testing verified this performance decline. Regarding the specific hypotheses tested: 1) iron-based sand substrate did not achieve more P removal than a gravel substrate, even with the significant difference in substrate size; 2) longer HRT did not increase P removal in the wetland cells, while a trend in the opposite direction as seen in the previous study was again suggested by these results 3) daily sampling time probably does have an impact on P removal performance monitoring, though no predictable trends could be established.

Regarding the changes made from the previous study, flow rate control with set levels of head was not capable of repeatedly regulating HRT between cells or over time. It was particularly difficult to regulate similar flow rates between substrates of different size. The persistent occurrence of fluidization presents a major downside to upward, vertical flow and indicates that this flow regime may actually be less capable than the downward, vertical flow at promoting mixing due to short-circuiting associated with fluidization. The siphon system was an effective method for maintaining flow to experimental cells. The long-term and short-term sampling sets suggested that more sampling was necessary to monitor variability in performance adequately. Long-term sampling suggested that variation in performance does occur over time as sorption capacity fills, and short-term sampling suggested that sampling is necessary over much shorter periods than once a day to capture all variation.

Acknowledgements

The authors would like to thank the National Science Foundation for providing support for two students, Steven Sell and Cherona Levy, who participated in this study as a part of the NSF Research Experiences for Undergraduates grant including taking photographs that are included in Appendix E.

Effect of humic acid on microbial reduction of iron and release of phosphorus from wetland substrates

S.E. Rosenquist, A. Egner, J. Pennington, M. J. Eick, D. H. Vaughan

Abstract

Declines in sorption capacity over time in wetland substrates have led to the development of novel techniques for the removal of adsorbed phosphorus (P). These techniques show promise in harvesting P from wetland substrates through facilitated Fe iron reduction, but require a faster cycle time for optimal field application. This study investigated the ability of humic acids to increase the rate of microbial iron reduction and the rate of associated P release. Experimental cells had humic acids introduced to P-saturated media at treatment concentrations of 0, 2, 20, and 200 mg/L. Results indicated a positive relationship between humic acid and microbial iron reduction and potentially with the subsequent release of P as well.

Introduction

In addition to a high affinity for sequestering phosphorus (P) by sorption processes, iron (Fe) oxides have demonstrated the ability to release P under anaerobic, reducing conditions such as in benthic sediments or saturated wetland soils (Komatsu et al., 2006; Aldous et al., 2007). This study is part of a larger effort to develop a controlled Fe-reduction process capable of periodic rejuvenation of P removal capacity in filtration substrates without replacement of substrate. While this process shows promise, the rejuvenation process is much slower than P sequestration by sorption and shortening of the cycle time will enable more practical field application.

The Fe reduction process is mainly dependent on microorganisms and varies according to their biotic requirements (Lovley, 1991; Kostka et al., 1996; Chen et al., 2003). These microbes reduce Fe as a part of an anaerobic or facultative aerobic respiration process where ferric iron (Fe^{3+}) serves as the terminal electron acceptor (Martinko and Madigan, 2006). Therefore, conditions which favor Fe reduction, and hence P release, should correspond to those which favor the growth of the microbial population. Factors which support microbial respiration include sufficient and bioavailable electron donors and acceptors as well as favorable environmental conditions such as temperature and optimal pH (Martinko and Madigan, 2006).

Several organic moieties have been tested to catalyze indirect Fe reduction by serving as electron shuttles, including nitrotriacetate (NTA), anthraquinone-2,6-disulfonate (AQDS), and humic acids (Lovley et al., 1998; Luu et al., 2003). Due to their ubiquity in the natural environment and typical freshwater biospheres, humic acids appear to be the most applicable electron shuttle for field application. Prevalent in aquatic and terrestrial environments, humic acids are a heterogeneous class of compounds resulting from the degradation of numerous organic sources including vascular plant material and algae (Steenson, 1994). While coming from such diverse sources, the chemical properties vary depending on the extent of breakdown and organic carbon source (Aiken et al., 1985). However, a shared characteristic is the ubiquity of organic radicals, or free, unpaired electrons, which result from chemical degradation. A majority of these radicals have been documented as quinone moieties, cyclic carbon structures with an even number of carbonyl groups (Scott et al., 1998). The presence of such organic radicals provides humic acids with large oxidation-reduction potential.

In the absence of humic acids or some other electron shuttling mechanism, Fe-reducing bacteria must be in physical contact with Fe^{3+} in order to donate an electron and allow respiration to occur (Lovley, 1991). This need for physical contact can prove to be a limiting factor to microbial growth due to insufficient bioavailability of the electron acceptor. However, the redox-active quinone groups of humic acid have great ability to both donate and receive electrons under favorable conditions. This ability allows for humic acids to accept electrons from Fe-reducing microbes during respiration and donate them to Fe^{3+} (Scott et al., 1998) as an 'electron shuttle' or redox mediator (Lovley et al., 1998). Therefore, the presence of humic acids generally increases Fe reduction by eliminating the requirement direct physical for electron transfer.

The addition of humic acid as an electron shuttle is also able to increase Fe reduction by interacting with a more diverse microbial population. Included in this phylogenetically diverse group are sulphate-reducing, methanogenic, and halo-respiring microorganisms as well as Fe-reducing bacteria, which are all able to reduce humic acids (Lovley et al., 1998; Cervantes et al., 2002; Coates et al., 2002). This diversity allows Fe^{3+} reduction to occur in more geographically diverse areas in which microbial populations may differ and with a larger variety of potential carbon-sources accessible to various types of bacteria. A more diverse biotic population should increase the rate of humic acid reduction and thereby provide for increased Fe reduction by decreasing the possibility of the process being environmentally or carbon-source limited.

Indirect Fe reduction by microorganisms with supplemented humic substances has resulted in rates up to seven times that of direct reduction by Fe-reducing bacteria (Jiang and Kappler, 2008). Even low concentrations of humic acids can significantly increase Fe reduction through the reuse of humics as a pseudo-catalyst (Nevin and Lovley, 2000).

While most studies documenting the effects of humic acid on microbial reduction of Fe have occurred in near ideal laboratory conditions, Fe reduction by native populations of microorganisms has demonstrated increase with the addition of humic substances (Rakshit et al., 2009) and the electron shuttling capabilities of humic acids have been documented in freshwater sediments (Kappler et al., 2004). Such cases provide evidence that comparable results could be possible under field conditions. Increased reduction in the presence of humic acids should also lead to increases in P release, but there has been little research in this area. As prior research shows that the rate of P release without further facilitation is too slow for practical usage as a renewal strategy for sorption capacity, studies examining the effect of humic acid on the kinetics of Fe reduction by microbes are critical to the development of the rejuvenation process.

The objective of this research is to examine the effects of humic acid on microbial Fe reduction and subsequent P release. Specifically, this research will evaluate the following research questions:

1. Does the inclusion of humic acids in a saturated wetland media increase not only the rate of Fe reduction but the rate of P release as well?;
2. Does the increase in Fe reduction or P release correlate to the amount of humic acid included?; and
3. Does the inclusion of humic acid affect the total mass of Fe reduced or P released?

Methods

Experimental Setup

A synthetic stormwater consisted of dilute phosphate solution with a concentration typical of rainwater runoff prepared with a naturally occurring pH buffer, sodium bicarbonate. The buffer was included to more accurately simulate stormwater alkalinity. The solution included 2 mM NaHCO₃ with 0.5 mg-P/L from reagent grade salts and deionized water.

USDA grade medium sand with total extractable Fe content between 0.2% - 0.7% by mass constituted the sorption media due to its Fe content and local availability in Blacksburg, VA. The required Fe content enabled P sorption mainly to Fe³⁺ sites. Hand mixing of 10 kg of the same ensured a homogeneous mixture. Then, we distributed 600 g quantities into each of 16 glass-jar cells (fig. A.17). In order for P sorption to occur, we added 600 mL of the synthetic stormwater solution to each cell. Plastic wrap covering the cells decreased evaporation while the P adsorption process occurred over 11 d.

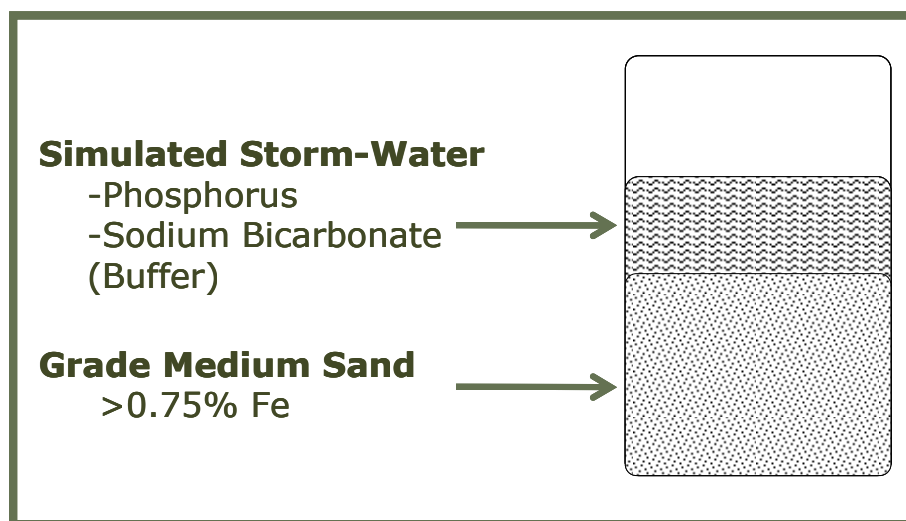


Figure A.17 - Layout of experimental cells including substrate and supernatant

Humic acid used in the experiment was from Aldrich Corporation. To ensure uniform addition to all cells within each treatment level, 20mL of extracted supernatant from each cell provided 80mL of water in which to dissolve the humic acid. Agitation of this solution for 30 minutes promoted dissolution and homogeneity. While the majority of humic acid dissolved, some particulate remained, especially in the highest treatment solution. Continuously agitation during transfer by pipette to the cells ensured that treatment remained uniform.

The glass jars had flat threaded rings and thin plastic wrap to provide an airtight seal, promoting an anaerobic environment. The plastic allowed for gas expansion but also sealed the cells, supporting the anaerobic conditions desired in a rejuvenation process. Optimum temperature for growth of mesophilic microorganisms, found in temperate aquatic climates, is between 30° C and 45° C (Madigan and Martinko, 2006). Therefore, cell incubation took place at 35° C to promote microbial activity and expedite the rejuvenation process under field-feasible temperature conditions.

Experimental Design

We divided the sixteen cells into four groups including a control and three humic acid treatment levels (Table A.3). All four groups received a uniform quantity (1000 mg/L) of organic carbon, in the form of granulated sucrose sugar. A high concentration of sucrose ensures that an electron donor source will not be a limiting factor in microbial growth.

Table A.3 – Initial cell treatment levels of humic acid

Treatment	Control	Level 1	Level 2	Level 3
Added Humic Acid (mg/L)	0	2	20	200
Organic Carbon (mg/L)	1000	1000	1000	1000

These treatment levels were chosen because it has been documented that microbial Fe reduction shows most correlation with humic acid concentrations between 5 mg/L - 25 mg/L (Jiang and Kappler, 2008). Therefore, it is advantageous to study the effects of humic acids within this range in order to determine any relationship between humic acid level and Fe reduction. Treatment level 3 was included to give the system an abundance of humic acid, ensuring that it is not a limiting factor to microbial growth. Four replications of each treatment provided greater statistical sample size and reduced standard error.

Sampling and Sample Analysis

In order to determine the percentage of total organic carbon attributable to humic acid, rather than the added sucrose, TOC occurred after the humic acid treatment but before sucrose addition (1000 mg/L).

Sample timing was three times per week (Monday, Wednesday, and Friday) over the course of four weeks. At each sampling time, we collected a 25 mL sample by syringe from the supernatant of each cell. Filtration to partition dissolved constituent was through a 0.45 μm mixed-cellulose-ester, sterile syringe filter. Acid-washed glass vials contained the samples and were stored in a refrigerator in advance of analysis.

After sample results for the first 14 d were analyzed, it was determined that the cells had not received adequate amounts of sucrose, and were probably carbon-source limited. An additional 50g sugar addition to each of the cells on day 15 remedied the carbon limitation, and sampling continued as scheduled. Sample analysis included the following elements and followed the procedures described below:

Total Dissolved Iron

Total dissolved iron (TDI) samples consisted of a 10 mL aliquot sent to Virginia Polytechnic University's Soil Chemistry Lab for analysis by Inductively-Coupled Plasma (ICP-AES) atomic emission spectroscopy.

Ferrous Iron

The 1,10 Phenanthroline Method was followed according to standard procedure (*Method 8146 Iron, Ferrous*, 2001). A spectrophotometer (Hach Co, Odyssey DR/2500 Spectrophotometer, Loveland, Colorado) provided the analysis. The method measures ferrous iron (Fe^{2+}) in concentrations up to 3.0 mg/L in 25 mL of sample. A 5 mL aliquot from each cell, diluted to 25 mL with DI water provided for the analysis. If concentrations of Fe^{2+} rose above detectable limits, further dilution of 1.0 mL and 0.5 mL aliquots occurred.

Total Dissolved Phosphorus

Total dissolved phosphorus (TDP) analysis included taking samples from a 10 mL aliquot and sending them to Virginia Polytechnic University's Soil Chemistry Lab for analysis by Inductively-Coupled Plasma (ICP-AES) atomic emission spectroscopy.

Dissolved Reactive Phosphorus

A 9 mL aliquot allowed for dissolved reactive phosphorus (DRP) analysis. We analyzed with a SEAL continuous flow analyzer (Seal Analytical GmbH, AutoAnalyzer 3, Norderstedt, Germany), and processed according to (*Phosphate in Water and Seawater, Total P in Pursulfate or Kjeldahl Digests*, 2008) .

Total Organic Carbon

The Sievers 900 Laboratory TOC Analyzer measured total organic carbon (General Electric Ionics Instrument Business Group, Sievers 900 Laboratory TOC Analyzer, Boulder, CO). We diluted 1 milliliter of sample with 29 mL of de-ionized water for analysis. The mean of three TOC measurements from each sample provided a TOC value for each cell.

pH

pH was measured using a portable probe rinsed thoroughly with distilled water and dried between sampling each cell (Hanna Instruments, Woonsocket, RI).

Data Analysis

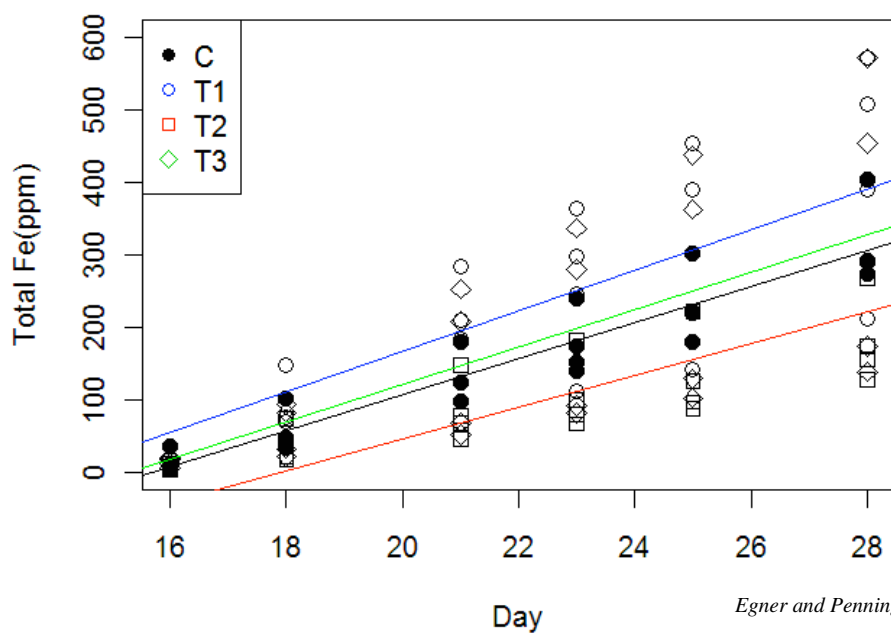
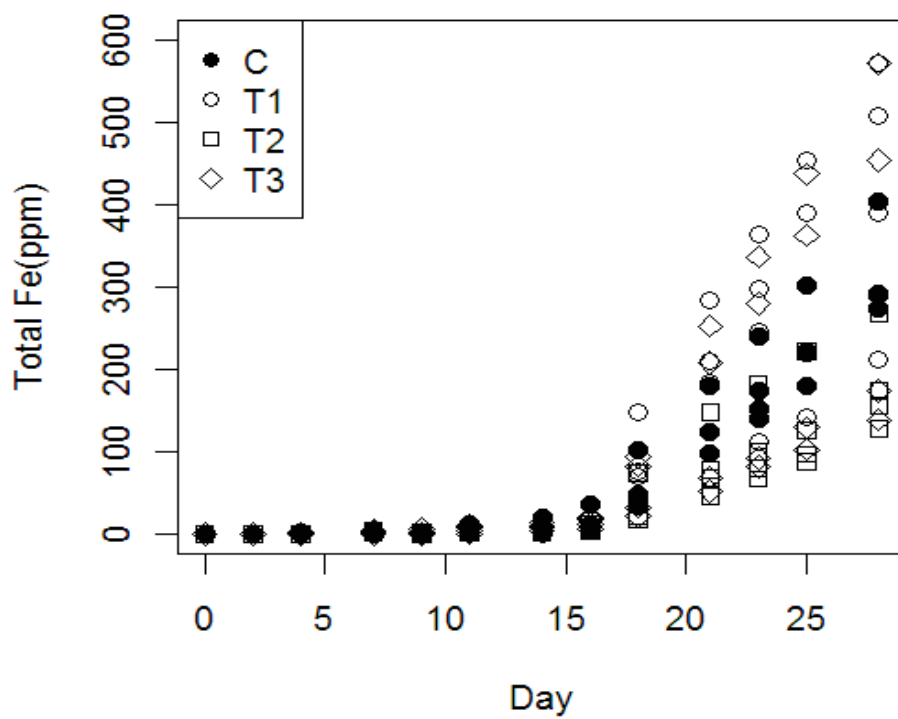
Multiple regression analysis was performed on the data using R-Project, v2.9.1, statistical software (R Development Core Team, 2009). The independent variables analyzed in each regression were time and treatment level and the dependent variable was the concentration of the various constituents (TDI, Fe^{2+} , TDP, and DRP). Indicator variables represented the treatment levels. Analysis of each data set included both the entire study period and from day 15 to the end, in order to recognize trends after additional carbon was included. P-values less than 0.05 indicated statistical significance.

Results and Discussion

After the 11-d adsorption period, day 0 measurements constituted a baseline for the Fe-reduction/P-release process. Baseline TDI levels were very low, ranging from 0.023 to 0.182 mg/L between cells. The level of TDP ranged from 0.138 to 0.202 mg/L between cells. Baseline Fe^{2+} levels were mostly undetectable by the analytical method used. Cell pH ranged from 7.62 to 8.02 between cells.

Total Dissolved Iron

The concentration of TDI increased over time (fig. A.18a). The most rapid release of Fe occurred during days 16-28 (fig. A.18b).



Egner and Pennington, R-Project

Figure A.18 - Total Fe Concentrations for the entire study (a, above) and after day 15 with associated regression models (b, below); lines from top to bottom represent T1, T3, C, and T2

Multiple linear regression analysis provided rate estimates for each treatment group in the following model ($R^2 = 0.67$). The general equation produced was:

$$y = -391.309 + 24.931(x_1) + 3.027(x_1)(x_2) - 3.059(x_1)(x_3) + 0.737(x_1)(x_4)$$

where:

x_1 = time (d)

x_2 = Treatment 1

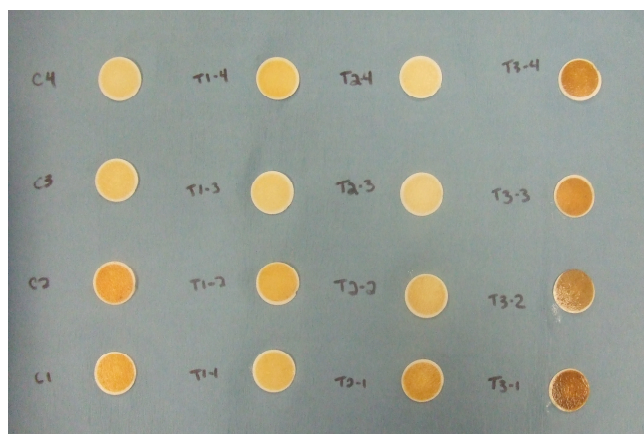
x_3 = Treatment 2

x_4 = Treatment 3

y = Fe concentration (mg/L)

The rate of Fe reduction for each treatment level corresponded to the equation, such that the slope of each regression line is the release of TDI in mg-Fe/L/d. The slope coefficient preceding each indicator variable is the change in rate in comparison to the control. The rate of Fe reduction after day 15 in treatment level one is significantly greater than that of the control, increasing the rate by 3.027 mg-Fe/L*d (p-value = 0.0053). Fe reduced after day 15 in treatment level two is significantly less than in the control, decreasing the rate by 3.059 mg-Fe/L*d (p-value = 0.0048). There was no significant difference between the Fe reduction rates of the control and treatment level three. The results for Fe reduction between the treatment levels was unexpected, as the lowest humic acid treatment level shows the greatest rate of Fe reduction, and the highest treatment level showed no effect on the rate of Fe reduction, while the second level of treatment has a negative effect on Fe reduction, in comparison to the control.

TDI data is inconclusive overall regarding the effects of humic acid on the rate of Fe release, due to the inconsistency of Fe released between treatment levels. Differences compared to results of previous studies (Nevin and Lovley, 2000; Jiang and Kappler, 2008; Rakshit et al., 2009) could be explained by sample filtration, specifically removal of Fe from the samples during the filtration process. Visual observations confirmed that red-brown particles, typical in Fe-rich soils, accumulated on filter papers (fig. A.19). Sample filtration was a possible source of the discrepancy seen between this study and previous studies for Fe reduction and humic acids and may suggest that Fe inclusion of suspended materials is necessary for complete quantification of Fe reduction in substrates.

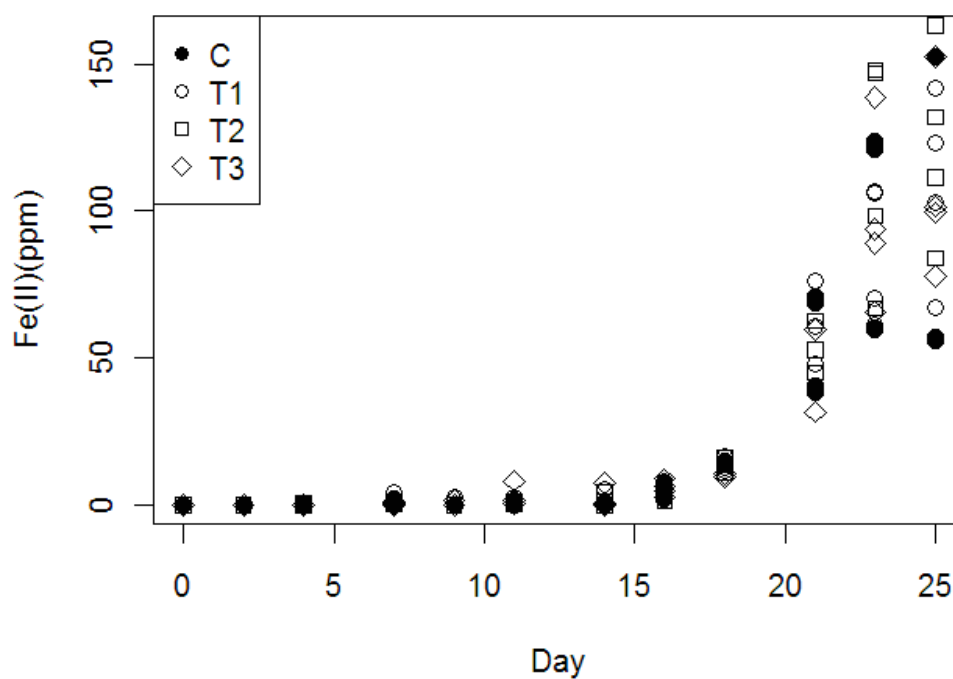


Egner and Pennington

Figure A.19 – Day-28 filter disks after filtration

Ferrous Iron

Fe^{2+} also increased during the study (fig. A.20a). Like TDI, The most rapid release of Fe^{2+} occurred during days 16-28 (fig. A.20b).



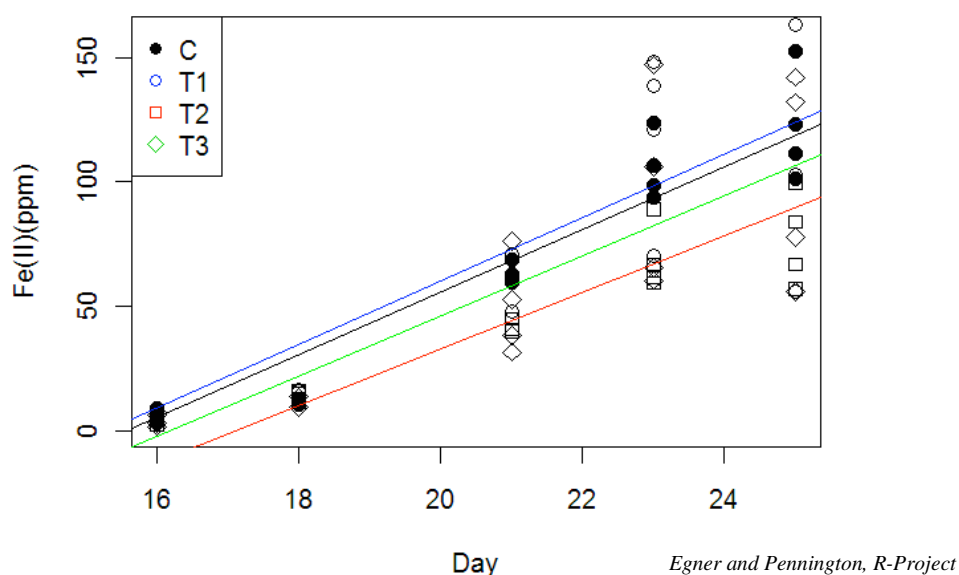


Figure A.20 - Fe^{2+} Concentrations for the entire study (a, above) and after day 15 with associated regression models (b, below); lines from top to bottom represent T1, C, T3, and T2

Multiple linear regression analysis provided rate estimates for each treatment group in the following model ($R^2 = 0.79$). The general equation produced was:

$$y = -194.476 + 12.515(x_1) + 0.217(x_1)(x_2) - 1.141(x_1)(x_3) - 0.476(x_1)(x_4)$$

where:

x_1 = time (d)

x_2 = Treatment 1

x_3 = Treatment 2

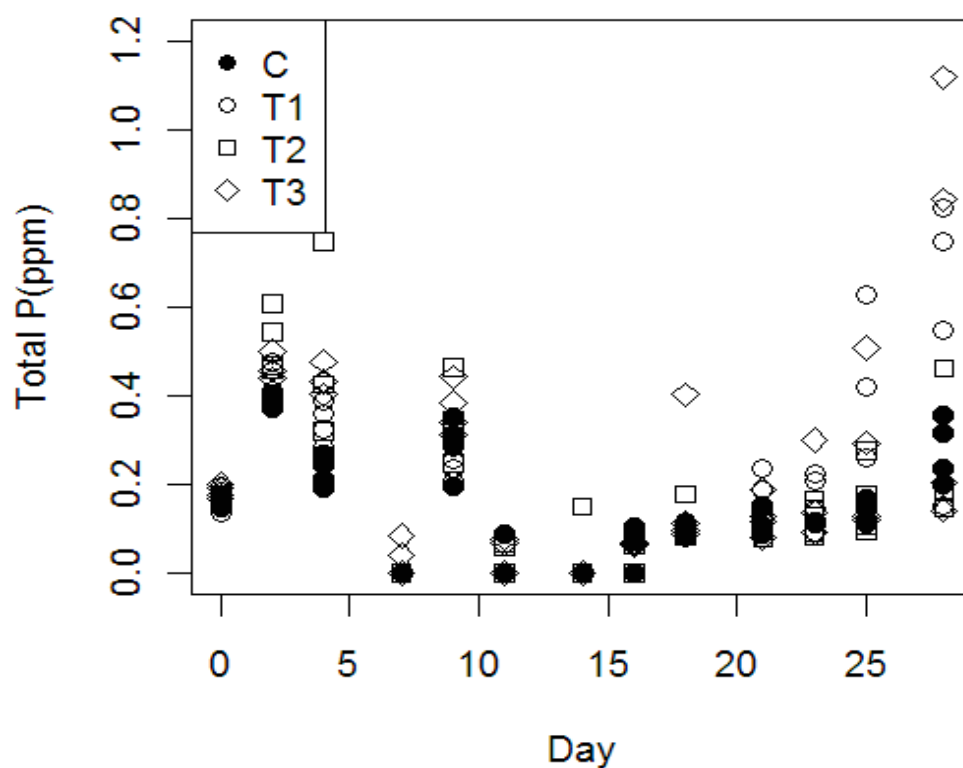
x_4 = Treatment 3

y = Fe^{2+} concentration (mg-Fe/L)

The Fe^{2+} release rate was not statistically different between the control and treatment levels one or three. The Fe^{2+} release rate for treatment level two was significantly less than the control, decreasing the rate of Fe reduction by 1.141 mg-Fe/L*d (p-value = 0.0021). This decrease in Fe reduction rate in treatment two was consistent with the results for TDI.

Total Dissolved Phosphorus

As expected, P concentrations increased during the study (fig. A.21), presumably due to corresponding reduction of Fe. The release of P into solution generally followed Fe reduction; however, unlike TDI or Fe^{2+} , TDP concentrations fluctuated widely from days 0 - 14. This decrease is possibly due to P re-adsorbing onto sorption sites remaining in the media. It is also possible, since very little Fe-reduction was observed before day 15, that these fluctuations in P concentration may be associated with ion exchange (outer-sphere interactions) and not specific adsorption (inner-sphere interactions). There does appear to be a positive relationship between time and P concentration after the additional carbon source was added on day 15 (fig. A.21b).



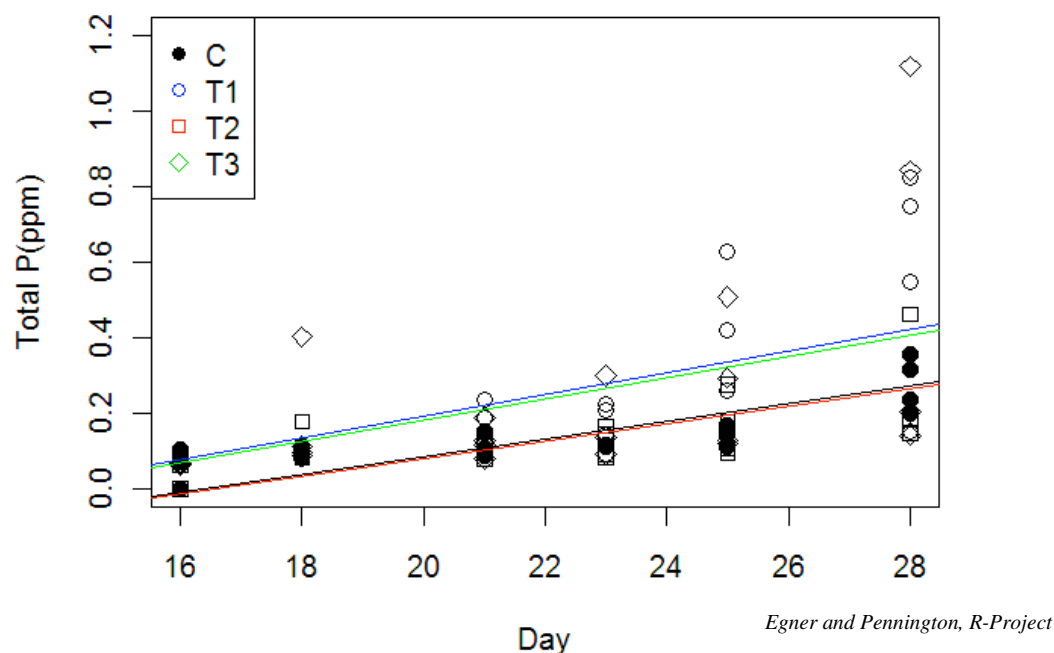


Figure A.21 - TDP Concentrations for the entire study (a, above) and after day 15 with associated regression models (b, below); lines from top to bottom represent T1, T3, C, and T2

Multiple linear regression analysis was performed on TDP after day 15 with time and treatment levels as predictor variables ($R^2 = 0.42$). The multiple regression model equation was:

$$y = -0.379 + 0.0232(x_1) + 0.00539(x_1)(x_2) - 0.000303(x_1)(x_3) + 0.00473(x_1)(x_4)$$

where:

x_1 = time (d)

x_2 = 1 for Treatment 1, 0 otherwise

x_3 = 1 for Treatment 2, 0 otherwise

x_4 = 1 for Treatment 3, 0 otherwise

y = P concentration (mg-P/L)

The rate of P release for treatment level one was significantly greater than the control, increasing the rate by 0.00539 mg-P/L*d (p-value = 0.00547). Similarly, rate of P release for treatment level three was significantly greater than the control, increasing the rate by 0.00473 mg-P/L*d (p-value = 0.0142). The rate of P release for treatment level two was not statistically different from the control. The significance increase in P release rate in treatments one and

three, but not in treatment two, follows approximately the results for Fe reduction above and indicates that the affect of humic acid on Fe reduction does carry over to P release. The possible effects of sample filtration discussed in relation to Fe could also have affected the results for P released due to associated with filtered material.

Dissolved Reactive Phosphate

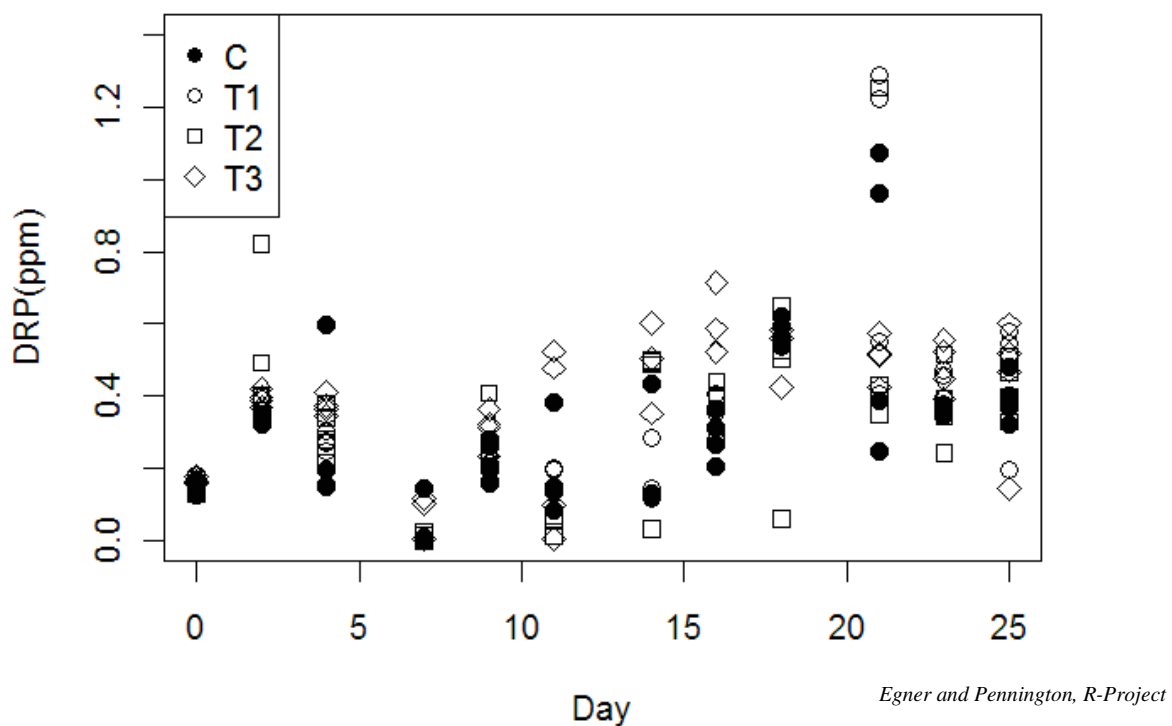


Figure A.22 - DRP concentrations during the humic acid study

In agreement with total P, the level of DRP fluctuated widely before day 15 (fig. A.22). However, the following days present confusing results as DRP concentrations continue to fluctuate. Unlike TDI, Fe^{2+} , and TDP, no significant relationships existed between DRP and time and/or treatments groups before or after the carbon source addition on day 15.

Total Organic Carbon

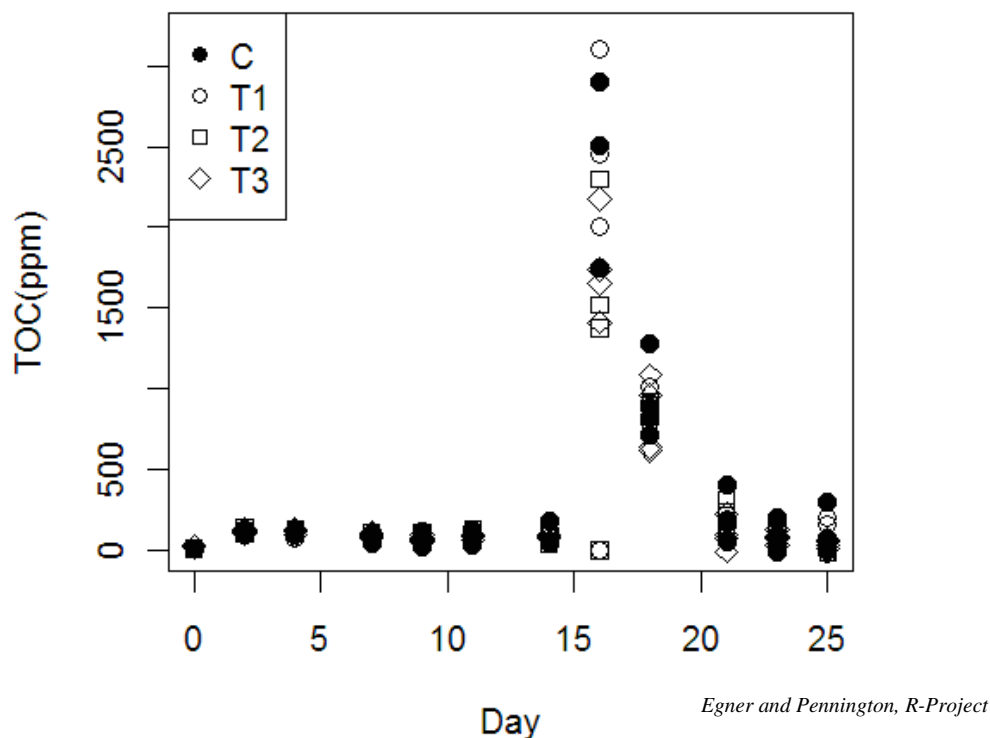


Figure A.23 - Total organic carbon concentrations during the humic acid study

Relatively little change occurs during the first 14 d of the experiment for TOC (fig. A.23). However, the addition of sugar on day 15 corresponds to a spike in TOC. Concentrations of TOC decrease relatively quickly in the next few sampling events. Microbial metabolism of the carbon source may explain this decrease and support the theory that the microorganism community was carbon-source limited during the first 14 d.

pH

Trends in pH were generally downward sloping (fig. A.24), with the greatest uniform decrease in pH occurring in the days following the addition of carbon on day 15. The trends in pH suggest that increased microbial growth decreased pH. A lack of microbial growth during days 5 and 15 may explain the steady or possibly upward sloping region during this time based on carbon limitation. The initial decrease in pH, while not accompanied by significant Fe

reduction, may explain the variation in TDP seen before day 15, since P adsorption is known to be dependent on pH (McBride, 1994).

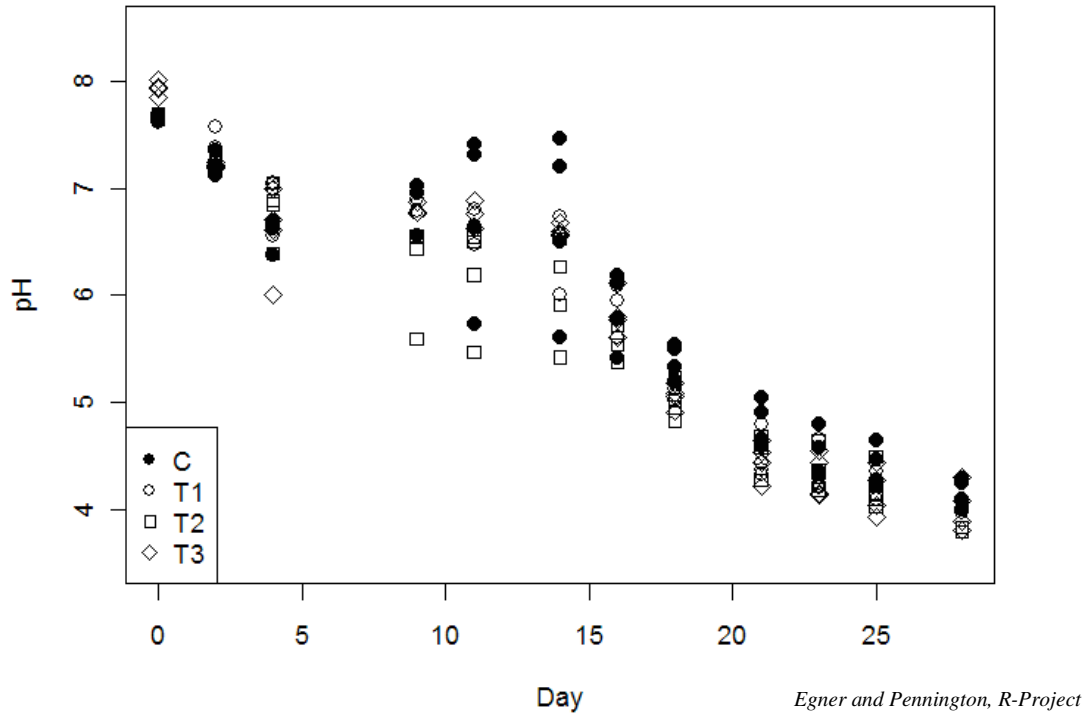


Figure A.24 - pH trends during the humic acid study

Conclusions

While this study provides no definitive conclusions regarding to the relationship between levels of humic acid and the rate of Fe reduction or P release, the results do suggest that the presence of humic acid does have some effect on Fe-reduction/p-release rate. TDI, Fe^{2+} , and TDP results all indicate some possible relationship with humic acid levels. The similar order observed in the magnitude of this effect between treatment levels across the various elements of interest (TDI, Fe^{2+} , and TDP) indicates that the whatever relationship exists between humic acid inclusion and Fe reduction is probably also present between humic acid inclusion and P release. However, with conflicting results for the treatment levels in TDI, Fe^{2+} , and TDP data, this study does not firmly support any conclusions about the correlation between humic acid level and the rates of Fe-reduction or P release.

Since neither Fe nor P concentrations reached an equilibrium position or peak level in this system, conclusions regarding the total capacity for Fe reduction or P release and any affect

of humic acid inclusion are not possible. Future research should include a longer sampling period to allow Fe and P levels to reach an equilibrium concentration so that conclusions regarding humic acid effects on total capacity of Fe reduction and P release are possible. Future experiments may also benefit from higher concentrations of P and by including sample analysis without filtration in the data set.

Acknowledgements

The authors would like to thank the National Science Foundation for providing support for students who worked on the project as a part of the NSF Research Experiences for Undergraduates grant. In addition, the authors would like to acknowledge assistance from many others in the Virginia Tech Biological Systems Engineering department.

References for Appendix A

- Aiken, G. R., D. M. McKnight, R. L. Wershaw, and P. MacCarthy. 1985. *Humic Substances in Soil, Sediment, and Water*. New York, NY: Wiley.
- Aldous, A. R., C. B. Craft, S. J. Carla, M. J. Barry, and B. B. Leslie. 2007. Soil phosphorus release from a restoration wetland, Upper Klamath Lake, Oregon. *Wetlands* 27 (4): 1025–1035.
- Arias, C. A., H. Brix, and N. H. Johansen. 2003. Phosphorus removal from municipal wastewater in an experimental two-stage vertical flow constructed wetland system equipped with a calcite filter. *Water Sci. Technol.* 48 (5): 51-58.
- Carleton, J. N., T. J. Grizzard, A. N. Godrej, H. E. Post, L. Lampe, and P. P. Kenel. 2000. Performance of a constructed wetlands in treating urban stormwater runoff. *Water Environ. Res.* 72 (3): 295-304.
- Cervantes, F. J., F. A. M. DeBok, D. T., A. J. M. Stams, G. Lettinga, and J. A. Field. 2002. Reduction of humic substances by halo-respiring, sulphate-reducing, and methanogenic microorganisms. *Environ. Microbiol.* 4 (1): 51-57.
- Chen, J., B. Gu, R. Royer, and W. Burgos. 2003. The roles of natural organic matter in chemical and microbial reduction of ferric iron. *The Science of the Total Environment* 307: 167-178.
- Chick, A. J., and D. S. Mitchell. 1995. A pilot study of vertical flow wetlands at Coffs Harbour, New South Wales, Australia. *Water Sci. Technol.* 32 (3): 103-109.
- Clesceri, L. S., A. E. Greenberg, and A. D. Eaton. 1999. *Standard Methods for the Evaluation of Water and Wastewater*. American Public Health Association.
- Coates, J. D., K. A. Cole, R. Charkraborty, S. M. O'Connor, and L. A. Achenbach. 2002. Diversity and ubiquity of bacteria capable of utilizing humic substances as electron donors for anaerobic respiration. *Appl. Environ. Microbiol.* 68 (5): 2445-2452.
- Comings, K. J., D. B. Booth, and R. R. Horner. 2000. Storm water pollutant removal by two wet ponds in Bellevue, Washington. *J. Environ. Eng.* 126 (4): 321-330.
- Correll, D. L. 1998. The role of phosphorus in the eutrophication of receiving waters: a review. *J. Environ. Qual.* 27: 261-266.

- Drizo, A., C. A. Frost, J. Grace, and K. A. Smith. 1999. Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Res.* 33 (17): 3595-3602.
- Farahbakhshazad, N., and G. M. Morrison. 2003. Phosphorus removal in a vertical upflow constructed wetland system. *Water Sci. Technol.* 48 (5): 43-50.
- Heal, K. V., K. E. Dobbie, E. Bozika, H. McHaffie, A. E. Simpson, and K. A. Smith. 2005. Enhancing phosphorus removal in constructed wetlands with ochre from mine drainage treatment. *Water Sci. Technol.* 51: 275-282.
- Hunt, W. F., and A. Wossink. 2003. The Economics of Structural Stormwater BMPs in North Carolina. UNC-WRRI-2003-344. Raleigh, NC: UNC-WRRI.
- Jiang, J., and A. Kappler. 2008. Kinetics of microbial and chemical reduction of humic substances: implications for electron shuttling. *Environ. Sci. Technol.* 42 (10): 3563-3569.
- Kadlec, R. H., and S. D. Wallace. 2009. *Treatment Wetlands*. Boca Raton, FL: CRC Press.
- Kappler, A., M. Benz, B. Schink, and A. Brune. 2004. Electron Shuttling via humic acids in microbial iron (III) reduction in a freshwater sediment. *FEMS Microbiol. Ecol.* 47: 85-92.
- Komatsu, E., T. Fukushima, and H. Shiraishi. 2006. Modeling of P-dynamics and algal growth in a stratified reservoir - mechanisms of P-cycle in water and interaction between overlying water and sediment. *Ecol. Model.* 197 (3/4): 331-349.
- Kostka, J. E., J. W. Stucki, K. H. Nealson, and J. Wu. 1996. Reduction of structural Fe(III) in smectite by a pure culture of shewanella putrefaciens strain MR-1. *Clays Clay Miner.* 44 (4): 522-529.
- Lovley, D. R. 1991. Dissimilatory Fe(III) and Mn(IV) Reduction. *Microbiological Reviews* 55 (2): 259-287.
- Lovley, D. R., J. L. Fraga, E. L. Blunt-Harris, L. A. Hayes, E. J. P. Phillips, and J. D. Coates. 1998. Humic Substances as a Mediator for Microbially Catalyzed Metal Reduction. *Acta Hydrochim. Hydrobiol.* 26: 152-157.
- Luu, Y., B. A. Ramsay, and J. A. Ramsay. 2003. Nitrilotriacetate stimulations of anaerobic Fe(III) respiration by mobilization of humic materials in soil. *Appl. Environ. Microbiol.* 69 (9): 5255-5262.
- Martinko, J. M., and M. T. Madigan. 2006. *Brock Biology of Microorganisms*. Pearson, Prentice Hall.

- Maynard, J. J., A. T. O'Geen, and R. A. Dahlgren. 2009. Spatial relationships of phosphorus sorption in a seasonally saturated constructed wetland soil. *Soil Sci. Soc. Am. J.* 73 (5): 1741-1753.
- McBride, M. B. 1994. *Environmental Chemistry of Soils*. New York, NY: Oxford.
- Method 8146 Iron, Ferrous. 2001. *Odyssey DR/2500 Spectrophotometer Procedure Manual*. Loveland, CO.: Hach Company.
- Namasivayam, C., A. Sakoda, and M. Suzuki. 2005. Removal of phosphate by adsorption onto oyster shell powder - kinetic studies. *J. Chem. Technol. Biotechnol.* 80 (3): 356-358.
- Naylor, S., J. Brisson, M. A. Labelle, A. Drizo, and Y. Comeau. 2003. Treatment of freshwater fish farm effluent using constructed wetlands: the role of plants and substrate. *Water Sci. Technol.* 48 (5): 215-222.
- Nevin, K. P., and D. R. Lovley. 2000. Potential for nonenzymatic reduction of Fe(III) via electron shuttling in subsurface sediments. *Environ. Sci. Technol.* 34: 2472-2478.
- Phosphate in Water and Seawater, Total P in Pursulfate or Kjeldahl Digests. 2008. *SEAL Autoanalyzer 3 High Resolution Operation Manual*. Norderstedt, Germany: Seal Analytical, Ltd.
- Prochaska, C. A., and A. I. Zouboulis. 2006. Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate. *Ecol. Eng.* 26 (3): 293-303.
- Rakshit, S., M. Uchimiya, and G. Sposito. 2009. Iron(III) bioreduction in soil in the presence of added humic substances. *Soil Sci. Soc. Am. J.* 73 (1): 65-71.
- Redshaw, C. J., C. F. Mason, C. R. Hayes, and R. D. Roberts. 1990. Factors influencing phosphate exchange across the sediment-water interface of eutrophic reservoirs. *Hydrobiologia* 192: 133-245.
- Scott, D. T., D. M. McKnight, E. L. Blunt-Harris, S. E. Kolesar, and D. R. Lovely. 1998. Quinone moieties act as electron acceptors in the reduction of humic substances by humic-reducing microorganisms. *Environ. Sci. Technol.* 32 (19): 2987-2989.
- Shang, C., J. W. B. Stewart, and P. M. Huang. 1992. pH effects on kinetics of adsorption of organic and inorganic phosphates by short-range ordered aluminum and iron precipitates. *Geoderma* 53 (1/2): 1-14.

- Shilton, A., S. Pratt, A. Drizo, B. Mahmood, S. Banker, L. Billings, S. Glenny, and D. Luo. 2005. 'Active' filters for upgrading phosphorus removal from pond systems. *Water Sci. Technol.* 51: 111-116.
- Steenson, F. J. 1994. *Humus Chemistry: Genesis, Composition, Reactions*. New York, NY: John Wiley & Sons.
- R Development Core Team. 2009. *R: A language and environment for statistical computing*. Vienna, Austria: R Foundation for Statistical Computing.
- USEPA. 2002. *Urban Stormwater BMP Performance Monitoring*. EPA 821-B-02-001. Washington, DC: US Environmental Protection Agency, Office of Water.
- Vymazal, J. 2005. Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. *Ecol. Eng.* 25 (5): 478-490.
- Westholm, L. J. 2006. Substrates for phosphorus removal - potential benefits for on-site wastewater treatment? *Water Res.* 40 (1): 23-36.
- Zhu, T., P. D. Jenssen, and T. Krogstad. 1997. Phosphorus sorption and chemical characteristics fo lightweight aggregates (LWA)-potential filter media in treatment wetlands *Water Sci. Technol.* 35 (5): 103-108.
- Zhu, T., T. Maehlum, P. D. Jenssen, and T. Krogstad. 2003. Phosphorus sorption characteristics of a light-weight aggregate. *Water Sci. Technol.* 48 (5): 93-100.

Appendix B: Comprehensive Materials and Methods

Variability in adsorptive phosphorus removal by structural stormwater best management practices

Based on copyright agreements, methods for this study are limited to those provided in chapter 2.

Facilitated Iron Reduction as a Means of Rejuvenating Phosphorus Removal Performance of Filtration Substrates

This study included two complementary experimental setups. The main portion of the study took place using flow-through wetland cells (FTWC) to investigate the central research questions with conditions approximating field installation. In addition, a set of batch reactor wetland cells (BRWC) were utilized to allow for testing of additional experimental factors, addressing additional research questions, and providing replicates of multiple factors for statistical power.

Flow-through wetland cells (FTWC)

Experimental Setup

The FTWC consisted of six, 20-L cylindrical containers filled with 25 kg of USDA-grade, medium sand media placed above a layer of limestone gravel (fig. 3.1). The sand media, sourced from a pit mine in New Castle, VA, had total Fe content between 0.2% and 0.7% by mass. The P-loading process was the main focus of another study in this research program and is described in detail by Rosenquist, et al. (In Review). The flow regime during P-loading was from bottom to top through the gravel layer then the sand media. The gravel layer served to distribute flow throughout the sand and promote piston-type flow. The filter media remained saturated throughout the loading process, but flow was intermittent and characterized by a 20-h flow period followed by "antecedent dry periods" of varying duration. Influent concentrations during P-loading were between 0.1 mg/L and 0.6 mg/L. The standard procedure for a given loading run with only before and after sampling included the following steps:

1. Turn on pump, making sure valve is set to recirculation only
2. Allow pump to cycle tank for 20-30 minutes to stir
3. Take a final pH reading for the previous cell and record
4. Take 3 samples from the top of the HT rising twice before taking the sample
5. Measure out the appropriate volume of stock solution and add to tank
6. Verify that the total volume in the tank is appropriate and add distilled water if evaporation has occurred
7. Take initial pH for the next cell and record

8. Switch hoses and clamps to prepare for flow into and out of the next cell
9. Allow 1-2 hours for tank to stir after addition of stock solution
10. Take 3 initial samples for the next cell by the same method as above
11. Move valve to open flow to the CHT
12. Set timer on pump and record start and stop times
13. After flow stabilizes, measure flow rate twice and record
14. Place samples in cooler for storage

During the reduction-reaction period conducted in this study, cells had opaque lids to minimize evaporation and algal growth.

Experimental Design

The FTWC included two treatment groups with three replications. For a control group (cells 1-3), no additional carbon-source was added, while the experimental treatment group (cells 4-6) involved exchanging the water in the FTWC with a sucrose solution carbon source by flow-through over a 2-h period. The final concentration of sucrose in the FTWC was between 100 mg/L and 150 mg/L, depending on the extent of the pore-water exchange.

Sampling and Sample Analysis Procedures

Sampling was from the standing water on top of each bucket in 20-mL volumes at the time of carbon addition and initially at one-day intervals. After temporal trends were established, sampling intervals increased to between 3-d and 7-d. Sampling included 306 samples overall from the six FTWC over a 253-d period. Gravimetric settling in the FTWC provided differentiation of dissolved constituents for sample analysis, as this portion of the study did not include sample filtration. All samples were analyzed by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) in accordance with EPA Method 200.7 (USEPA, 1994) to determine total dissolved phosphorus (TDP) and total dissolved iron (TDI) for each sample. Along with the above sampling schedule, a handheld pH meter (Hanna Instruments, Woonsocket, RI) provided pH measurements and a handheld dissolved oxygen meter (YSI Incorporated, Yellow Spring, OH) provided dissolved oxygen measurements. Dissolved oxygen served as a surrogate for estimating gross changes in redox potential. Periodic calibration of both the pH and dissolved oxygen instruments followed in accordance with the manufacturer's instructions.

Data Analysis

Graphical analysis included the following variables: 1) pH, 2) dissolved oxygen, 3) TDP, 4) TDI, and 5) TDP/TDI correlation. After a distinct break in the TDP/TDI correlation appeared, including two linear regions of differing slope, a least-squares breakpoint analysis determined the threshold concentration between the two linear regions. This procedure preceded a segmented linear regression analysis using a model with an indicator variable for the breakpoint between the two slope regions. This process tested for a correlation between Fe reduction and release of previously adsorbed P into solution, and for differences in the slope observed in the two regions. Lastly, a comparison between the final concentrations in the carbon-treated FTWC and the influent concentrations used to load the FTWC enabled concentration comparison and estimates the percentage of previously adsorbed P released. Statistical analyses were performed with software from the R-project (R Development Core Team, 2009). For data values below the analytical limits of the instrument, the analytical limit served for calculations.

Batch-reactor wetland cells (BRWC)

Experimental Setup

The BRWC consisted of 36, 250-mL NalgeneTM containers containing 100 g of USDA-grade-medium sand of the same type described under the FTWC setup. The addition of 90 mL of distilled water and 10 mL of 350-mg/L stock P solution enabled the saturation of the sand in each BRWC was saturated with P. The BRWC were agitated for 72 h and dewatered by vacuum filtration. After filtration, the glass-fiber filter used became part of the dewatered sample to conserve P in the cell.

Experimental Design

Once saturated with P, the 36 BRWC became four experimental groups based on the carbon source provided. These carbon sources included: 1) distilled water (control), 2) 250 g/L sucrose solution, 3) surface water grab sample from a local retention pond (with slight P-contribution accounted for), and 4) a 50% combination of sucrose solution and surface-water sample. These groups subdivided into one-day, two-day, and three-day reaction times. There were three replications for each carbon-source and reaction-time combination. Each BRWC had

100 mL of the designated carbon source added gravimetrically. Each BRWC received a cap, 30 s of agitation, and storage in a dark, climate-controlled space.

Sampling and Sample Analysis Procedures

After the dewatering process in the BRWC, gravimetric analysis enabled estimation of the extent of dewatering and together with sample taken for TDP analysis provided an estimate of un-sorbed P remaining. After the designated reaction time, a sample taken from each BRWC by pipetting from the standing water on top of the substrate and filtering through 0.45- μm glass-fiber filter provided for analysis. Additional samples taken in the same manner from three BRWC of each carbon-source type after 20-d and 36-d reaction times provided for extended monitoring. One filtered sample and one filtrate weight was lost in processing resulting in two lost data points from the set. The remaining 59 samples were analyzed by ICP-AES in accordance with EPA Method 200.7 (USEPA, 1994) to determine TPD and TDI for each sample.

Data Analysis

Three calculated values for each of the 36 BRWC provided for further analysis: 1) the mass of P initially adsorbed, 2) the mass of P released at each time interval, and 3) the percentage of initially-adsorbed P released at each time interval. For data values below the analytical limits of the instrument, the analytical limit served for calculations. Due to a lack of normality among residuals, a Kruskal non-parametric test applied to the data tested for differences between means with pairwise multiple comparisons with a Bonferroni correction factor to determine which means were different. Statistical analyses were again performed with software from the R-project (R Development Core Team, 2009).

The Urban Wetland Filter: Field Results in the Development of a Renewable Practice for Managing Phosphorus in Stormwater Runoff from High Land-Value Areas

Six, rectangular, plastic containers (38 cm tall x 46 cm L x 33 cm W) contained the scaled wetland cells (fig. 4.1). Cell construction began with 8 cm of limestone gravel containing a slotted section of plastic pipe. This pipe connected to a bulkhead fitting on one end of the container to function as the water outlet for the cell. Above the gravel, 8.5 L of substrate including USDA grade medium sand (0.2% - 0.7% Fe by mass) sourced from Newcastle, VA and in some cases a cast-iron filing waste product sourced from a local machining operation. The water inlet and flow control structure was located above the wetland substrate and connected through another bulkhead fitting in the opposite end of the container from the outlet. Cells were set up with downward, vertical flow. Between 5 cm and 6 cm of head remained above the substrate due to a constant-head float valve (Hudson Valve Company, Bakersville, CA) that restricted flow to a single direction.

A siphon system fed stormwater simultaneously to two wetland cells from a stormwater retention pond located on the Virginia Tech campus (fig. 4.2). A section of slotted well screen (slot width of 0.5 mm) pre-filtered the water to exclude trash and detritus. The retention pond used in this study drains several areas that are likely contributors of P through runoff including a dairy farm, a recently active construction area with associated erosion of high-P sediments, and heavily fertilized turf areas.

Experimental Design

This study had two experimental factors, sand-only versus iron/sand substrates and pre-rejuvenation versus post-rejuvenation runs of the wetland cells. The iron/sand cells, included sand thoroughly mixed with cast-iron filings at a 2:1 volumetric ratio, which corresponded roughly to a 1:1 mass ratio. There were three replicates of each type of cell, but only six cells in total since a given cell provided both a pre- and post-rejuvenation filtration run (fig. 4.3). The rejuvenation cycle consisted of adding 1000 g of sucrose sugar to each of the saturated cells without flow to initiate Fe-reduction, then storing them for 50 days to promote the release of adsorbed P. Cells were stored in a climate-controlled space, which maintained a temperature

between 18°C and 26°C. Each 48-h filtration run included one sand-only cell and one iron/sand cell run simultaneously. Three of these runs occurred before and three occurred after the rejuvenation cycle.

Sampling and Sample Analysis

Water sampling during each run involved three automated samplers (ISCO 3700, Lincoln, NE), one located at the inlet to both cells and one located at each outlet. Preparation of automated samplers included rinsing of lines with approximately 5L of distilled water to prevent contamination. During each filtration run, the automated sampler gathered 24 multiplexed samples consisting of four, 200 mL samples taken at 30-min intervals combined to form each multiplexed sample. The result of tests runs with longer sampling intervals (4h or more) that did not sufficiently capture trending in performance led to the 30-min sampling intervals. During one of the six runs, specifically the second post-rejuvenation run, automated sampler failure resulted in 12 missing inlet samples. A triplicate grab sample, taken at the end of the run and interpolated with the last sample taken by the automated sampler estimated the inlet concentration during this period. A pH measurement taken from each of the 24 sample bottles after the run by a handheld pH meter (Hanna Instruments, Woonsocket, RI) tracked any changes in pH during the run. An additional sample bottle positioned at each outlet, received effluent from the cells and held 1000mL of continuously overflowing effluent for collection by two of the automated samplers. The third automated sampler collected influent samples from the inlet structure behind the float valves. Volumetric capture involving a graduate cylinder and stopwatch provided flow rate measurements for the beginning and the end of each filtration run (Table 1). Interpolation of these two values provided flow rate estimates for each sampling time during a particular run.

Grab samples, taken from the top of the cells at day 0, day 33, and day 50 captured the changes occurring during the rejuvenation cycle. Sampling on day 50 included a composite sample in addition to the grab sample and a pH measurement. A volume measurement of the water resident in the cells when they were gravity drained allowed for mass calculations. The rejuvenation cycle did not include any cell rinsing prior to the post-rejuvenation filtration runs. After some consideration of whether the foam in the iron/sand cells should be part of the removed liquid or part of the retained solid, it remained as part of the retained solid with only a

small sampled removed for possible further analysis. However, additional foaming did occur in the drain bucket.

Sample preparation involved digestion of all samples by the ascorbic acid method (Stream_Team 2008). A colorimetric autoanalyzer (SEAL Analytical, Mequon, WI) used in accordance with standard operating procedures (Stream_Team 2008) provided analysis for total phosphorus (TP) from six filtration runs. Quality control measures for the analytical runs on the colorimetric autoanalyzer included lab blanks, duplicates on 10% of samples, and spikes on 5% of samples. Based on concerns of color interference, inductively coupled plasma atomic emission spectroscopy (ICP-AES) conducted according to EPA method 200.7 (USEPA 1994) provided analysis of TP and total iron (TI) for samples from the rejuvenation cycle.

Data Analysis

Filtration Runs

Visual analysis included graphing observed TP and pH trends for all filtration runs. For each 2-hr period in the filtration runs, a P-mass removal rate (mg/h) calculation drew on the associated influent concentration, effluent concentration, and flow rate data. Because of a lack of normality among residuals (Shapiro-Wilkes Test, p-value < 2.2E-16) and the overall likelihood of non-normality in environmental sampling the Kruskal-Wallis Test was the best choice to test for any differences both between treatment types including all cells and within treatment groups between replicate cells. Pairwise analysis with a bonferroni correction factor to adjust p-values followed the initial test to determine which groups were different from each other. A bootstrap method (Chernick 1999) with 10^6 iterations provided confidence intervals for P-mass removal rates and P-mass in solution during rejuvenation. Software from R-project (R Development Core Team 2009) provided for all statistical analyses in this study.

Rejuvenation Process

A linear regression model using an indicator variable for substrate type tested the relationship between Fe and P in solution for to the rejuvenation data. A significant relationship between these two variables supported the Fe-reduction process as a means to release adsorbed P from CW substrate. Pairwise analysis with a bonferroni correction factor, using P-mass in solution as an estimate of the amount of P released through rejuvenation of the substrate, enabled

comparisons between substrate types and sampling times during rejuvenation. Confidence intervals gathered by the bootstrap method cited above, provided additional comparison between substrate types and sampling time and between estimated rejuvenation totals and estimated filtration totals. Pairwise analysis with a bonferroni correction factor also provided testing for significant differences in pH between rejuvenation and filtration.

Modeling Variability in Removal

Multivariate linear regression with backward selection was applied to the removal rate data to test for correlations with suspected variables including time, Effluent pH, influent concentration, and the maximum previous effluent concentration at each point during the run (since this concentration should represent the existing substrate/solution equilibrium point). Effluent pH data were only included for analysis of pre-rejuvenation runs since the relationship between pH and removal was confounded in post-rejuvenation runs by carryover from the rejuvenation process. A bonferroni correction factor provided adjustment to the p-value to account for model application to subsets of the data.

Quality Control

Use of the pH meter in this study included periodical calibration in accordance with manufacturer specifications. Because TP and not TDP was used to measure differences in P removal (due to sample collection and preservation requirements), measurements of total suspended solids (TSS) ensured that any differences in removal between cells could not be attributed to differences in physical removal processes. Measurements of TSS included a randomly selected group of five inlet, five sand-only effluent, and five iron/sand effluent samples. Mean TSS removals for the cells were was 3.44 mg/L (sand-only) and 1.76 mg/L (iron/sand). Analysis indicated no significant difference between mean TSS removal in the two substrate types (p-value = 0.15), thereby supporting the assumption of similar physical removal properties in the two substrate types. Visual analysis of the filtered solids indicates that some of the solid mass filtered from the iron/sand effluent may be Fe exported from the cells. Another quality control measure was the inclusion of a known standard to compare results for TP between the two analytical instrument types. Means for the standard analyzed in three separate runs on each instrument were 0.77 mg/L (ICP-AES) and 0.75 mg/L (colorimetric autoanalyzer). Analysis indicated no significant difference between these means (p-value = 0.16). A test of the

sampling bottles ensured that variations in sample holding time were not affecting measured concentrations. This test revealed no significant correlation between time and TP in samples including influent, sand-only effluent, and iron/sand effluent held in bottles up to 9 days (all p-values ≥ 0.26). To eliminate interference caused by carryover from the rejuvenation process, data management included omission of the first two data points for all post-rejuvenation cells from the removal rate comparison between treatment groups and the multivariate regression analysis for variability in removal rate.

Adsorption Isotherm Experiment

This supporting experiment was conducted in a soil science department laboratory, closely following the methods described by (Arias et al., 2001). The dependent variable was final equilibrium concentration of phosphorus in the water, while the independent variable was the initial concentration of phosphorus in the water. The sand used (fig. 1) was a sample from the bulk sand in the experiments described above that not been used in a previous experiment. Approximately 10g of sand started each of the 200mL plastic containers, with a total fill volume adding water up to 200mL. The experiment included fourteen containers, with two at each concentration including 5, 10, 15, 20, 25, 30, and 35 mg-P/L. A stir plate provided agitation for approximately 24 hours to mix the sand and water. Then containers were all titrated to a pH of 7, with the volume of acid or base required recorded. After another 24-h stir plate period to reach equilibrium, samples taken from each of the containers and filtered through a 0.45-micron filter provided for analysis. ICP-AAS provided for analysis of samples for dissolved phosphorus. Calculations for the mass of phosphorus adsorbed included the initial and final concentrations, along with the specific amounts of sand and water added to each container. The data collected and applied to the Langmuir isotherm model, shown as equation 1, determined a theoretical maximum for adsorption to this substrate.

$$C/q = 1/kb + C/b \quad (1)$$

Where C is the equilibrium concentration of adsorptive, q is the adsorbed quantity, k is the rate constant, and b is the adsorption maximum. An estimate of the percentage of the maximum sorption capacity based on the isotherm curve produced and the maximum influent concentrations utilized in bench-scale testing predicts that cumulative sorption will only reach 10% of the theoretical maximum.



FROEHLING & ROBERTSON, INC.
 GEOTECHNICAL • ENVIRONMENTAL • MATERIALS
 ENGINEERS • LABORATORIES
 "OVER ONE HUNDRED YEARS OF SERVICE"
 1734 Selbel Drive, N.E. • Roanoke, Virginia 24012
 PHONE: (540) 344-7939 • FAX: (540) 344-3657

LABORATORY REPORT

Deborah Lindsey
 Castle Sands Co
 2832 Fairway Forest Dr
 Salem VA 24153

Report Date: 09/13/07
 Purchase Order #: AMEX.Lindsey.DL100
 Fax Number: 540-864-5113

Record No: C62-193T

REPORT OF LABORATORY TEST FOR LIGHT CASTLE SAND

Castle Sand Company
 Route 2 Box 737 Star Route 609
 New Castle, Virginia 24127

Subject: Light Castle Sand
 Laboratory Testing Services

Attention: David G. Lindsey, Jr.

F&R Lab No.: 79031

Gentlemen:

The following tables summarize the aggregate testing completed by our office on the above referenced project. This work was performed according to the standards referenced below.

Sieve Analysis of Coarse and Fine Aggregates (ASTM C-136)

Sieve Size	Individual Weight (g)	Individual % Retained	Accumulative Weight (g)	Accumulative % Retained	Percent Passing
#4	0.0	0.0	0.0	0.0	100.0
#8	2.4	0.3	2.4	0.3	99.7
#16	9.3	1.2	11.7	1.5	98.5
#30	65.1	8.6	76.8	10.1	89.9
#50	528.4	69.6	605.2	79.7	20.3
#100	140.3	18.5	745.5	98.2	1.8
#200	7.7	1.0	753.2	99.2	0.8
Pan	5.6	0.7	758.8	99.9	0.1

Magnesium Sulfate Soundness Test (ASTM C-88)

Sieve Size	Original % Retained	Weight of Sample Before	Weight of Sample After	% Passing Actual % Loss	Weighted Average Corrected % Loss	
#16	#30	8.6	100	94.8	5.20	0.45
#30	#50	69.6	100	95.7	4.30	2.99
Total % Loss					3.44	

Authorized Release of Data

Pat DeLozier
 Pat DeLozier
 Production Coordinator

PD/yb A1 This report shall not be reproduced, except in full, without the written approval of the laboratory. Page 1 of 1
 Custom reports are available upon request; additional charges may apply.

HEADQUARTERS: 3015 DUNBARTON ROAD • BOX 27524 • RICHMOND, VA 23261-7524
 TELEPHONE (804) 264-2701 • FAX (804) 264-1302 • www.F&R.com

BRANCHES: ASHEVILLE, NC • BALTIMORE, MD • CHARLOTTE, NC • CHESAPEAKE, VA
 CROZET, VA • FAYETTEVILLE, NC • FREDERICKSBURG, VA
 GREENVILLE, SC • RALEIGH, NC • ROANOKE, VA • STEUBENS, VA

Mailing: P.O. Box 51610 | Knoxville, TN 37950-1610
 Toll Free: 1.877.449.8797

Shipping: 2323 Sycamore Dr. | Knoxville, TN 37921-1700
 Fax: 865.546.7209

www.galbraith.com

Provided by Castle Sands Company, fair use

Figure B.1 – Chemical and physical properties reports for sand sourced from New Castle, VA

Retention Pond Survey

Four ponds in the local Blacksburg, VA area (fig. 2) were studied to assess the typical chemical conditions of a retention pond. Properties measured included depth at sampling locations, pH and phosphorus concentrations.

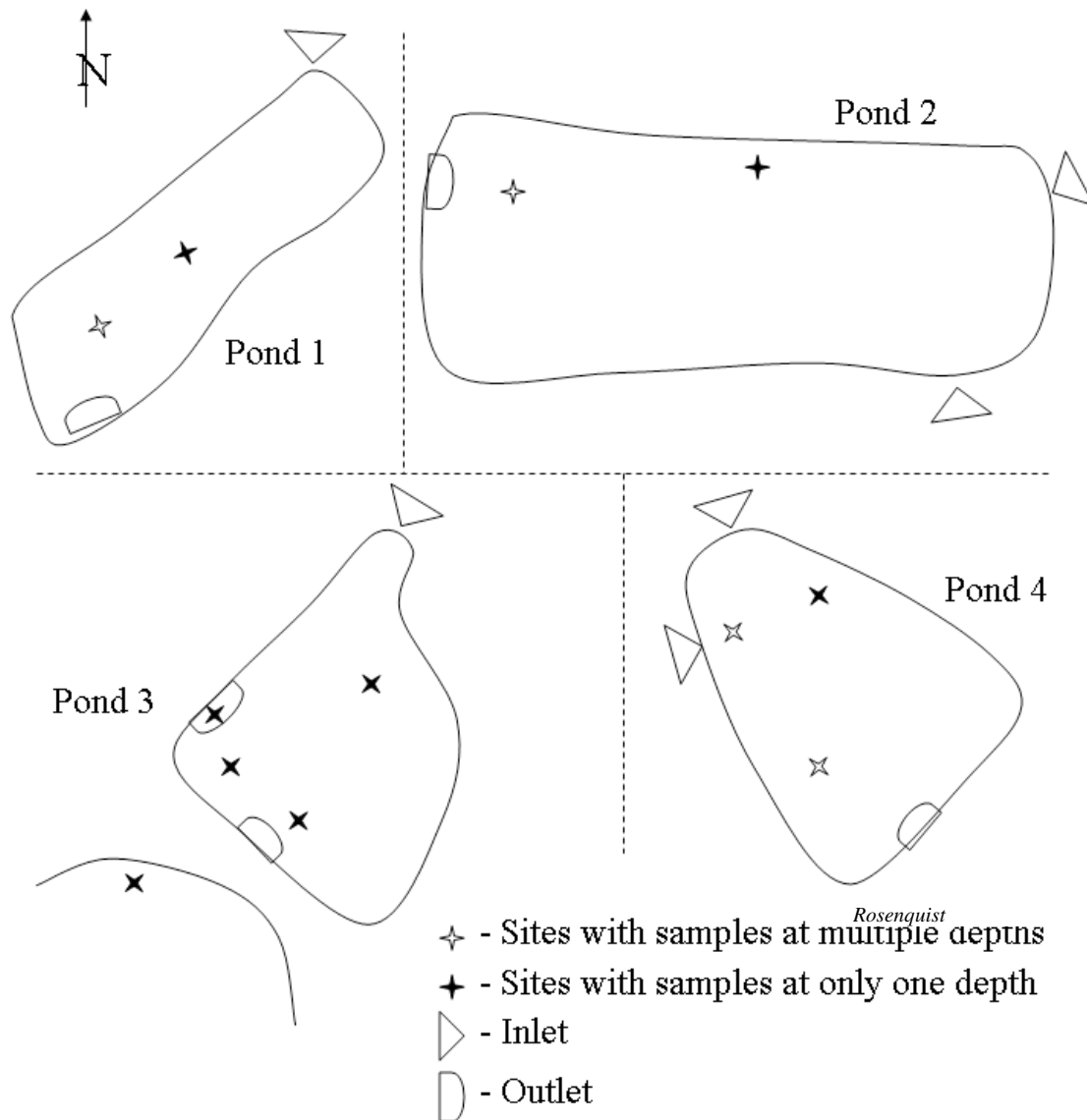


Figure B.2 – Location and number of samples in the four retention ponds included in this study

Re-oxidation/Precipitation Experiment

The purpose of this supporting experiment was to determine the feasibility of precipitating Fe-P solids from the water contained in post-rejuvenation cells that contained high concentrations of dissolved iron and phosphorus. Theoretically, aeration of the samples (presumed to be anaerobic) might initiate precipitation based on redox potential. Approximately 60mL of water removed from each of three rejuvenation cells into beakers provided sample for this experiment. Preparation for all glassware and the air hose used in this experiment included acid washing to prevent contamination and DI rinsing between samples. Unfiltered and filtered 20-mL subsamples provided controls for the experiment. After aeration of the remaining 20-mL of sample in a graduated cylinder with a small aquarium-style bubbler for 1.5 h there was no indication of precipitation. This lack of precipitation indicated that no further sample analysis was necessary to confirm the lack of effectiveness of this method for precipitating Fe-P solids. An explanation proposed for the lack of success was the possible organic complexation of Fe and/or P, making them resistant to oxidation. Oxidation may be possible with a stronger oxidizer, but the practicality of using a chemical oxidizer at full-scale is questionable.

Appendix C: Primary Data Sets

Variability in Adsorptive Phosphorus Removal by Structural Stormwater Best Management Practices

Cell	Run	Time	Start Date		Stop Date		pH	Flow Rates				Concentration Data																						
			Time	Date	Time	Date		Rest Time	Method	Initial	Final	Tank Volume (L)	Test Volume(L)	Rate 1(L/min)	Rate 2 (L/min)	Added SS (mg)	SS (mg/L)	0	5	10	15	20												
1	1	4:00 PM	1/18/2008	12:00 PM	1/19/2008		Hach		218	5	0.179	0.179							0.15	0.17	0.15	0.31	0.4	0.31	0.34	0.33	0.26	0.17	0.24	0.26	0.06	0.06	0.07	
2	1	3:45 PM	1/21/2008	11:45 AM	1/22/2008		Hach		218	0.5	0.227	0.227							0.20	0.18	0.20	0.46	0.43	0.48	0.38	0.37	0.44	0.40	0.36	0.42	0.10	0.09	0.09	
3	1	4:45 PM	1/24/2008	12:45 PM	1/25/2008		Hach		218	0.5	0.194	0.203							0.14	0.10	0.11	0.22	0.21	0.24	0.20	0.16	0.34	0.19	0.17	0.16	0.07	0.04	0.03	
4	1	4:45 PM	1/25/2008	12:45 PM	1/26/2008		Hach		218	0.5	0.207	0.222							0.18	0.18	0.15	0.30	0.46	0.51	0.32	0.35	0.38	0.33	0.3	0.37	0.08	0.07	0.08	
5	1	3:30 PM	1/27/2008	11:30 AM	1/28/2008		Hach		218	0.5	0.188	0.200							0.09	0.16	0.13	0.35	0.33	0.32	0.33	0.31	0.27	0.59	0.22	0.2	0.07	0.06	0.06	
6	1	5:15 PM	1/28/2008	1:15 PM	1/29/2008		Hach		218	0.5	0.166	0.168							0.15	0.14	0.14	0.35	0.37	0.37	0.35	0.35	0.34	0.26	0.25	0.32	0.07	0.07	0.09	
1	2	5:00 PM	1/29/2008	1:00 PM	1/30/2008	10	Hach		218	0.5	0.194	0.188							0.12	0.13	0.13	0.34	0.31	0.34	0.26	0.26	0.28	0.20	0.21	0.21	0.05	0.05	0.07	
2	2	4:45 PM	1/31/2008	12:45 PM	2/1/2008	9	Hach		218	0.5	0.201	0.201							0.19	0.17	0.18	0.47	0.47	0.46	0.41	0.42	0.44	0.30	0.36	0.28	0.10	0.09	0.09	
3	2	3:30 PM	2/4/2008	11:30 AM	2/5/2008	10	Hach		218	0.5	0.194	0.192							0.11	0.12	0.15	0.54	0.3	0.33	0.29	0.27	0.31	0.21	0.22	0.25	0.06	0.07	0.07	
4	2	2:30 PM	2/6/2008	10:30 AM	2/7/2008	11	Hach		218	0.5	0.210	0.204							0.13	0.14	0.15	0.31	0.32	0.38	0.23	0.25	0.31	0.21	0.32	0.33	0.07	0.06	0.06	
5	2	7:00 PM	2/7/2008	3:00 PM	2/8/2008	10	Hach		218	0.5	0.207	0.208							0.15	0.22	0.23	0.44	0.43	0.54	0.42	0.35	0.32	0.35	0.51	0.42	0.09	0.08	0.06	
6	2	2:15 PM	2/11/2008	10:15 AM	2/12/2008	13	Hach		218	0.5	0.169	0.169							0.17	0.15	0.16	0.45	0.35	0.78	0.47	0.45	0.48	0.37	0.31	0.5	0.11	0.16	0.09	
1	3	2:10 PM	2/18/2008	10:10 AM	2/19/2008	19	Hach		218	0.5	0.227	0.227							0.12	0.13	0.11	0.34	0.34	0.3	0.35	0.34	0.25	0.26	0.27	0.23	0.07	0.11	0.09	
2	3	3:00 PM	2/20/2008	11:00 AM	2/21/2008	19	ICP		218	0.5	0.197	0.197							0.09	0.09	0.11	0.27	0.30	0.26	0.24	0.17	0.27	0.20	0.23	0.19	0.03	0.04	0.04	
3	3	5:45 PM	2/20/2008	1:45 PM	2/21/2008	15	ICP		218	0.5	0.173	0.178							0.11	0.14	0.14	0.39	0.36	0.34	0.24	0.33	0.31	0.21	0.22	0.22	0.07	0.06	0.06	
4	3	4:00 PM	2/25/2008	12:00 PM	2/26/2008	18	Hach		218	0.5	0.196	0.197							0.13	0.12	0.11	0.29	0.39	0.43	0.34	0.3	0.32	0.32	0.28	0.27	0.08	0.06	0.07	
5	3	4:15 PM	2/28/2008	12:15 PM	2/29/2008	20	ICP	7.8	7.3	218	0.5	0.190	0.197							0.12	0.13	0.13	0.29	0.29	0.32	0.26	0.25	0.25	0.18	0.15	0.16	0.06	0.05	0.05
6	3	2:00 PM	3/3/2008	10:00 AM	3/4/2008	20	ICP	7.1	7.2	218	0.5	0.170	0.165							0.09	0.09	0.09	0.22	0.23	0.21	0.19	0.20	0.19	0.13	0.17	0.17	0.04	0.04	0.04
1	4	2:00 PM	3/4/2008	10:00 AM	3/5/2008	14	ICP	7.1	7.0	218	0.5	0.201	0.214							0.07	0.09	0.09	0.18	0.20	0.22	0.14	0.16	0.19	0.06	0.16	0.08	0.02	0.04	0.04
2	4	2:30 PM	3/5/2008	10:30 AM	3/6/2008	13	ICP	6.4	7.3	218	0.5	0.191	0.185	65.00	744.48					0.10	0.11	0.06	0.18	0.25	0.23	0.18	0.16	0.10	0.07	0.13	0.14	0.02	0.02	0.02
3	4	2:20 PM	3/6/2008	10:20 AM	3/7/2008	14	ICP	6.9	7.2	218	0.5	0.179	0.173	60.00	744.48					0.10	0.10	0.08	0.21	0.23	0.26	0.17	0.15	0.16	0.12	0.17	0.18	0.03	0.04	0.05
4	4	11:50 AM	3/7/2008	7:50 AM	3/8/2008	10	ICP	7.6	7.4	218	0.5	0.197	0.199	70.60	744.48					0.11	0.13	0.05	0.22	0.23	0.28	0.15	0.2	0.18	0.14	0.15	0.05	0.04	0.04	0.04
5	4	2:20 PM	3/9/2008	10:20 AM	3/10/2008	9	ICP	7.6	7.6	218	0.5	0.179	0.182	59.00	744.48					0.05	0.10	0.06	0.31	0.23	0.22	0.29	0.19	0.21	0.15	0.18	0.16	0.04	0.03	0.00
6	4	4:05 PM	3/10/2008	12:05 PM	3/11/2008	6	ICP	7.2	7.2	218	0.5	0.157	0.165	63.80	744.48					0.11	0.11	0.11	0.29	0.29	0.29	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
1	5	3:45 PM	3/13/2008	11:45 AM	3/14/2008	8	ICP	7.4	7.4	218	0.5	0.180	0.155	66.50	744.48					0.12	0.14	0.12	0.27	0.3	0.28	0.21	0.23	0.25	0.14	0.18	0.2	0.05	0.05	0.06
2	5	4:02 PM	3/17/2008	12:02 PM	3/18/2008	11	ICP	7.8	7.8	218	0.5	0.191	0.197	70.90	744.48					0.11	0.13	0.13	0.27	0.28	0.29	0.19	0.22	0.19	0.16	0.16	0.17	0.04	0.04	0.04
3	5	5:30 PM	3/19/2008	1:30 PM	3/20/2008	12	ICP	7.5	7.8	218	0.5	0.169	0.169	76.00	744.48					0.19	0.14	0.13	0.29	0.29	0.29	0.28	0.21	0.24	0.25	0.16	0.17	0.17	0.04	0.04
4	5	3:55 PM	3/24/2008	11:55 AM	3/25/2008	16	ICP	6.8	7.1	208	0.5	0.190	0.194	69.50	744.48					0.12	0.13	0.13	0.26	0.26	0.26	0.19	0.19	0.2	0.13	0.15	0.14	0.03	0.04	0.04
5	5	3:42 PM	3/25/2008	11:42 AM	3/26/2008	15	ICP	7.1	7.6	208	0.5	0.191	0.194	74.90	744.48					0.13	0.13	0.13	0.12	0.25	0.29	0.27	0.2	0.2	0.21	0.15	0.17	0.16	0.03	0.04
6	5	4:30 PM	3/27/2008	12:30 PM	3/28/2008	16	ICP	7.5	7.6	218	0.5	0.179	0.164	45.60	744.48					0.08	0.08	0.08	0.09	0.21	0.21	0.22	0.16	0.16	0.14	0.14	0.14	0.03	0.04	0.03
1	6	3:25 PM	4/7/2008	11:25 AM	4/8/2008	24	ICP	7.7	7.7	218	0.5	0.152	0.151	70.40	1202.31					0.16	0.17	0.17	0.39	0.42	0.42	0.31	0.34	0.33	0.26	0.26	0.27	0.07	0.08	0.07
2	6	4:40 PM	4/10/2008	12:40 PM	4/11/2008	21	ICP	7.5	7.8	218	0.5	0.203	0.193	73.20	1202.31					0.21	0.24	0.21	0.44	0.48	0.47	0.34	0.34	0.37	0.28	0.28	0.27	0.06	0.06	0.09
3	6	3:40 PM	4/14/2008	11:40 AM	4/15/2008	25	ICP	7.9	7.3	218	0.5	0.190	0.132	71.80	1202.31					0.20	0.21	0.21	0.51	0.51	0.5	0.42	0.48	0.43	0.36	0.38	0.37	0.09	0.10	0.09
4	6	4:55 PM	4/17/2008	12:55 PM	4/18/2008	23	ICP	7.8	7.5	218	0.5	0.181	0.188	63.20	1202.31					0.21	0.22	0.22	0.63	0.69	0.68							0.07	0.07	0.08
5	6	3:40 PM	4/21/2008	11:40 AM	4/22/2008	26	ICP	7.2	7.6	218	0.5	0.171	0.170	70.50	1202.31					0.17	0.18	0.17										0.06	0.07	0.06
6	6	-	4/22/2008	-	4/23/2008	25	ICP	7.8	7.7	218	0.5	0.227	0.227	69.50	1202.31					0.21	0.20	0.18										0.08	0.07	0.06
1	7	5:30 PM	4/23/2008	1:30 PM	4/24/2008	15	ICP	7.8	7.8	218	0.5	0.135	0.134	71.70	1202.31					0.18	0.18	0.17										0.09	0.09	0.08
2	7	4:30 PM	4/24/2008	12:30 PM	4/25/2008	15	ICP	7.8	7.7	218	0.5	0.219	0.189	73.20	1202.31					0.25	0.25	0.24	0.24									0.10	0.09	0.09
3	7	5:00 PM	4/28/2008	1:00 PM	4/29/2008	13	ICP	7.9	7.9	218	0.5	0.190	0.124	67.45	1202.31					0.22	0.21	0.21										0.10	0.08	0.09
4	7	1:00 PM	4/30/2008	9:00 AM	5/1/2008	12	ICP	7.8	7.8	218	0.5	0.192	0.183	71.10	1202.31					0.24	0.23	0.25										0.10	0.08	0.07
5	7	-	-	-	-	-	ICP	7.7	7.7	218	0.5	-	-	-	-					0.22	0.23	0.24										0.11	0.11	0.11
6	7	5:10 PM	5/4/2008	1:10 PM	5/5/2008	11	ICP	7.8	7.8	218	0.5	0.138	0.146	68.10	1202.31					0.24	0.24	0.25	0.24									0.12	0.12	0.12
1	8	11:15 AM	5/7/2008	7:15 AM	5/8/2008	13	ICP	7.7	7.7	218	0.5	0.136	0.136	60.43	1202.31					0.25	0.2													

Facilitated Iron Reduction as a Means of Rejuvenating Phosphorus Removal Performance of Filtration Substrates

Date	Day	Cell	Fe	P	pH	DO	Date	Day	Cell	Fe	P	pH	DO	Date	Day	Cell	Fe	P	pH	DO	Date	Day	Cell	Fe	P	pH	DO
7/15/2008			0.100	0.208			7/24/2008	9	6	78.105	0.180	3.7	3.1	8/5/2008	21	1	0.005	0.240			8/18/2008	34	2	0.005	0.326	7.8	7.7
7/15/2008		Bucket	0.048	0.176			7/25/2008	10	1	0.098	0.327	6.8	7.8	8/5/2008	21	2	0.015	0.279			8/18/2008	34	3	0.005	0.256	7.9	7.5
7/15/2008	0	1	0.040	0.391			7/25/2008	10	2	0.118	0.342	7.1	7.8	8/5/2008	21	3	0.035	0.063			8/18/2008	34	4	315.732	1.465	3.8	1.8
7/15/2008	0	2	0.078	0.407			7/25/2008	10	3	0.055	0.287	7.0	7.6	8/5/2008	21	4	224.606	0.435			8/18/2008	34	5	351.666	1.328	3.9	1.9
7/15/2008	0	3	0.110	0.398			7/25/2008	10	4	63.171	0.204	3.7	3.8	8/5/2008	21	5	259.725	0.475			8/18/2008	34	6	350.003	0.968	4.0	2.0
7/15/2008	0	4	0.107	0.401			7/25/2008	10	5	64.154	0.177	3.7	3.4	8/5/2008	21	6	277.464	0.441			8/19/2008	35	1	0.018	0.298	7.7	7.9
7/15/2008	0	5	0.091	0.383			7/25/2008	10	6	105.881	0.173	3.8	2.8	8/6/2008	22	1	0.213	0.268			8/19/2008	35	2	0.005	0.317	7.8	7.7
7/15/2008	0	6	0.098	0.393			7/26/2008	11	1	0.140	0.339	7.1	7.8	8/6/2008	22	2	0.005	0.345			8/19/2008	35	3	0.005	0.265	7.8	7.6
7/15/2008	0	1	0.070	0.398	5.7	7.8	7/26/2008	11	2	0.081	0.387	7.2	7.7	8/6/2008	22	3	0.005	0.263			8/19/2008	35	4	320.612	1.566	3.8	1.9
7/15/2008	0	2	0.075	0.383	5.7	7.5	7/26/2008	11	3	0.065	0.275	7.1	7.6	8/6/2008	22	4	240.827	0.498			8/19/2008	35	5	354.401	1.368	3.8	1.9
7/15/2008	0	3	0.028	0.286	5.7	7.3	7/26/2008	11	4	79.578	0.190	3.7	3.4	8/6/2008	22	5	271.830	0.550			8/19/2008	35	6	348.112	0.958	4.0	1.8
7/15/2008	0	4	0.023	0.243	5.5	6.4	7/26/2008	11	5	98.951	0.219	3.8	2.7	8/6/2008	22	6	285.906	0.468			8/20/2008	36	1	0.005	0.889	7.6	8.0
7/15/2008	0	5	0.015	0.242	5.6	6.6	7/26/2008	11	6	145.590	0.215	3.9	2.5	8/7/2008	23	1	0.164	0.274			8/20/2008	36	2	0.005	0.354	7.8	7.8
7/15/2008	0	6	0.062	0.234	5.6	6.4	7/27/2008	12	1	0.087	0.291	7.1	7.5	8/7/2008	23	2	0.005	0.336			8/20/2008	36	3	0.005	0.244	7.7	7.7
7/16/2008	1	1	0.079	0.398	6.3	8.3	7/27/2008	12	2	0.056	0.346	7.2	7.5	8/7/2008	23	3	0.005	0.277			8/20/2008	36	4	324.136	1.670	3.8	1.8
7/16/2008	1	2	0.083	0.395	6.3	7.9	7/27/2008	12	3	0.075	0.272	6.7	7.6	8/7/2008	23	4	248.862	0.566			8/20/2008	36	5	357.288	1.443	3.8	1.8
7/16/2008	1	3	0.008	0.331	6.3	7.9	7/27/2008	12	4	93.608	0.199	3.7	3.7	8/7/2008	23	5	281.937	0.572			8/20/2008	36	6	355.561	1.044	3.9	1.8
7/16/2008	1	4	0.091	0.265	6.0	7.8	7/27/2008	12	5	105.214	0.199	3.8	2.6	8/7/2008	23	6	292.287	0.508			8/21/2008	37	1	0.009	0.284	7.7	8.0
7/16/2008	1	5	0.072	0.252	6.0	7.9	7/27/2008	12	6	153.190	0.224	3.9	2.6	8/8/2008	24	1	0.005	0.262			8/21/2008	37	2	0.009	0.317	7.9	7.9
7/16/2008	1	6	0.101	0.245	6.1	7.8	7/28/2008	13	1	0.092	0.293	7.3	7.7	8/8/2008	24	2	0.005	0.334			8/21/2008	37	3	0.009	0.260	7.9	7.8
7/17/2008	2	1	0.015	0.217	6.3	8.1	7/28/2008	13	2	0.059	0.320	7.2	7.7	8/8/2008	24	3	0.005	0.243			8/21/2008	37	4	372.028	2.000	3.8	1.8
7/17/2008	2	2	0.074	0.383	6.3	7.7	7/28/2008	13	3	0.072	0.286	7.0	7.6	8/8/2008	24	4	260.552	0.587			8/21/2008	37	5	406.006	1.801	3.8	1.7
7/17/2008	2	3	0.004	0.294	6.0	7.1	7/28/2008	13	4	122.252	0.241	3.8	3.7	8/8/2008	24	5	289.031	0.613			8/21/2008	37	6	412.179	1.223	4.0	1.7
7/17/2008	2	4	0.207	0.218	5.6	2.7	7/28/2008	13	5	145.880	0.259	3.9	2.4	8/8/2008	24	6	296.378	0.555			8/22/2008	38	1	0.067	0.294	8.1	7.9
7/17/2008	2	5	0.158	0.204	5.7	3.0	7/28/2008	13	6	190.623	0.268	3.9	2.4	8/9/2008	25	1	0.005	0.547	7.3	7.8	8/22/2008	38	2	0.009	0.316	8.0	7.8
7/17/2008	2	6	0.143	0.225	5.8	3.0	7/29/2008	14	1	0.048	0.295	7.3	7.7	8/9/2008	25	2	0.005	0.334	7.2	7.8	8/22/2008	38	3	0.009	0.271	8.0	7.7
7/18/2008	3	1	0.008	0.316	6.1	7.6	7/29/2008	14	2	0.050	0.325	7.4	7.8	8/9/2008	25	3	0.131	0.165	6.9	7.5	8/22/2008	38	4	375.490	2.054	3.9	1.7
7/18/2008	3	2	0.072	0.379	6.1	8.0	7/29/2008	14	3	0.061	0.286	7.4	7.7	8/9/2008	25	4	265.825	0.719	3.9	2.3	8/22/2008	38	5	411.180	1.882	3.9	1.5
7/18/2008	3	3	0.004	0.282	5.9	7.1	7/29/2008	14	4	135.008	0.266	3.8	3.0	8/9/2008	25	5	292.022	0.701	3.9	2.4	8/22/2008	38	6	413.295	1.289	4.0	1.5
7/18/2008	3	4	1.381	0.215	5.2	2.8	7/29/2008	14	5	162.463	0.311	3.9	2.7	8/9/2008	25	6	300.771	0.588	3.9	2.5	8/23/2008	39	1	0.009	0.284	7.6	7.7
7/18/2008	3	5	0.245	0.199	5.6	3.0	7/29/2008	14	6	207.073	0.305	3.9	2.7	8/11/2008	27	1	0.005	0.378			8/23/2008	39	2	0.009	0.338	7.8	7.5
7/18/2008	3	6	0.165	0.206	5.9	2.9	7/30/2008	15	1	0.141	0.327	7.4	7.8	8/11/2008	27	2	0.005	0.360			8/23/2008	39	3	0.009	0.251	7.8	7.5
7/19/2008	4	1	0.020	0.320	5.9	7.4	7/30/2008	15	2	0.064	0.382	7.6	7.8	8/11/2008	27	3	0.005	0.236			8/23/2008	39	4	381.485	2.233	3.8	1.9
7/19/2008	4	2	0.089	0.361	6.2	8.4	7/30/2008	15	3	0.103	0.328	7.6	7.7	8/11/2008	27	4	279.222	0.922			8/23/2008	39	5	420.424	1.992	3.8	1.7
7/19/2008	4	3	0.022	0.204	6.1	7.7	7/30/2008	15	4	129.893	0.238	4.2	2.6	8/11/2008	27	5	304.365	0.894			8/23/2008	39	6	421.234	1.399	3.9	1.8
7/19/2008	4	4	2.446	0.216	4.0	3.3	7/30/2008	15	5	157.734	0.264	4.3	2.4	8/11/2008	27	6	313.717	0.722			8/25/2008	41	1	0.009	0.292	7.8	15.5
7/19/2008	4	5	0.855	0.169	4.7	3.1	7/30/2008	15	6	195.874	0.265	4.3	2.4	8/12/2008	28	1	0.005	0.373			8/25/2008	41	2	0.009	0.317	7.9	15.9
7/19/2008	4	6	1.386	0.185	4.8	3.1	7/31/2008	16	1	0.174	0.328	7.8	7.7	8/12/2008	28	2	0.005	0.344			8/25/2008	41	3	0.009	0.241	7.9	16.2
7/20/2008	5	1	0.093	0.320	6.4	8.1	7/31/2008	16	2	0.059	0.367	7.8	7.9	8/12/2008	28	3	0.005	0.230			8/25/2008	41	4	396.206	2.420	4.0	3.2
7/20/2008	5	2	0.113	0.356	6.4	8.3	7/31/2008	16	3	0.089	0.307	7.8	7.8	8/12/2008	28	4	280.337	0.941			8/25/2008	41	5	431.154	2.233	3.9	2.9
7/20/2008	5	3	0.082	0.231	6.2	6.9	7/31/2008	16	4	144.204	0.266	4.3	2.6	8/12/2008	28	5	314.392	0.867			8/25/2008	41	6	424.730	1.488	4.0	2.9
7/20/2008	5	4	5.186	0.160	3.7	3.6	7/31/2008	16	5	179.874	0.340	4.3	2.4	8/12/2008	28	6	319.002	0.699			8/26/2008	42	1	0.009	0.282	7.8	10.1
7/20/2008	5	5	4.938	0.174	4.0	2.8	7/31/2008	16	6	222.308	0.305	4.0	2.4	8/13/2008	29	1	0.005	0.363			8/26/2008	42	2	0.009	0.311	7.8	10.1
7/20/2008	5	6	9.292	0.174	3.9	3.0	8/1/2008	17	1	0.129	0.292	7.5	7.9	8/13/2008	29	2	0.005	0.346			8/26/2008	42	3	0.009	0.266	7.9	10.1
7/21/2008	6	1	0.166	0.310	6.6	7.5	8/1/2008	17	2	0.099	0.337	7.5	8.1	8/13/2008	29	3	0.005	0.244			8/26/2008	42	4	396.298	2.465	4.0	1.8
7/21/2008	6	2	0.219	0.372	6.4	7.7	8/1/2008	17	3	0.089	0.287	7.5	7.7	8/13/2008	29	4	294.943	1.061			8/26/2008	42	5	436.053	2.293	3.9	1.9
7/21/2008	6	3	0.128	0.281	6.2	7.0	8/1/2008	17	4	160.235	0.333	5.1	2.5	8/13/2008	29	5	319.042	0.973			8/26/2008	42	6	424.706	1.480	4.0	2.0
7/21/2008	6	4	8.726	0.165	3.7	4.4	8/1/2008	17	5	208.888	0.405	5.1	2.3	8/13/2008	29	6	320.830	0.751			8/27/2008	43	1	0.009	0.270	7.5	7.9
7/21/2008	6	5	14.370	0.155	3.9	3.6	8/1/2008																				

Appendix C

Date	Day	Cell	Fe	P	pH	DO	Date	Day	Cell	Fe	P	pH	DO	Date	Day	Cell	Fe	P	pH	DO	Date	Day	Cell	Fe	P	pH	DO
8/30/2008	46	3	0.009	0.242	7.7	7.3	9/17/2008	64	3	0.016	0.209	8.7	11.4	10/17/2008	94	3	0.011	0.200	7.8	7.0	12/5/2008	143	3	0.011	0.229	7.0	7.9
8/30/2008	46	4	416.965	2.922	4.0	1.9	9/17/2008	64	4	355.934	2.711	3.5	2.0	10/17/2008	94	4	570.279	5.510	3.2	1.5	12/5/2008	143	4	685.801	8.570	3.2	1.6
8/30/2008	46	5	454.706	2.755	3.9	1.7	9/17/2008	64	5	382.084	2.440	3.4	1.9	10/17/2008	94	5	582.223	4.968	3.2	1.3	12/5/2008	143	5	665.116	7.828	3.2	1.3
8/30/2008	46	6	440.343	1.728	4.0	1.7	9/17/2008	64	6	403.303	2.130	3.5	1.9	10/17/2008	94	6	600.796	4.460	3.3	1.5	12/5/2008	143	6	695.607	7.046	3.4	1.5
9/1/2008	48	1	0.009	0.260	7.4	7.5	9/18/2008	65	1	0.413	0.350	8.5	11.3	10/20/2008	97	1	0.011	0.417	8.1	8.7	12/8/2008	146	1	0.009	0.312	6.8	8.4
9/1/2008	48	2	0.009	0.298	7.6	7.4	9/18/2008	65	2	0.094	0.241	8.6	11.0	10/20/2008	97	2	0.011	0.263	8.1	8.5	12/8/2008	146	2	0.009	0.342	6.9	8.2
9/1/2008	48	3	0.009	0.244	7.7	7.4	9/18/2008	65	3	0.040	0.178	8.7	10.5	10/20/2008	97	3	0.011	0.246	8.1	8.2	12/8/2008	146	3	0.009	0.140	6.9	7.7
9/1/2008	48	4	417.020	3.140	3.9	1.7	9/18/2008	65	4	364.628	2.745	3.4	1.8	10/20/2008	97	4	580.567	5.647	3.2	1.1	12/8/2008	146	4	706.673	8.662	3.2	1.7
9/1/2008	48	5	460.482	2.931	3.9	1.7	9/18/2008	65	5	388.773	2.451	3.4	2.0	10/20/2008	97	5	589.860	5.068	3.2	1.1	12/8/2008	146	5	676.933	7.907	3.2	1.3
9/1/2008	48	6	448.192	1.888	3.9	1.7	9/18/2008	65	6	406.559	2.158	3.4	1.9	10/20/2008	97	6	610.465	4.644	3.4	1.1	12/8/2008	146	6	704.284	7.017	3.4	1.4
9/2/2008	49	1	0.009	0.298	7.7	7.9	9/19/2008	66	1	0.009	0.380	7.9	11.4	10/22/2008	99	1	0.011	0.379	8.1	8.3	12/12/2008	150	1	0.009	0.301	6.7	8.2
9/2/2008	49	2	0.009	0.300	8.1	7.7	9/19/2008	66	2	0.009	0.239	8.3	11.2	10/22/2008	99	2	0.011	0.294	8.1	8.1	12/12/2008	150	2	0.009	0.302	6.8	7.8
9/2/2008	49	3	0.009	0.254	8.2	7.7	9/19/2008	66	3	0.012	0.232	8.4	11.1	10/22/2008	99	3	0.011	0.242	8.1	7.7	12/12/2008	150	3	0.009	0.197	6.8	7.4
9/2/2008	49	4	421.873	3.216	3.5	1.6	9/19/2008	66	4	366.702	2.807	3.4	2.1	10/22/2008	99	4	577.012	5.716	3.2	1.4	12/12/2008	150	4	708.655	8.936	3.2	1.2
9/2/2008	49	5	461.343	3.063	3.4	1.6	9/19/2008	66	5	393.152	2.547	3.3	2.2	10/22/2008	99	5	584.612	5.188	3.2	1.3	12/12/2008	150	5	679.239	8.200	3.2	1.2
9/2/2008	49	6	452.810	2.020	3.5	1.7	9/19/2008	66	6	403.575	2.218	3.4	2.1	10/22/2008	99	6	623.701	4.837	3.3	1.2	12/12/2008	150	6	711.493	7.207	3.4	1.2
9/3/2008	50	1	0.009	0.285	8.2	7.6	9/20/2008	67	1	0.291	0.406	7.9	8.0	10/27/2008	104	1	0.011	0.369	7.6	8.1	12/15/2008	153	1	0.009	0.251	6.8	8.1
9/3/2008	50	2	0.009	0.308	8.4	7.5	9/20/2008	67	2	0.097	0.248	8.2	8.1	10/27/2008	104	2	0.011	0.290	7.4	8.0	12/15/2008	153	2	0.009	0.270	7.2	7.9
9/3/2008	50	3	0.009	0.270	8.4	7.2	9/20/2008	67	3	0.046	0.214	8.5	7.9	10/27/2008	104	3	0.011	0.255	7.5	8.5	12/15/2008	153	3	0.009	0.224	7.3	7.6
9/3/2008	50	4	425.995	3.245	3.5	1.7	9/20/2008	67	4	365.059	2.829	3.6	3.0	10/27/2008	104	4	604.597	6.222	3.1	1.9	12/15/2008	153	4	733.914	9.200	3.2	1.2
9/3/2008	50	5	466.349	3.053	3.4	1.6	9/20/2008	67	5	398.721	2.631	3.4	1.7	10/27/2008	104	5	606.091	5.522	3.1	1.8	12/15/2008	153	5	678.825	8.308	3.2	1.3
9/3/2008	50	6	455.229	2.052	3.4	1.8	9/20/2008	67	6	411.361	2.282	3.4	1.6	10/27/2008	104	6	636.106	5.161	3.3	1.5	12/15/2008	153	6	723.248	7.369	3.3	1.4
9/4/2008	51	1	0.009	0.293	8.1	7.6	9/22/2008	69	1	0.027	0.341	8.4	15.1	10/28/2008	105	1	0.011	0.698	6.9	8.0	12/19/2008	157	1	0.009	0.291	6.9	7.7
9/4/2008	51	2	0.009	0.321	8.2	7.5	9/22/2008	69	2	0.009	0.239	8.4	14.8	10/28/2008	105	2	0.011	0.260	7.3	8.3	12/19/2008	157	2	0.009	0.235	7.1	7.3
9/4/2008	51	3	0.009	0.232	8.2	7.5	9/22/2008	69	3	0.015	0.207	8.5	14.4	10/28/2008	105	3	0.011	0.199	7.4	8.6	12/19/2008	157	3	0.009	0.205	7.1	7.5
9/4/2008	51	4	429.268	3.321	3.5	1.7	9/22/2008	69	4	371.735	2.889	3.2	2.8	10/28/2008	105	4	603.632	6.256	3.1	1.7	12/19/2008	157	4	735.222	9.272	3.0	1.3
9/4/2008	51	5	466.084	3.063	3.4	1.6	9/22/2008	69	5	393.853	2.633	3.3	2.5	10/28/2008	105	5	599.982	5.540	3.1	2.2	12/19/2008	157	5	691.211	8.380	3.0	1.3
9/4/2008	51	6	463.179	2.107	3.4	1.6	9/22/2008	69	6	420.584	2.350	3.4	2.6	10/28/2008	105	6	645.519	5.156	3.2	1.6	12/19/2008	157	6	720.446	7.498	3.1	1.3
9/5/2008	52	1	0.009	0.374	7.7	9.7	9/23/2008	70	1	0.191	0.367	8.3	10.0	11/3/2008	111	1	0.011	0.372			12/29/2008	167	1	0.009	0.319	6.8	7.9
9/5/2008	52	2	0.009	0.306	8.2	9.7	9/23/2008	70	2	0.084	0.237	8.5	9.7	11/3/2008	111	2	0.011	0.255			12/29/2008	167	2	0.009	0.296	6.7	7.5
9/5/2008	52	3	0.009	0.241	8.4	9.6	9/23/2008	70	3	0.053	0.217	8.6	9.5	11/3/2008	111	3	0.011	0.259			12/29/2008	167	3	0.009	0.193	6.8	6.8
9/5/2008	52	4	430.377	3.429	3.5	2.3	9/23/2008	70	4	373.695	2.893	3.1	1.8	11/3/2008	111	4	620.093	6.462			12/29/2008	167	4	762.494	9.771	3.0	1.7
9/5/2008	52	5	468.458	3.129	3.4	1.9	9/23/2008	70	5	393.002	2.673	3.2	1.8	11/3/2008	111	5	616.234	5.802			12/29/2008	167	5	707.702	8.819	2.9	1.7
9/5/2008	52	6	468.074	2.193	3.4	1.8	9/23/2008	70	6	417.096	2.406	3.4	2.0	11/3/2008	111	6	656.758	5.555			12/29/2008	167	6	749.874	8.181	3.2	1.7
9/6/2008	53	1	0.009	0.354	7.6	11.7	9/25/2008	72	1	0.031	0.374			11/6/2008	114	1	0.011	0.399			1/5/2009	174	1	0.009	0.397	6.9	7.5
9/6/2008	53	2	0.009	0.331	8.2	12.0	9/25/2008	72	2	0.012	0.257			11/6/2008	114	2	0.011	0.324			1/5/2009	174	2	0.009	0.277	7.1	6.6
9/6/2008	53	3	0.017	0.219	8.5	11.8	9/25/2008	72	3	0.013	0.212			11/6/2008	114	3	0.011	0.258			1/5/2009	174	3	0.009	0.201	7.2	7.3
9/6/2008	53	4	437.638	3.454	3.5	2.4	9/25/2008	72	4	379.987	3.047			11/6/2008	114	4	636.374	6.775			1/5/2009	174	4	784.821	10.193	3.0	1.4
9/6/2008	53	5	471.969	3.224	3.4	2.4	9/25/2008	72	5	399.199	2.776			11/6/2008	114	5	630.593	6.089			1/5/2009	174	5	706.716	9.079	3.0	1.5
9/6/2008	53	6	472.773	2.335	3.4	2.1	9/25/2008	72	6	415.039	2.420			11/6/2008	114	6	656.374	5.584			1/5/2009	174	6	746.879	8.445	3.1	1.7
9/8/2008	55	1	0.009	0.490	8.4	8.4	9/26/2008	73	1	0.274	0.400			11/7/2008	115	1	0.011	0.578			1/12/2009	181	1	0.009	0.367	6.6	8.3
9/8/2008	55	2	0.009	0.314	8.4	8.3	9/26/2008	73	2	0.071	0.255			11/7/2008	115	2	0.011	0.328			1/12/2009	181	2	0.009	0.251	6.6	8.0
9/8/2008	55	3	0.009	0.255	8.4	8.0	9/26/2008	73	3	0.024	0.204			11/7/2008	115	3	0.011	0.205			1/12/2009	181	3	0.009	0.218	6.7	6.3
9/8/2008	55	4	440.160	3.525	3.5	1.5	9/26/2008	73	4	374.665	3.048			11/7/2008	115	4	640.159	6.885			1/12/2009	181	4	792.093	10.625	3.0	1.5
9/8/2008	55	5	472.218	3.377	3.1	1.6	9/26/2008	73	5	400.305	2.833			11/7/2008	115	5	621.227	6.116			1/12/2009	181	5	715.756	9.406	2.9	1.7
9/8/2008	55	6	483.212	2.473	3.2	1.3	9/26/2008	73	6	420.440	2.462			11/7/2008	115	6	657.099	5.634			1/12/2009	181	6	777.275	8.951	3.1	1.7
9/9/2008	56	1	0.121	0.400	8.1	10.5	9/29/2008	76	1	0.012	0.310			11/14/2008	122	1	0.011	0.679			1/19/2009	188	1	0.011	0.436	6.6	7.9
9/9/200																											

The Urban Wetland Filter: Field Results in the Development of a Renewable Practice for Managing Phosphorus in Stormwater Runoff from High Land-Value Areas

Time (h)	Run	Group	Cell	Sample	TP(ppm)	Duplicate	Spikes (1.0 / 0.1 ppm)	Spike Recovery	pH	Flow Rate (L/m)
2	Pre	IN	1	1	0.041				7.93	
4	Pre	IN	1	2	0.022				8.05	
6	Pre	IN	1	3	0.032				8.11	
8	Pre	IN	1	4	0.031				8.15	
10	Pre	IN	1	5	0.027				8.16	
12	Pre	IN	1	6	0.024	0.024			8.22	
14	Pre	IN	1	7	0.028				8.23	
16	Pre	IN	1	8	0.024				8.22	
18	Pre	IN	1	9	0.021				8.22	
20	Pre	IN	1	10	0.020				8.21	
22	Pre	IN	1	11	0.026				8.27	
24	Pre	IN	1	12	0.028				8.31	
26	Pre	IN	1	13	0.024				8.33	
28	Pre	IN	1	14	0.023				8.38	
30	Pre	IN	1	15	0.021				8.42	
32	Pre	IN	1	16	0.020				8.49	
34	Pre	IN	1	17	0.019				8.54	
36	Pre	IN	1	18	0.018				8.55	
38	Pre	IN	1	19	0.020				8.52	
40	Pre	IN	1	20	0.021	0.019			8.46	
42	Pre	IN	1	21	0.018				8.39	
44	Pre	IN	1	22	0.019				8.33	
46	Pre	IN	1	23	0.017				8.31	
48	Pre	IN	1	24	0.020				8.29	
2	Pre	SO	1	1	0.017				8.25	0.52
4	Pre	SO	1	2	0.020				8.28	
6	Pre	SO	1	3	0.027				8.34	
8	Pre	SO	1	4	0.027				8.36	
10	Pre	SO	1	5	0.030				8.38	
12	Pre	SO	1	6	0.032				8.38	
14	Pre	SO	1	7	0.030				8.36	
16	Pre	SO	1	8	0.026				8.35	
18	Pre	SO	1	9	0.017				8.32	
20	Pre	SO	1	10	0.026				8.30	
22	Pre	SO	1	11	0.024				8.29	
24	Pre	SO	1	12	0.026	0.026			8.30	
26	Pre	SO	1	13	0.027				8.32	
28	Pre	SO	1	14	0.028				8.35	
30	Pre	SO	1	15	0.032				8.40	
32	Pre	SO	1	16	0.035				8.46	
34	Pre	SO	1	17	0.034	0.033			8.52	
36	Pre	SO	1	18	0.031				8.55	
38	Pre	SO	1	19	0.022				8.54	
40	Pre	SO	1	20	0.021				8.51	
42	Pre	SO	1	21	0.021				8.50	
44	Pre	SO	1	22	0.019				8.40	
46	Pre	SO	1	23	0.017				8.38	
48	Pre	SO	1	24	0.018				8.38	0.59
2	Pre	IS	1	1	0.032	0.034	1.043	100.90%	8.41	0.48
4	Pre	IS	1	2	0.027				8.43	
6	Pre	IS	1	3	0.027				8.45	
8	Pre	IS	1	4	0.020				8.48	
10	Pre	IS	1	5	0.024				8.46	
12	Pre	IS	1	6	0.021				8.46	
14	Pre	IS	1	7	0.020				8.46	
16	Pre	IS	1	8	0.018				8.46	
18	Pre	IS	1	9	0.017				8.44	
20	Pre	IS	1	10	0.018				8.42	
22	Pre	IS	1	11	0.019				8.43	
24	Pre	IS	1	12	0.020				8.43	
26	Pre	IS	1	13	0.016	0.015	0.957	94.20%	8.45	
28	Pre	IS	1	14	0.016				8.46	
30	Pre	IS	1	15	0.016				8.47	
32	Pre	IS	1	16	0.015				8.49	
34	Pre	IS	1	17	0.017				8.48	
36	Pre	IS	1	18	0.014				8.49	
38	Pre	IS	1	19	0.016				8.49	
40	Pre	IS	1	20	0.017				8.45	
42	Pre	IS	1	21	0.013				8.41	
44	Pre	IS	1	22	0.014				8.37	
46	Pre	IS	1	23	0.012				8.34	
48	Pre	IS	1	24	0.015				8.30	0.63

Appendix C

Time (h)	Run	Group	Cell	Sample	TP(ppm)	Duplicate	Spikes (1.0 / 0.1 ppm)	Spike Recovery	pH	Flow Rate (L/m)
2	Pre	IN	2	1	0.101				8.14	
4	Pre	IN	2	2	0.087				8.14	
6	Pre	IN	2	3	0.072				8.13	
8	Pre	IN	2	4	0.062				8.11	
10	Pre	IN	2	5	0.054				8.08	
12	Pre	IN	2	6	0.042	0.044			8.06	
14	Pre	IN	2	7	0.030				8.04	
16	Pre	IN	2	8	0.029				8.02	
18	Pre	IN	2	9	0.024				8.00	
20	Pre	IN	2	10	0.022				8.00	
22	Pre	IN	2	11	0.023				7.96	
24	Pre	IN	2	12	0.017				7.97	
26	Pre	IN	2	13	0.021				7.98	
28	Pre	IN	2	14	0.024				8.02	
30	Pre	IN	2	15	0.015				8.01	
32	Pre	IN	2	16	0.013				8.00	
34	Pre	IN	2	17	0.013				8.04	
36	Pre	IN	2	18	0.019				8.07	
38	Pre	IN	2	19	0.015				8.11	
40	Pre	IN	2	20	0.019	0.018			8.14	
42	Pre	IN	2	21	0.013				8.14	
44	Pre	IN	2	22	0.011				8.13	
46	Pre	IN	2	23	0.016				8.13	
48	Pre	IN	2	24	0.016				8.13	
2	Pre	SO	2	1	0.037				8.13	0.60
4	Pre	SO	2	2	0.040				8.16	
6	Pre	SO	2	3	0.046				8.16	
8	Pre	SO	2	4	0.043				8.16	
10	Pre	SO	2	5	0.048				8.16	
12	Pre	SO	2	6	0.040				8.16	
14	Pre	SO	2	7	0.036				8.16	
16	Pre	SO	2	8	0.026				8.16	
18	Pre	SO	2	9	0.031				8.16	
20	Pre	SO	2	10	0.027				8.16	
22	Pre	SO	2	11	0.027				8.17	
24	Pre	SO	2	12	0.023	0.025			8.21	
26	Pre	SO	2	13	0.026				8.23	
28	Pre	SO	2	14	0.025				8.26	
30	Pre	SO	2	15	0.025				8.28	
32	Pre	SO	2	16	0.030				8.28	
34	Pre	SO	2	17	0.029	0.030			8.26	
36	Pre	SO	2	18	0.032				8.21	
38	Pre	SO	2	19	0.029				8.15	
40	Pre	SO	2	20	0.030				8.09	
42	Pre	SO	2	21	0.029				8.03	
44	Pre	SO	2	22	0.023				7.96	
46	Pre	SO	2	23	0.022				7.90	
48	Pre	SO	2	24	0.019				7.83	0.53
2	Pre	IS	2	1	0.003	0.006			7.95	0.58
4	Pre	IS	2	2	0.008				7.90	
6	Pre	IS	2	3	0.012				7.93	
8	Pre	IS	2	4	0.020				7.96	
10	Pre	IS	2	5	0.021				7.97	
12	Pre	IS	2	6	0.021				7.98	
14	Pre	IS	2	7	0.021				8.02	
16	Pre	IS	2	8	0.022				8.05	
18	Pre	IS	2	9	0.023				8.07	
20	Pre	IS	2	10	0.020				8.07	
22	Pre	IS	2	11	0.017				8.09	
24	Pre	IS	2	12	0.017				8.11	
26	Pre	IS	2	13	0.017	0.020			8.13	
28	Pre	IS	2	14	0.008				8.18	
30	Pre	IS	2	15	0.010				8.20	
32	Pre	IS	2	16	0.006				8.23	
34	Pre	IS	2	17	0.005				8.25	
36	Pre	IS	2	18	0.006				8.28	
38	Pre	IS	2	19	0.006				8.29	
40	Pre	IS	2	20	0.006				8.29	
42	Pre	IS	2	21	0.006				8.29	
44	Pre	IS	2	22	0.006				8.27	
46	Pre	IS	2	23	0.006				8.24	
48	Pre	IS	2	24	0.005				8.24	0.30

Appendix C

Time (h)	Run	Group	Cell	Sample	TP(ppm)	Duplicate	Spikes (1.0 / 0.1 ppm)	Spike Recovery	pH	Flow Rate (L/m)
2	Pre	IN	1	1	0.041				7.93	
4	Pre	IN	3	2	0.022				8.08	
6	Pre	IN	3	3	0.023				8.13	
8	Pre	IN	3	4	0.020				8.21	
10	Pre	IN	3	5	0.028				8.26	
12	Pre	IN	3	6	0.023	0.018	1.027	100.90%	8.29	
14	Pre	IN	3	7	0.023				8.29	
16	Pre	IN	3	8	0.022				8.28	
18	Pre	IN	3	9	0.021				8.27	
20	Pre	IN	3	10	0.026				8.26	
22	Pre	IN	3	11	0.022				8.24	
24	Pre	IN	3	12	0.017				8.24	
26	Pre	IN	3	13	0.022				8.25	
28	Pre	IN	3	14	0.026				8.27	
30	Pre	IN	3	15	0.013				8.29	
32	Pre	IN	3	16	0.017				8.31	
34	Pre	IN	3	17	0.010				8.33	
36	Pre	IN	3	18	0.012				8.33	
38	Pre	IN	3	19	0.019				8.30	
40	Pre	IN	3	20	0.014	0.012	1.028	101.60%	8.28	
42	Pre	IN	3	21	0.015				8.25	
44	Pre	IN	3	22	0.022				8.27	
46	Pre	IN	3	23	0.012				8.26	
48	Pre	IN	3	24	0.007				8.26	
2	Pre	SO	3	1	0.016				8.28	0.72
4	Pre	SO	3	2	0.015				8.29	
6	Pre	SO	3	3	0.025				8.30	
8	Pre	SO	3	4	0.025				8.32	
10	Pre	SO	3	5	0.028				8.34	
12	Pre	SO	3	6	0.028				8.36	
14	Pre	SO	3	7	0.029				8.36	
16	Pre	SO	3	8	0.023				8.34	
18	Pre	SO	3	9	0.022				8.32	
20	Pre	SO	3	10	0.026				8.31	
22	Pre	SO	3	11	0.017				8.26	
24	Pre	SO	3	12	0.014	0.011	1.056	104.50%	8.24	
26	Pre	SO	3	13	0.011				8.23	
28	Pre	SO	3	14	0.012				8.25	
30	Pre	SO	3	15	0.016				8.29	
32	Pre	SO	3	16	0.016				8.29	
34	Pre	SO	3	17	0.016	0.015			8.28	
36	Pre	SO	3	18	0.016				8.29	
38	Pre	SO	3	19	0.016				8.29	
40	Pre	SO	3	20	0.013				8.26	
42	Pre	SO	3	21	0.015				8.27	
44	Pre	SO	3	22	0.014				8.27	
46	Pre	SO	3	23	0.010				8.24	
48	Pre	SO	3	24	0.016				8.24	0.68
2	Pre	IS	3	1	0.018	0.015			8.32	0.74
4	Pre	IS	3	2	0.004				8.34	
6	Pre	IS	3	3	0.003				8.37	
8	Pre	IS	3	4	0.003				8.38	
10	Pre	IS	3	5	0.002				8.37	
12	Pre	IS	3	6	-0.001				8.35	
14	Pre	IS	3	7	0.002				8.34	
16	Pre	IS	3	8	0.001				8.32	
18	Pre	IS	3	9	0.007				8.32	
20	Pre	IS	3	10	0.013				8.31	
22	Pre	IS	3	11	0.005				8.29	
24	Pre	IS	3	12	0.011				8.31	
26	Pre	IS	3	13	0.005	0.002			8.30	
28	Pre	IS	3	14	0.010				8.32	
30	Pre	IS	3	15	0.002				8.33	
32	Pre	IS	3	16	0.005				8.34	
34	Pre	IS	3	17	0.005				8.34	
36	Pre	IS	3	18	-0.003				8.32	
38	Pre	IS	3	19	-0.001				8.31	
40	Pre	IS	3	20	0.006				8.29	
42	Pre	IS	3	21	0.008				8.27	
44	Pre	IS	3	22	0.005				8.28	
46	Pre	IS	3	23	0.004				8.25	
48	Pre	IS	3	24	0.014				8.26	0.50

Appendix C

Time (h)	Run	Group	Cell	Sample	TP(ppm)	Duplicate	Spikes (1.0 / 0.1 ppm)	Spike Recovery	pH	Flow Rate (L/m)
2	Pre	IN	1	1	0.041				7.93	
4	Post	IN	1	2	0.080				8.32	
6	Post	IN	1	3	0.060				8.40	
8	Post	IN	1	4	0.062				8.44	
10	Post	IN	1	5	0.051				8.45	
12	Post	IN	1	6	0.045				8.45	
14	Post	IN	1	7	0.045				8.44	
16	Post	IN	1	8	0.039				8.43	
18	Post	IN	1	9	0.038				8.43	
20	Post	IN	1	10	0.038				8.46	
22	Post	IN	1	11	0.041				8.52	
24	Post	IN	1	12	0.041				8.58	
26	Post	IN	1	13	0.038	0.031	0.133	102.00%	8.63	
28	Post	IN	1	14	0.031				8.63	
30	Post	IN	1	15	0.033				8.62	
32	Post	IN	1	16	0.032				8.59	
34	Post	IN	1	17	0.031				8.56	
36	Post	IN	1	18	0.028				8.51	
38	Post	IN	1	19	0.029				8.48	
40	Post	IN	1	20	0.025				8.46	
42	Post	IN	1	21	0.027				8.45	
44	Post	IN	1	22	0.025	0.022	0.122	100.00%	8.53	
46	Post	IN	1	23	0.025				8.66	
48	Post	IN	1	24	0.027				8.77	
2	Post	SO	1	1	0.393	0.394	0.477	83.00%	5.92	0.71
4	Post	SO	1	2	0.093				6.87	
6	Post	SO	1	3	0.081				7.01	
8	Post	SO	1	4	0.080				7.11	
10	Post	SO	1	5	0.081				7.22	
12	Post	SO	1	6	0.066				7.30	
14	Post	SO	1	7	0.066				7.40	
16	Post	SO	1	8	0.054				7.44	
18	Post	SO	1	9	0.048				7.60	
20	Post	SO	1	10	0.047				7.71	
22	Post	SO	1	11	0.048				7.75	
24	Post	SO	1	12	0.047				7.81	
26	Post	SO	1	13	0.047				7.87	
28	Post	SO	1	14	0.045				7.83	
30	Post	SO	1	15	0.047				7.98	
32	Post	SO	1	16	0.040				8.02	
34	Post	SO	1	17	0.045				8.04	
36	Post	SO	1	18	0.040				8.07	
38	Post	SO	1	19	0.039				8.07	
40	Post	SO	1	20	0.036	0.034	0.135	101.00%	8.08	
42	Post	SO	1	21	0.034				8.08	
44	Post	SO	1	22	0.035				8.09	
46	Post	SO	1	23	0.037				8.12	
48	Post	SO	1	24	0.036				8.22	0.57
2	Post	IS	1	1	0.054				6.02	0.50
4	Post	IS	1	2	0.048				6.67	
6	Post	IS	1	3	0.044				6.88	
8	Post	IS	1	4	0.043				7.02	
10	Post	IS	1	5	0.038				7.14	
12	Post	IS	1	6	0.032				7.22	
14	Post	IS	1	7	0.030				7.30	
16	Post	IS	1	8	0.031				7.35	
18	Post	IS	1	9	0.029				7.41	
20	Post	IS	1	10	0.028				7.48	
22	Post	IS	1	11	0.029				7.55	
24	Post	IS	1	12	0.028				7.57	
26	Post	IS	1	13	0.024				7.61	
28	Post	IS	1	14	0.023				7.62	
30	Post	IS	1	15	0.023				7.65	
32	Post	IS	1	16	0.021				7.66	
34	Post	IS	1	17	0.023	0.023	0.120	97.00%	7.68	
36	Post	IS	1	18	0.019				7.71	
38	Post	IS	1	19	0.021				7.71	
40	Post	IS	1	20	0.022				7.74	
42	Post	IS	1	21	0.019				7.76	
44	Post	IS	1	22	0.019				7.78	
46	Post	IS	1	23	0.024				7.80	
48	Post	IS	1	24	0.017	0.018	0.119	101.00%	7.80	0.54

Appendix C

Time (h)	Run	Group	Cell	Sample	TP(ppm)	Duplicate	Spikes (1.0 / 0.1 ppm)	Spike Recovery	pH	Flow Rate (L/m)
2	Pre	IN	1	1	0.041				7.93	
4	Post	IN	2	2	0.033	0.027			8.75	
6	Post	IN	2	3	0.029				8.71	
8	Post	IN	2	4	0.028	0.024			8.69	
10	Post	IN	2	5	0.032				8.67	
12	Post	IN	2	6	0.029				8.63	
14	Post	IN	2	7	0.030				8.63	
16	Post	IN	2	8	0.026				8.61	
18	Post	IN	2	9	0.023				8.63	
20	Post	IN	2	10	0.022				8.68	
22	Post	IN	2	11	0.069				8.79	
24	Post	IN	2	12						
26	Post	IN	2	13						
28	Post	IN	2	14						
30	Post	IN	2	15						
32	Post	IN	2	16						
34	Post	IN	2	17						
36	Post	IN	2	18						
38	Post	IN	2	19						
40	Post	IN	2	20						
42	Post	IN	2	21						
44	Post	IN	2	22						
46	Post	IN	2	23						
48	Post	IN	2	24	0.055				8.86	
2	Post	SO	2	1	0.562				5.96	0.55
4	Post	SO	2	2	0.090				6.96	
6	Post	SO	2	3	0.071	0.062			7.24	
8	Post	SO	2	4	0.062				7.48	
10	Post	SO	2	5	0.054				7.65	
12	Post	SO	2	6	0.049				7.81	
14	Post	SO	2	7	0.046				7.91	
16	Post	SO	2	8	0.043	0.039			8.03	
18	Post	SO	2	9	0.040				8.11	
20	Post	SO	2	10	0.044				8.18	
22	Post	SO	2	11	0.048				8.25	
24	Post	SO	2	12	0.054				8.31	
26	Post	SO	2	13	0.051				8.39	
28	Post	SO	2	14	0.048				8.46	
30	Post	SO	2	15	0.050				8.51	
32	Post	SO	2	16	0.046				8.53	
34	Post	SO	2	17	0.044				8.51	
36	Post	SO	2	18	0.041				8.48	
38	Post	SO	2	19	0.040				7.70	
40	Post	SO	2	20	0.039				8.00	
42	Post	SO	2	21	0.040				8.20	
44	Post	SO	2	22	0.044				8.30	
46	Post	SO	2	23	0.045				8.38	
48	Post	SO	2	24	0.046				7.63	0.45
2	Post	IS	2	1	0.030				6.37	0.51
4	Post	IS	2	2	0.017				6.84	
6	Post	IS	2	3	0.020				7.11	
8	Post	IS	2	4	0.021				7.26	
10	Post	IS	2	5	0.019				7.43	
12	Post	IS	2	6	0.019				7.57	
14	Post	IS	2	7	0.019	0.024			7.70	
16	Post	IS	2	8	0.022				7.79	
18	Post	IS	2	9	0.019				7.84	
20	Post	IS	2	10	0.021				7.91	
22	Post	IS	2	11	0.020				7.96	
24	Post	IS	2	12	0.019				7.95	
26	Post	IS	2	13	0.018				7.93	
28	Post	IS	2	14	0.018				7.93	
30	Post	IS	2	15	0.019				7.95	
32	Post	IS	2	16	0.019	0.018			7.95	
34	Post	IS	2	17	0.018				7.95	
36	Post	IS	2	18	0.019				7.95	
38	Post	IS	2	19	0.019				7.94	
40	Post	IS	2	20	0.019				7.93	
42	Post	IS	2	21	0.019				7.93	
44	Post	IS	2	22	0.022				7.92	
46	Post	IS	2	23	0.019				7.90	
48	Post	IS	2	24	0.019				7.89	0.25

Appendix C

Time (h)	Run	Group	Cell	Sample	TP(ppm)	Duplicate	Spikes (1.0 / 0.1 ppm)	Spike Recovery	pH	Flow Rate (L/m)
2	Pre	IN	1	1	0.041				7.93	
4	Post	IN	3	2	0.022				8.82	
6	Post	IN	3	3	0.023				8.85	
8	Post	IN	3	4	0.022	0.016			8.88	
10	Post	IN	3	5	0.021				8.88	
12	Post	IN	3	6	0.021				8.88	
14	Post	IN	3	7	0.020				8.85	
16	Post	IN	3	8	0.019				8.82	
18	Post	IN	3	9	0.022				8.80	
20	Post	IN	3	10	0.022				8.79	
22	Post	IN	3	11	0.024				8.78	
24	Post	IN	3	12	0.025				8.77	
26	Post	IN	3	13	0.021				8.77	
28	Post	IN	3	14	0.023				8.79	
30	Post	IN	3	15	0.020				8.80	
32	Post	IN	3	16	0.020				8.81	
34	Post	IN	3	17	0.020				8.79	
36	Post	IN	3	18	0.020				8.77	
38	Post	IN	3	19	0.023				8.73	
40	Post	IN	3	20	0.022				8.70	
42	Post	IN	3	21	0.025	0.023			8.64	
44	Post	IN	3	22	0.021				8.59	
46	Post	IN	3	23	0.021				8.58	
48	Post	IN	3	24	0.020				8.68	
2	Post	SO	3	1	0.882				5.88	0.53
4	Post	SO	3	2	0.113				7.05	
6	Post	SO	3	3	0.084				7.54	
8	Post	SO	3	4	0.070				7.80	
10	Post	SO	3	5	0.056				8.18	
12	Post	SO	3	6	0.050				8.29	
14	Post	SO	3	7	0.045				8.36	
16	Post	SO	3	8	0.041	0.041			8.41	
18	Post	SO	3	9	0.035				8.44	
20	Post	SO	3	10	0.036				8.46	
22	Post	SO	3	11	0.038				8.46	
24	Post	SO	3	12	0.033				8.45	
26	Post	SO	3	13	0.033				8.45	
28	Post	SO	3	14	0.032				8.46	
30	Post	SO	3	15	0.035				8.47	
32	Post	SO	3	16	0.033				8.49	
34	Post	SO	3	17	0.033	0.032			8.49	
36	Post	SO	3	18	0.038				8.47	
38	Post	SO	3	19	0.033				8.43	
40	Post	SO	3	20	0.032				8.38	
42	Post	SO	3	21	0.049				8.34	
44	Post	SO	3	22	0.038				8.29	
46	Post	SO	3	23	0.035				8.27	
48	Post	SO	3	24	0.044				8.29	0.43
2	Post	IS	3	1	0.031				6.48	0.39
4	Post	IS	3	2	0.022				7.05	
6	Post	IS	3	3	0.019				7.21	
8	Post	IS	3	4	0.018				7.43	
10	Post	IS	3	5	0.017				7.49	
12	Post	IS	3	6	0.017				7.57	
14	Post	IS	3	7	0.016				7.64	
16	Post	IS	3	8	0.076				7.69	
18	Post	IS	3	9	0.016				7.76	
20	Post	IS	3	10	0.016				7.83	
22	Post	IS	3	11	0.015				7.89	
24	Post	IS	3	12	0.016	0.018			7.93	
26	Post	IS	3	13	0.016				7.96	
28	Post	IS	3	14	0.019				7.98	
30	Post	IS	3	15	0.017				8.01	
32	Post	IS	3	16	0.016				8.02	
34	Post	IS	3	17	0.016				8.04	
36	Post	IS	3	18	0.016				8.07	
38	Post	IS	3	19	0.016	0.015			8.07	
40	Post	IS	3	20	0.016				8.06	
42	Post	IS	3	21	0.020				8.07	
44	Post	IS	3	22	0.015				8.05	
46	Post	IS	3	23	0.015				8.02	
48	Post	IS	3	24	0.015				8.02	0.35

Appendix C

Time (d)	Group	Cell	Sampling Location	Volume Drained (L)	TP (ppm)	Duplicates	Spikes (1ppm)	Spike Recovery	P Solution(mg)	TI (ppm)	Dups	Spikes (18.5 ppm)	Spike Recovery
0	SO	1	Top	12.0	0.04				0.47	0.67			
0	SO	2	Top	12.0	0.05				0.62	0.18			
0	SO	3	Top	11.5	0.06				0.67	0.35			
0	IS	1	Top	12.0	0.03	0.03	1.01	107%	0.41	0.52	0.34	19.81	107%
0	IS	2	Top	12.0	0.11				1.33	2.11			
0	IS	3	Top	16.0	0.03				0.54	0.06			
33	SO	1	Top	12.0	0.88				10.60	544.07			
33	SO	2	Top	12.0	1.21	1.21	1.99	97%	14.56	544.57	543.88	516.32	120%
33	SO	3	Top	11.5	1.20				13.85	595.99			
33	IS	1	Top	12.0	0.25	0.19	0.33	18%	3.01	2872.80	2443.66	2292.06	388%
33	IS	2	Top	12.0	0.33				3.90	3225.60			
33	IS	3	Top	16.0	0.37				5.89	2163.05			
50	SO	1	Drained Effluent	12.0	3.27				39.26	922.96			
50	SO	2	Drained Effluent	12.0	2.89	2.59			34.62	868.18	876.64		
50	SO	3	Drained Effluent	11.5	3.39				39.02	936.31			
50	IS	1	Drained Effluent	12.0	0.33				4.00	4914.80			
50	IS	2	Drained Effluent	12.0	0.32	0.32			3.84	4245.60	4236.01		
50	IS	3	Drained Effluent	16.0	0.28				4.48	3340.40			
50	SO	1	Top	12.0	2.26				27.10	765.39			
50	SO	2	Top	12.0	1.43				17.17	728.24			
50	SO	3	Top	11.5	2.51				28.82	763.16			
50	IS	1	Top	12.0	0.24				2.87	3660.40			
50	IS	2	Top	12.0	0.24				2.86	3711.80			
50	IS	3	Top	16.0	0.27	0.26			4.30	2900.80	3132.20		

Field-Scale Study of Phosphorus Removal by Sorption: Comparison of Substrates and Residence Times

Orthophosphorus (mg/L PO₄-)					
Experimental Cell	7/15/07	7/17/07	7/19/07	721/07	
1	0.11	0.12	0.17	0.15	
2	0.26	0.23	0.15	0.1	
3	0.14	0.18	0.12	0.12	
4	0.34	0.11	0.16	0.11	
5	0.1	0.09	0.13	0.11	
6	0.19	0.17	0.1	0.1	
7	0.3	0.2	0.11	0.09	
8	0.47	0.19	0.17	0.11	
9	0.26	0.2	0.12	0.1	
10	0.27	0.22	0.17	0.12	
11	0.24	0.15	0.1	0.11	
12	0.32	0.26	0.22	0.08	
T	0.31	0.17	0.15	0.13	

Total Phosphorus (mg/L PO₄-)					
Experimental Cell	7/13/07	7/15/07	7/17/07	7/19/07	721/07
1	0.44	0.20	0.61	0.63	0.26
2	0.36	0.23	0.23	0.20	0.17
3	0.29	0.28	1.04	0.45	0.40
4	0.27	0.28	0.48	0.20	0.40
5	0.70	0.25	0.31	0.39	0.17
6	0.63	0.23	0.18	0.56	0.25
7	0.41	0.27	0.35	0.57	0.20
8	0.57	0.49	0.31	0.51	0.49
9	0.90	0.31	0.32	0.31	0.22
10	1.09	0.19	0.25	0.36	0.27
11	1.02	0.59	0.27	0.21	0.16
12	1.45	0.23	0.28	0.33	0.20
T	0.70	0.31	0.23	0.51	0.43
Standard (2 +/- 0.10mg/L)		2.18	2.02	2.30	

Standard-Adjusted Total Phosphorus					
Standard Adjustment:	0.00	-0.08	0.00	-0.20	0.00
Experimental Cell	7/13/07	7/15/07	7/17/07	7/19/07	721/07
1	0.44	0.12	0.61	0.43	0.26
2	0.36	0.15	0.23	0.00	0.17
3	0.29	0.20	1.04	0.25	0.40
4	0.27	0.20	0.48	0.00	0.40
5	0.70	0.17	0.31	0.19	0.17
6	0.63	0.15	0.18	0.36	0.25
7	0.41	0.19	0.35	0.37	0.20
8	0.57	0.41	0.31	0.31	0.49
9	0.90	0.23	0.32	0.11	0.22
10	1.09	0.11	0.25	0.16	0.27
11	1.02	0.51	0.27	0.01	0.16
12	1.45	0.15	0.28	0.13	0.20
T	0.70	0.23	0.23	0.31	0.43

Field-Scale Study of Phosphorus Removal by Sorption: Substrate and Residence Time Study Follow-up

Long-term Data Set												
Cell	Type	Type2	Date	Day	Water Temp (C)	Dissolved Oxygen (mg/L)	Air Temp (C)	pH	Total Iron (mg/L)	Total P (mg/L)	Flow (L/min)	
1	Low	S	6/24/2008	0	31.0	4.00	26	6.6	0.011	0.112	0.37	
2	Med	S	6/24/2008	0	28.7	8.00	26	6.8	0.000	0.000	0.79	
3	High	S	6/24/2008	0	27.9	8.00	26	7.0	0.011	0.047	1.25	
4	High	S	6/24/2008	0	28.0		26	7.0	0.000	0.043	1.25	
5	Con	C	6/24/2008	0	27.7	10.00	26	8.7	0.000	0.000	0.88	
6	Low	S	6/24/2008	0	29.9		26	6.8	0.024	0.000	0.28	
7	Con	C	6/24/2008	0	27.4		26	8.8	0.022	0.130	1.25	
8	High	S	6/24/2008	0	27.9		26	7.0	0.039	0.044	1.15	
9	Med	S	6/24/2008	0	28.1		26	7.1	0.080	0.046	0.83	
10	Low	S	6/24/2008	0	29.6		26	6.9	0.077	0.108	0.33	
11	Med	S	6/24/2008	0	28.6		26	6.9	0.000	0.000	0.63	
12	Con	C	6/24/2008	0	28.5		26	8.2	0.084	0.000	0.50	
T		T	6/24/2008	0	27.5	10.00	26	9.0	0.023	0.103		
1	Low	S	7/9/2008	15	23.4	4.85	25	7.5	0.033	0.183	0.17	
2	Med	S	7/9/2008	15	23.5	5.21	25	7.5	0.068	0.046	0.10	
3	High	S	7/9/2008	15	23.5	4.95	25	7.5	0.076	0.048	0.10	
4	High	S	7/9/2008	15	23.5	5.02	25	7.6	0.038	0.042	0.13	
5	Con	C	7/9/2008	15	24.3	7.10	25	7.6	0.042	0.016	1.50	
6	Low	S	7/9/2008	15	23.3	4.96	25	7.5	0.021	0.050	0.13	
7	Con	C	7/9/2008	15	24.7	7.00	25	7.7	0.097	0.050	1.50	
8	High	S	7/9/2008	15	23.7	5.27	25	7.5	0.030	0.038	0.10	
9	Med	S	7/9/2008	15	23.6	5.04	25	7.5	0.052	0.056	0.13	
10	Low	S	7/9/2008	15	23.3	6.00	25	7.5	0.019	0.042	0.13	
11	Med	S	7/9/2008	15	23.3	5.38	25	7.5	0.014	0.013	0.12	
12	Con	C	7/9/2008	15	23.3	5.55	25	7.6	0.023	0.011	0.16	
T		T	7/9/2008	15	24.4	7.77	25	7.7	0.038	0.032		
1	Low	S	7/16/2008	22	33.2	6.75	28	7.6	0.161	0.101	0.12	
2	Med	S	7/16/2008	22	32.8	5.20	28	7.4	0.155	0.053	0.18	
3	High	S	7/16/2008	22	33.2	6.21	28	7.5	0.069	0.056	0.14	
4	High	S	7/16/2008	22	33.0	5.16	28	7.5	0.219	0.096	0.24	
5	Con	C	7/16/2008	22	30.7	7.25	28	7.7	0.048	0.019	0.49	
6	Low	S	7/16/2008	22	33.0	6.04	28	7.6	0.020	0.033	0.24	
7	Con	C	7/16/2008	22	31.7	5.88	28	7.6	0.130	0.028	0.41	
8	High	S	7/16/2008	22	32.8	4.79	28	7.4	0.014	0.052	0.29	
9	Med	S	7/16/2008	22	33.1	5.28	28	7.5	0.067	0.041	0.24	
10	Low	S	7/16/2008	22	33.2	6.19	28	7.7	0.067	0.056	0.20	
11	Med	S	7/16/2008	22	33.2	5.74	28	7.6	0.062	0.027	0.12	
12	Con	C	7/16/2008	22	31.8	6.42	28	7.6	0.140	0.040	0.51	
T		T	7/16/2008	22	30.8	8.16	28	7.7	0.042	0.040		
1	Low	S	7/23/2008	29	30.1	8.34	26	8.3	0.242	0.067	0.07	
2	Med	S	7/23/2008	29	30.4	5.18	26	7.9	0.097	0.066	0.18	
3	High	S	7/23/2008	29	30.3	7.31	26	8.0	0.034	0.043	0.11	
4	High	S	7/23/2008	29	30.1	6.05	26	8.1	0.037	0.043	0.26	
5	Con	C	7/23/2008	29	30.1	8.09	26	8.3	0.090	0.033	0.40	
6	Low	S	7/23/2008	29	30.0	7.53	26	8.0	0.326	0.094	0.09	
7	Con	C	7/23/2008	29	30.2	6.24	26	8.1	0.196	0.025	0.42	
8	High	S	7/23/2008	29	30.3	5.19	26	7.9	0.094	0.041	0.29	
9	Med	S	7/23/2008	29	30.1	5.63	26	7.9	0.147	0.069	0.22	
10	Low	S	7/23/2008	29	30.1	7.25	26	7.9	0.237	0.179	0.06	
11	Med	S	7/23/2008	29	29.8	7.57	26	8.0	0.207	0.158	0.06	
12	Con	C	7/23/2008	29	30.0	7.08	26	8.2	0.075	0.033	0.48	
T		T	7/23/2008	29	30.0	8.26	26	8.3	0.434	0.151		
1	Low	S	7/31/2008	37	24.8	5.38	7.9	0.050	0.099	0.081	0.18	
2	Med	S	7/31/2008	37	25.6	4.32	7.8	0.150	0.084	0.084	0.48	
3	High	S	7/31/2008	37	25.4	4.94	7.8	0.078	0.065	0.22		
4	High	S	7/31/2008	37	25.4	5.90	7.8	0.176	0.119	1.80		
5	Con	C	7/31/2008	37	24.5	7.30	8.0	0.034	0.019	0.62		
6	Low	S	7/31/2008	37	24.7	5.27	7.8	0.011	0.062	0.16		
7	Con	C	7/31/2008	37	25.1	4.84	7.7	0.098	0.013	1.38		
8	High	S	7/31/2008	37	25.8	5.58	7.7	0.109	0.028	1.00		
9	Med	S	7/31/2008	37	25.5	4.60	7.7	0.061	0.059	0.43		
10	Low	S	7/31/2008	37	24.8	4.94	7.8	0.047	0.065	0.16		
11	Med	S	7/31/2008	37	24.9	4.81	7.8	0.018	0.057	0.19		
12	Con	C	7/31/2008	37	24.4	6.80	8.0	0.067	0.013	1.64		
T		T	7/31/2008	37	26.0	6.68	7.7	0.091	0.021			
T		T	8/8/2008	45	26.1	7.39	7.9	0.153	0.027			
T		T	8/8/2008	45	26.1	7.39	7.9	0.144	0.025			
T		T	8/8/2008	45	26.1	7.39	7.9	0.137	0.041			
1	Low	S	8/8/2008	45	25.5	7.23	7.8	0.131	0.081	0.02		
2	Med	S	8/8/2008	45	26.4	6.03	7.6	0.222	0.056	3.78		
3	High	S	8/8/2008	45	25.6	5.88	7.8	0.089	0.049	0.09		
4	High	S	8/8/2008	45	26.7	5.88	7.7	0.206	0.061	0.74		
5	Con	C	8/8/2008	45	26.2	5.45	7.9	0.069	0.025			
6	Low	S	8/8/2008	45	25.3	6.56	7.8	0.397	0.114	0.03		
7	Con	C	8/8/2008	45	27.0	5.48	7.6	0.111	0.013	0.80		
8	High	S	8/8/2008	45	26.8	5.69	7.7	0.129	0.022	0.48		
9	Med	S	8/8/2008	45	26.4	5.54	7.6	0.152	0.043	0.18		
10	Low	S	8/8/2008	45	25.3	7.42	7.9	0.242	0.083	0.02		
11	Med	S	8/8/2008	45	25.3	6.78	7.8	0.131	0.075	0.02		
12	Con	C	8/8/2008	45	26.0	5.78	7.9	0.084	0.034	0.05		
1	Low	S	8/13/2008	50	25.7	10.50		0.283	0.110	0.01		
2	Med	S	8/13/2008	50	25.5	5.78		0.096	0.026	1.52		
3	High	S	8/13/2008	50	25.9	6.24		0.065	0.058	0.13		
4	High	S	8/13/2008	50	26.2	6.43		0.333	0.064	0.80		
5	Con	C	8/13/2008	50	25.8	8.60		0.161	0.054	0.15		
6	Low	S	8/13/2008	50	25.7	10.70		1.706	0.167	0.01		

Long-term Data Set											
Cell	Type	Type2	Date	Day	Water Temp (C)	Dissolved Oxygen (mg/L)	Air Temp (C)	pH	Total Iron (mg/L)	Total P (mg/L)	Flow (L/min)
7	Con	C	8/13/2008	50	26.2	6.28			0.224	0.043	0.64
8	High	S	8/13/2008	50	26.3	5.96			0.194	0.051	0.28
9	Med	S	8/13/2008	50	26.0	6.10			0.231	0.105	0.08
10	Low	S	8/13/2008	50	25.9	9.32			0.304	0.117	0.01
11	Med	S	8/13/2008	50	25.7	9.88			0.270	0.183	0.02
12	Con	C	8/13/2008	50	26.0	8.70			0.125	0.051	0.48
T		T	8/13/2008	50	25.3	8.33			0.281	0.054	
T		T	8/13/2008	50	25.3	8.33			0.113	0.013	
T		T	8/13/2008	50	25.3	8.33			0.078	0.013	
1	Low	S	8/22/2008	59	18.9	8.66	8.4		0.196	0.098	0.01
2	Med	S	8/22/2008	59	20.3	4.82	7.8		0.101	0.134	0.32
3	High	S	8/22/2008	59	19.9	4.57	7.8		0.095	0.027	0.21
4	High	S	8/22/2008	59	20.4	4.59	7.8		0.108	0.032	0.46
5	Con	C	8/22/2008	59	20.3	5.52	7.9		0.138	0.038	0.12
6	Low	S	8/22/2008	59	19.3	9.05	8.4		0.325	0.127	0.00
7	Con	C	8/22/2008	59	21.0	5.52	7.9		0.117	0.013	0.26
8	High	S	8/22/2008	59	20.3	4.81	7.9		0.171	0.048	0.33
9	Med	S	8/22/2008	59	19.2	5.11	8.0		0.244	0.052	0.10
10	Low	S	8/22/2008	59	18.9	9.72	8.7		0.407	0.073	0.00
11		S	8/22/2008	59	19.6	11.45	8.7		0.244	0.148	
12	Con	C	8/22/2008	59	21.8	9.74	8.1		0.086	0.041	2.04
T		T	8/22/2008	59	22.3	9.98	8.2		0.095	0.013	
T		T	8/22/2008	59	22.3	9.98	8.2		0.213	0.091	
T		T	8/22/2008	59	22.3	9.98	8.2		0.093	0.041	
1	Low	S	8/28/2008	65	17.5	7.66	7.9		0.195	0.131	
2	Med	S	8/28/2008	65	17.0	2.87	7.7		0.105	0.013	0.19
3	High	S	8/28/2008	65	17.3	3.08	7.6		0.074	0.013	0.34
4	High	S	8/28/2008	65	16.7	2.97	7.6		0.293	0.057	0.26
5	Con	C	8/28/2008	65	16.6	9.45	8.3		0.047	0.013	0.00
6	Low	S	8/28/2008	65	16.6	8.17	8.3		0.172	0.143	0.00
7	Con	C	8/28/2008	65	17.0	4.46	7.8		0.176	0.029	0.16
8	High	S	8/28/2008	65	17.1	3.05	7.7		0.150	0.077	0.27
9	Med	S	8/28/2008	65	16.8	4.19	7.9		0.143	0.049	0.07
10	Low	S	8/28/2008	65	16.7	8.11	8.3		0.142	0.314	0.08
11	Med	S	8/28/2008	65	16.7	8.12	8.3		0.261	0.260	0.08
12	Con	C	8/28/2008	65	16.6	5.44	8.0		0.077	0.028	0.26
T		T	8/28/2008	65	19.1	7.18	7.9		0.238	0.046	
T		T	8/28/2008	65	19.1	7.18	7.9		0.189	0.047	
T		T	8/28/2008	65	19.1	7.18	7.9		0.121	0.041	
1	Low	S	9/4/2008	72	23.1	6.43	8.6		0.170	0.098	0.02
2	Med	S	9/4/2008	72	25.0	3.50	8.2		0.188	0.048	0.53
3	High	S	9/4/2008	72	25.0	3.57	8.2		0.073	0.023	0.82
4	High	S	9/4/2008	72	25.0	3.78	8.2		0.081	0.013	4.74
5	Con	C	9/4/2008	72	24.3	4.78	8.4		0.060	0.013	0.12
6	Low	S	9/4/2008	72	23.5	6.06	8.7		0.145	0.074	0.02
7	Con	C	9/4/2008	72	25.1	4.58	8.6		0.105	0.028	0.72
8	High	S	9/4/2008	72	25.6	3.56	8.4		0.110	0.044	0.80
9	Med	S	9/4/2008	72	23.6	3.84	8.5		0.289	0.047	0.25
10	Low	S	9/4/2008	72	22.7	6.34	9.0		0.090	0.090	0.02
11	Med	S	9/4/2008	72	23.0	5.91	8.7		0.055	0.075	0.02
12	Con	C	9/4/2008	72	25.0	8.52	8.8		0.123	0.013	2.64
T		T	9/4/2008	72	25.0	8.46	8.9		0.111	0.038	
T		T	9/4/2008	72	25.0	8.46	8.9		0.087	0.032	
T		T	9/4/2008	72	25.0	8.46	8.9		0.093	0.032	
1	Low	S	9/25/2008	93	16.8	10.20	9.3		0.176	0.040	0.02
2	Med	S	9/25/2008	93	17.9	6.60	9.0		0.115	0.031	0.40
3	High	S	9/25/2008	93	17.9	6.20	8.9		0.135	0.030	0.96
4	High	S	9/25/2008	93	16.8	7.30	9.1		0.080	0.013	0.20
5	Con	C	9/25/2008	93	16.4	9.30	9.4		0.052	0.013	0.02
6	Low	S	9/25/2008	93	16.2	10.10	9.6		0.101	0.063	0.00
7	Con	C	9/25/2008	93	17.9	7.00	9.1		0.052	0.025	0.70
8	High	S	9/25/2008	93	17.7	4.30	8.8		0.040	0.013	0.57
9	Med	S	9/25/2008	93	17.3	6.40	9.0		0.055	0.032	0.34
10	Low	S	9/25/2008	93	16.6	9.30	9.5		0.283	0.043	0.00
11	Med	S	9/25/2008	93	16.5	9.70	9.5		0.344	0.050	0.00
12	Con	C	9/25/2008	93	17.7	18.50	9.3		0.325	0.057	0.80
T		T	9/25/2008	93	18.6	7.80	9.2		0.084	0.013	
T		T	9/25/2008	93	18.6	7.80	9.2		0.111	0.039	
T		T	9/25/2008	93	18.6	7.80	9.2		0.124	0.038	
1	Low	S	10/23/2008	121	8.0	8.30	8.6		0.872	0.468	0.01
2	Med	S	10/23/2008	121	8.2	5.70	8.1		0.280	0.046	0.02
3	High	S	10/23/2008	121	10.2	7.90	8.3		0.942	0.046	0.00
4	High	S	10/23/2008	121	7.7	5.40	8.0		0.462	0.046	0.02
5	Con	C	10/23/2008	121	7.7	6.20	8.2		0.208	0.046	0.00
6	Low	S	10/23/2008	121	7.6	7.80	8.6		0.182	0.202	0.00
7	Con	C	10/23/2008	121	9.9	7.10	8.5		0.284	0.046	0.01
8	High	S	10/23/2008	121	8.6	5.50	8.1		0.278	0.046	0.02
9	Med	S	10/23/2008	121	8.8	6.10	8.9		0.328	0.046	0.01
10	Low	S	10/23/2008	121	7.3	7.80	8.6		0.600	0.180	0.00
11	Med	S	10/23/2008	121	7.8	7.20	8.5		0.770	0.046	0.01
12	Con	C	10/23/2008	121	8.7	8.40	8.6		0.206	0.046	0.01
T		T	10/23/2008	121	10.5	9.00	8.7		0.892	0.268	
T		T	10/23/2008	121	10.5	9.00	8.7		0.650	0.288	
T		T	10/23/2008	121	10.5	9.00	8.7		0.768	0.192	

Appendix D: Comprehensive References

References

- Abelson, P. H. 1999. A potential phosphate crisis. *Science* 283 (5410): 2015.
- Aiken, G. R., D. M. McKnight, R. L. Wershaw, and P. MacCarthy. 1985. *Humic Substances in Soil, Sediment, and Water*. New York, NY: Wiley.
- Aldous, A. R., C. B. Craft, S. J. Carla, M. J. Barry, and B. B. Leslie. 2007. Soil phosphorus release from a restoration wetland, Upper Klamath Lake, Oregon. *Wetlands* 27 (4): 1025–1035.
- Anderson, B. H., and F. R. Magdoff. 2005. Relative movement and soil fixation of soluble organic and inorganic phosphorus. *J. Environ. Qual.* 34 (6): 2228-2233.
- Anderson, C. J., and W. J. Mitsch. 2006. Sediment, carbon, and nutrient accumulation at two 10-year-old created riverine marshes. *Wetlands* 26 (3):
- Arai, Y., and D. L. Sparks. 2007. Phosphate reaction dynamics in soils and soil components: A multiscale approach. *Advances in Agronomy* 94: 136-179.
- Arias, C. A., and H. Brix. 2005. Phosphorus removal in constructed wetlands: can suitable alternative media be identified? *Water Sci. Technol.* 51 (9): 267-273.
- Arias, C. A., H. Brix, and N. H. Johansen. 2003. Phosphorus removal from municipal wastewater in an experimental two-stage vertical flow constructed wetland system equipped with a calcite filter. *Water Sci. Technol.* 48 (5): 51-58.
- Arias, C. A., M. d. Bubba, and H. Brix. 2001. Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. *Water Res.* 35 (5): 1159-1168.
- Atasoy, M., R. B. Palmquist, and D. J. Phaneuf. 2006. Estimating the effects of urban residential development on water quality using microdata. *J. Environ. Manage.* 79: 399-408.
- Axt, J. R., and M. R. Walbridge. 1999. Phosphate removal capacity of palustrine forested wetlands and adjacent uplands in Virginia. *Soil Sci. Soc. Am. J.* 63 (4): 1019-1031.
- Baker, B. J., K. W. King, and H. A. Torbert. 2007. Runoff losses of dissolved reactive phosphorus from organic fertilizer applied to sod. *Trans. ASABE* 50 (2): 449-454.
- Birch, G. F., C. Matthai, M. S. Fazeli, and J. Suh. 2004. Efficiency of a constructed wetland in removing contaminants from stormwater. *Wetlands* 24 (2): 459-466.
- Boesch, D. F., R. B. Brinsfield, and R. E. Magnien. 2001. Chesapeake bay eutrophication: scientific understanding, ecosystem restoration, and challenges for agriculture. *J. Environ. Qual.* 30: 303-320.

- Brady, N.C. and R.R. Weil. 2002. *The Nature and Properties of Soils*. Upper Saddle River, N.J.: Prentice Hall.
- Bubba, M. d., C. A. Arias, and H. Brix. 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. *Water Res* 37 (14): 3990-3400.
- Calder, N., B. C. Anderson, and D. G. Martin. 2006. Field investigation of advanced filtration for phosphorus removal from constructed treatment wetland effluents. *Environ. Technol.* 27 (10): 1063-1071.
- Camargo, J. A., and A. Alonso. 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. *Environ. Int.* 32: 831-849.
- Carleton, J. N., T. J. Grizzard, A. N. Godrej, H. E. Post, L. Lampe, and P. P. Kenel. 2000. Performance of a constructed wetlands in treating urban stormwater runoff. *Water Environ. Res.* 72 (3): 295-304.
- Cervantes, F. J., F. A. M. DeBok, D. T., A. J. M. Stams, G. Lettinga, and J. A. Field. 2002. Reduction of humic substances by halo-respiring, sulphate-reducing, and methanogenic microorganisms. *Environ. Microbiol.* 4 (1): 51-57.
- Chen, J., B. Gu, R. Royer, and W. Burgos. 2003. The roles of natural organic matter in chemical and microbial reduction of ferric iron. *The Science of the Total Environment* 307: 167-178.
- Chernick, M. R. 1999. *Bootstrap Methods: A Practitioners Guide*. New York, N.Y.: Wiley-Interscience.
- Chick, A. J., and D. S. Mitchell. 1995. A pilot study of vertical flow wetlands at Coffs Harbour, New South Wales, Australia. *Water Sci. Technol.* 32 (3): 103-109.
- Chiew, H., M. L. Sampson, S. Huch, S. Ken, and B. C. Bostick. 2009. Effect of groundwater iron and phosphate on the efficacy of arsenic removal by iron-amended biosand filters. *Environ. Sci. Technol.* 43 (16): 6295-6300.
- Chorus, I., and J. Bartram. 1999. *Toxic Cyanobacteria in Water: A Guide to their Public Health Consequences, Monitoring, and Management*. London & New York: E & FN Spon.
- Clesceri, L. S., A. E. Greenberg, and A. D. Eaton. 1999. *Standard Methods for the Evaluation of Water and Wastewater*. American Public Health Association.

- Coates, J. D., D. J. Ellis, E. L. Blunt-Harris, C. V. Gaw, E. E. Roden, and D. R. Lovley. 1998. Recovery of humic-reducing bacteria from a diversity of environments. *Appl. Environ. Microbiol.* 64 (4): 1504-1509.
- Coates, J. D., K. A. Cole, R. Charkraborty, S. M. O'Connor, and L. A. Achenbach. 2002. Diversity and ubiquity of bacteria capable of utilizing humic substances as electron donors for anaerobic respiration. *Appl. Environ. Microbiol.* 68 (5): 2445-2452.
- Comeau, Y., J. Brisson, J. P. Réville, C. Forget, and A. Drizo. 2001. Phosphorus removal from trout farm effluents by constructed wetlands. *Water Sci. Technol.* 44: 55-60.
- Comings, K. J., D. B. Booth, and R. R. Horner. 2000. Storm water pollutant removal by two wet ponds in Bellevue, Washington. *J. Environ. Eng.* 126 (4): 321-330.
- Correll, D. L. 1998. The role of phosphorus in the eutrophication of receiving waters: a review. *J. Environ. Qual.* 27: 261-266.
- Coveney, M. F., D. L. Stites, E. F. Lowe, and R. C. Battoe. 2002. Nutrient removal from eutrophic lake water by wetland filtration. *Ecol. Eng.* 19: 141-159.
- Cucarella, V., and G. Renman. 2009. Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments - A comparative study. *J. Environ. Qual.* 38: 381-392.
- Daniels, J. L., G. P. Das, and M. T. S. Hernandez. 2006. Coastal pollution mitigation with lime and zero valent iron. *Marine Georesources and Geotechnology* 24: 183-191.
- Darke, A. K., and M. R. Walbridge. 2000. Al and Fe biogeochemistry in a floodplain forest: implications for P retention. *Biogeochemistry* 51 (1): 1-32.
- Dowling, D. C. 2009. Virginia Stormwater Management Program (VSMP) Permit Regulations. 4VAC50-60. Richmond, VA: Virginia Soil and Water Conservation Board, Virginia Code Commission.
- Drizo, A., C. A. Frost, J. Grace, and K. A. Smith. 1999. Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Res.* 33 (17): 3595-3602.
- Drizo, A., C. A. Frost, J. Grace, and K. A. Smith. 2000. Phosphate and ammonium distribution in a pilot-scale constructed wetland with horizontal subsurface flow using shale as a substrate. *Water Res* 34 (9): 2483-2490.

- Drizo, A., C. Forget, R. P. Chapuis, and Y. Comeau. 2006. Phosphorus removal by electric arc furnace steel slag and serpentinite. *Water Res.* 40 (8): 1547-1554.
- Drizo, A., Y. Comeau, C. Forget, and R. P. Chapuis. 2002. Phosphorus saturation potential: A parameter for estimating the longevity of constructed wetland systems. *Environ. Sci. Technol.* 36 (21): 4642-4648.
- Erickson, A. J., J. S. Gulliver, and P. T. Weiss. 2007. Enhanced sand filtration for stormwater phosphorus removal. *J. Environ. Eng.* 133 (5): 485-497.
- Evans, E. A., and K. A. Rusch. 2007. Phosphorus treatment capability of the marshland upwelling system under low background salinity conditions. *Ecol. Eng.* 30: 250-263.
- Farahbakhshazad, N., and G. M. Morrison. 2003. Phosphorus removal in a vertical upflow constructed wetland system. *Water Sci. Technol.* 48 (5): 43-50.
- Fisher, M. M., and K. R. Reddy. 2001. Phosphorus flux from wetland soils affected by long-term nutrient loading. *J. Environ. Qual.* 30: 261-271.
- Fisher, T. R., E. R. Peele, J. W. Ammerman, and L. W. Harding. 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Mar. Ecol. Prog. Ser.* 82 (1): 51-63.
- Frossard, E., J. P. Bauer, and F. Lothe. 1997. Evidence of vivianite in FeSO₄-floculated sludges. *Water Res* 31 (10): 2449-2454.
- Georgantas, D. A., V. M. Matsis, and H. P. Grigoropoulou. 2006. Soluble phosphorus removal through adsorption on spent alum sludge. *Water Sci. Technol.* 27 (10): 1081-1088.
- Griffioen, J. 2006. Extent of immobilization of phosphate during aeration of nutrient-rich, anoxic groundwater. *Journal of Hydrology* 320 (3/4): 359-369.
- Hammer, D. 1992. Designing constructed wetlands systems to treat agricultural nonpoint source pollution. *Ecol. Eng.* 1 (1/2): 49-82.
- Heal, K. V., K. E. Dobbie, E. Bozika, H. McHaffie, A. E. Simpson, and K. A. Smith. 2005. Enhancing phosphorus removal in constructed wetlands with ochre from mine drainage treatment. *Water Sci. Technol.* 51: 275-282.
- Hogan, D. M., and M. R. Waldbridge. 2007. Best management practices for nutrient and sediment retention in urban stormwater runoff. *J. Environ. Qual.* 36: 386-395.
- Holley, J. W., R. M. Chambers, and G. S. Hancock. 2007. Water quality in headwater streams: A test of best management practices. Virginia/West Virginia Water Research Symposium. Blacksburg, VA: Virginia Water Resources Research Center.

- Hunt, W. F., and A. Wossink. 2003. The Economics of Structural Stormwater BMPs in North Carolina. UNC-WRRI-2003-344. Raleigh, NC: UNC-WRRI.
- Hunt, W. F., and B. Lord. 2006. Maintenance of Stormwater Wetlands and Wet Ponds. Raleigh, NC: North Carolina Cooperative Extension Service.
- Hupfer, M., P. Fischer, and K. Friese. 1998. Phosphorous retention mechanisms in the sediment of an eutrophic mining lake. *Water Air Soil Pollution* 108: 341-352.
- Janda, V., P. Vasek, J. Bizova, and Z. Belohlav. 2004. Kinetic models for volatile chlorinated hydrocarbons removal by zero-valent iron. *Chemosphere* 54: 917-925.
- Jiang, J., and A. Kappler. 2008. Kinetics of microbial and chemical reduction of humic substances: implications for electron shuttling. *Environ. Sci. Technol.* 42 (10): 3563-3569.
- Jones, H. P., and O. J. Schmitz. 2009. Rapid Recovery of Damaged Ecosystems. *Plos ONE* 4 (5): e5653.
- Kadlec, R. H. 2000. The inadequacy of first-order treatment wetland models. *Ecol. Eng.* 15: 105-119.
- Kadlec, R. H. 2005. Phosphorus removal in emergent free surface wetlands. *J. Environ. Sci. Health, Pt. A: Environ. Sci. Eng. Toxic Hazard. Subst. Control* 40 (6): 1293-1306.
- Kadlec, R. H., and S. D. Wallace. 2009. *Treatment Wetlands*. Boca Raton, FL: CRC Press.
- Kaplan, D. 2004. Enhanced contaminant desorption induced by phosphate mineral additions to sediment. *Environ. Sci. Technol.* 38 (11): 31-53.
- Kappler, A., M. Benz, B. Schink, and A. Brune. 2004. Electron Shuttling via humic acids in microbial iron (III) reduction in a freshwater sediment. *FEMS Microbiol. Ecol.* 47: 85-92.
- Keppler, A. M., and J. F. Martin. 2008. Investigating the performance of a laboratory-scale ecological system to treat dairy wastewater. *Trans. ASABE* 51 (5): 1837-1846.
- Komatsu, E., T. Fukushima, and H. Shiraishi. 2006. Modeling of P-dynamics and algal growth in a stratified reservoir - mechanisms of P-cycle in water and interaction between overlying water and sediment. *Ecol. Model.* 197 (3/4): 331-349.
- Kostka, J. E., J. W. Stucki, K. H. Nealson, and J. Wu. 1996. Reduction of structural Fe(III) in smectite by a pure culture of *Shewanella putrefaciens* strain MR-1. *Clays Clay Miner.* 44 (4): 522-529.
- Langergraber, G., R. Haberl, J. Laber, and A. Pressl. 2003. Evaluation of substrate clogging processes in vertical flow constructed wetlands. *Water Sci. Technol.* 48 (5): 25-34.

- Lantzke, I. R., A. D. Heritage, G. Pistillo, and D. S. Mitchell. 1998. Phosphorus removal rates in bucket size planted wetlands with a vertical hydraulic flow. *Water Res.* 32 (4): 1280-1286.
- Lantzke, I. R., D. S. Mitchell, A. D. Heritage, and K. P. Sharma. 1999. A model of factors controlling orthophosphate removal in planted vertical flow wetlands. *Ecol. Eng.* 12 (1): 93-105.
- Li, H., and A. P. Davis. 2009. Water quality improvement through reduction of pollutant loads using bioretention. *J. Environ. Eng.* 135 (8): 567-576.
- Lijklema, L. 1995. Development and eutrophication: experiences and perspectives. *Water Sci. Technol.* 31 (9): 11-15.
- Lindsay, W. L. 1979. *Chemical Equilibria in Soils*. New York: John Wiley and Sons.
- Line, D. E., G. D. Jennings, M. B. Shaffer, J. Calabria, and W. F. Hunt. 2008. Evaluating the effectiveness of two stormwater wetlands in North Carolina. *Trans. ASABE* 51 (2): 521-528.
- Lovely, D. R., E. J. P. Phillips, and D. J. Lonergan. 1991. Enzymatic versus nonenzymatic mechanisms for Fe(III) reduction in aquatic sediments. *Environ. Sci. Technol.* 25 (6): 1062-1067.
- Lovley, D. R. 1991. Dissimilatory Fe(III) and Mn(IV) Reduction. *Microbiological Reviews* 55 (2): 259-287.
- Lovley, D. R., J. L. Fraga, E. L. Blunt-Harris, L. A. Hayes, E. J. P. Phillips, and J. D. Coates. 1998. Humic Substances as a Mediator for Microbially Catalyzed Metal Reduction. *Acta Hydrochim. Hydrobiol.* 26: 152-157.
- Luederitz, V., and F. Gerlach. 2002. Phosphorous removal in different constructed wetlands. *Acta Biotechnology* 22 (1/2): 91-99.
- Luederitz, V., E. Eckert, M. Lange-Weber, A. Lange, and R. M. Gersberg. 2001. Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands. *Ecol. Eng.* 18: 157-171.
- Luu, Y., B. A. Ramsay, and J. A. Ramsay. 2003. Nitritotriacetate stimulations of anaerobic Fe(III) respiration by mobilization of humic materials in soil. *Appl. Environ. Microbiol.* 69 (9): 5255-5262.
- Martinko, J. M., and M. T. Madigan. 2006. *Brock Biology of Microorganisms*. Pearson, Prentice Hall.

- Masscheleyn, P. H., J. H. Pardue, R. D. DeLaune, and W. H. Patrick, Jr. 1992. Phosphorus release and assimilatory capacity of two lower Mississippi Valley freshwater wetland soils. *Water Resources Bulletin* 28 (4): 763-773.
- Maynard, J. J., A. T. O'Geen, and R. A. Dahlgren. 2009. Spatial relationships of phosphorus sorption in a seasonally saturated constructed wetland soil. *Soil Sci. Soc. Am. J.* 73 (5): 1741-1753.
- McBride, M. B. 1994. *Environmental Chemistry of Soils*. New York, NY: Oxford.
- McGechan, M. B., and D. R. Lewis. 2002. Sorption of phosphorus by soil, part 1: Principles, equations, and models. *Biosys. Eng.* 82 (1): 1-24.
- Method 8146 Iron, Ferrous. 2001. *Odyssey DR/2500 Spectrophotometer Procedure Manual*. Loveland, CO.: Hach Company.
- Mitsch, W. J., and J. G. Gosselink. 2000. *Wetlands*. New York, NY: Wiley.
- Namasivayam, C., A. Sakoda, and M. Suzuki. 2005. Removal of phosphate by adsorption onto oyster shell powder - kinetic studies. *J. Chem. Technol. Biotechnol.* 80 (3): 356-358.
- Naylor, S., J. Brisson, M. A. Labelle, A. Drizo, and Y. Comeau. 2003. Treatment of freshwater fish farm effluent using constructed wetlands: the role of plants and substrate. *Water Sci. Technol.* 48 (5): 215-222.
- Nevin, K. P., and D. R. Lovley. 2000. Potential for nonenzymatic reduction of Fe(III) via electron shuttling in subsurface sediments. *Eviron. Sci. Technol.* 34: 2472-2478.
- Noubactep, C., and P. Woafu. 2008. *Elemental Iron for Better Drinking Water in Rural Areas of Developing Countries. Uranium, Mining and Hydrogeology*. Springer Berlin Heidelberg.
- Novotny, V. 2003. *Water Quality*. Hoboken, NJ: John Wiley and Sons, Inc.
- Oguz, E. 2005. Thermodynamic and kinetic investigations of PO adsorption on blast furnace slag. *J. Colloid Interface Sci.* 281 (1): 62-67.
- Osborne, L. L., and M. J. Wiley. 1988. Empirical relationships between land use/cover and stream water quality in an agricultural watershed. *J. Environ. Manage.* 26: 9-27.
- Pant, H. K., K. R. Reddy, and E. Lemon. 2001. Phosphorus retention capacity of root bed media of sub-surface flow constructed wetlands. *Ecol. Eng.* 17 (4): 345-355.
- Parry, R. 1998. Agricultural phosphorous and water quality: A US environmental protection agency perspective. *J. Environ. Qual.* 27: 258-261.

- Paul, M. J., and J. L. Meyer. 2001. Streams in the urban landscape. *Annu. Rev. Ecol. Syst.* 32: 333-365.
- Peretyazhko, T., and G. Sposito. 2005. Iron(III) reduction and phosphorous solubilization in humid tropical forest soils. *Geochimica et Cosmochimica Acta* 69 (14): 3643–3652.
- Phosphate in Water and Seawater, Total P in Pursulfate or Kjeldahl Digests. 2008. SEAL Autoanalyzer 3 High Resolution Operation Manual. Norderstedt, Germany: Seal Analytical, Ltd.
- Prochaska, C. A., and A. I. Zouboulis. 2006. Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate. *Ecol. Eng.* 26 (3): 293-303.
- Puls, R. W., C. J. Paul, and R. M. Powell. 1999. The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test. *Appl. Geochem.* 14: 989-1000.
- R Development Core Team. 2009. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing.
- Rakshit, S., M. Uchimiya, and G. Sposito. 2009. Iron(III) bioreduction in soil in the presence of added humic substances. *Soil Sci. Soc. Am. J.* 73 (1): 65-71.
- Reddy, K. R., R. H. Kadlec, E. Flaig, and P. M. Gale. 1999. Phosphorus retention in streams and wetlands: a review. *Critical Review in Environmental Science and Technology* 29 (1): 83-146.
- Redshaw, C. J., C. F. Mason, C. R. Hayes, and R. D. Roberts. 1990. Factors influencing phosphate exchange across the sediment-water interface of eutrophic reservoirs. *Hydrobiologia* 192: 133-245.
- Reed, S. C., and D. Brown. 1995. Subsurface flow wetlands: A performance evaluation. *Water Environ. Res.* 67 (2): 244-248.
- Regimi, T. P., A. L. Thompson, and D. M. Sievers. 2003. Comparative studies of vegetated and non-vegetated submerged-flow wetlands treating primary lagoon effluent. *Trans. ASAE* 46 (1): 17-27.
- Rohlich, G. A. 1969. *Eutrophication: Causes, Consequences, Correctives*. Washington, DC: National Academy of Sciences.

- Rosenquist, S. E., C. L. Levy, S. T. Sell, W. C. Hession, M. J. Eick, and D. H. Vaughan. In Review. Facilitated iron reduction as a means of rejuvenating phosphorus removal performance of filtration substrate. *Trans. ASABE*:
- Rosenquist, S. E., W. C. Hession, M. J. Eick, and D. H. Vaughan. 2010. Variability in adsorptive phosphorus removal by structural stormwater best management practices. *Ecol. Eng.*: In Press. <http://dx.doi.org/10.1016/j.ecoleng.2009.12.008>.
- Rousseau, D. P. L., P. A. Vanrolleghem, and N. De Pauw. 2004. Model-based design of horizontal subsurface flow constructed treatment wetlands: a review. *Water Res.* 38 (6): 1484–1493.
- Russell, M. J., D. E. Weller, T. E. Jordan, K. J. Sigwart, and K. J. Sullivan. 2008. Net anthropogenic phosphorus inputs: spatial and temporal variability in the Chesapeake Bay region. *Biogeochemistry* 88: 285-304.
- Sano, D., A. Hodges, and R. Degner. 2005. *Economic Analysis of Water Treatments for Phosphorus Removal in Florida*. Gainesville, FL: Florida Cooperative Extension Service.
- Scheibe, T. D., Y. Fang, C. J. Murray, E. E. Roden, and J. Chen. 2006. Transport and biogeochemical reaction of metals in a physically and chemically heterogeneous aquifer. *Geosphere* 2 (4): 220-235.
- Schueler, T. R. 1996. Irreducible pollutant concentrations discharged from urban BMPs. *Watershed Protection Techniques* 2: 369-372.
- Scott, D. T., D. M. McKnight, E. L. Blunt-Harris, S. E. Kolesar, and D. R. Lovely. 1998. Quinone moieties act as electron acceptors in the reduction of humic substances by humic-reducing microorganisms. *Environ. Sci. Technol.* 32 (19): 2987-2989.
- Shang, C., J. W. B. Stewart, and P. M. Huang. 1992. pH effects on kinetics of adsorption of organic and inorganic phosphates by short-range ordered aluminum and iron precipitates. *Geoderma* 53 (1/2): 1-14.
- Shilton, A., S. Pratt, A. Drizo, B. Mahmood, S. Banker, L. Billings, S. Glenney, and D. Luo. 2005. 'Active' filters for upgrading phosphorus removal from pond systems. *Water Sci. Technol.* 51: 111-116.
- Shumway, S. E. 1990. A review of the effects of algal blooms on shellfish and aquaculture. *Journal for the World Aquaculture Society* 21: 65-104.

- Simeral, K. D. 1998. Using constructed wetlands for removing contaminants from livestock wastewater. A-5-98. Columbus: The Ohio State University Extension Office.
- Smith, J. T., W. F. Hunt, and S. Jadlocki. 2005. Conversion of an urban pond to a water quality treatment pond. World Water and Environmental Resources Congress. Anchorage, AK: ASCE.
- Smith, S. V., W. H. Renwick, J. D. Bartley, and R. W. Budemeier. 2002. Distribution and significance of small, artificial water bodies across the United States landscape. *Sci. Total Environ.* 299: 21-36.
- Sonzogni, W. C., G. Chesters, D. R. Coote, D. N. Jeffs, J. C. Konrad, R. C. Ostry, and J. B. Robinson. 1980. Pollution from land runoff. *Environ. Sci. Technol.* 14 (2): 148-153.
- Stenson, F. J. 1994. *Humus Chemistry: Genesis, Composition, Reactions*. New York, NY: John Wiley & Sons.
- Strecker, E. W., M. M. Quigley, B. R. Urbonas, and J. J. Jones. 2001. Determining urban storm water BMP effectiveness. *Journal of Water Resources Planning and Management* 127 (3): 144-149.
- Swenson, K., and D. Catchpoole. 2000. After devastation...the recovery. *Creation ex nihilo*. 22 (2): 33-37.
- Tenenbaum, D. J. 2004. Constructed wetlands: Borrowing a concept from nature. *Environ. Health Perspect.* 112 (1): 44-48.
- USDA. 1986. *Urban Hydrology for Small Watersheds*. Technical Release No. 55. Washington, DC: Soil Conservation Service, US Government Printing Office.
- USEPA. 1974. *The Relationships of Phosphorus and Nitrogen to the Trophic State of Northeast and North-Central Lakes and Reservoirs*. Working Paper No. 23. Corvallis, OR: US Environmental Protection Agency, Office of Water.
- USEPA. 1983. *Results of the Nationwide Urban Runoff Program*. EPA 832-R-83-112. Washington, DC: US Environmental Protection Agency, Office of Water.
- USEPA. 1994. *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry*. EPA Method 200.7. Cincinnati, OH: US Environmental Protection Agency, Office of Research and Development.
- USEPA. 2000. *Nutrient Criteria Technical Guidance Manual*. EPA-822-B00-001. Washington, DC: US Environmental Protection Agency, Office of Water.

- USEPA. 2002. Urban Stormwater BMP Performance Monitoring. EPA 821-B-02-001. Washington, DC: US Environmental Protection Agency, Office of Water.
- VDCR. 1999. Virginia Stormwater Management Handbook. Richmond, VA: Department of Conservation and Recreation, Division of Soil and Water Conservation.
- Virginia Tech Department of Biology. 2008. Simultaneous Persulfate Digestion for Total Nitrogen and Total Phosphorous in Water. Standard Operating Procedure. Blacksburg, VA: Virginia Polytechnic Institute and State University.
- Vymazal, J. 2005. Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. *Ecol. Eng.* 25 (5): 478-490.
- Ward, A. D., and S. W. Trimble. 2004. Environmental Hydrology. Boca Raton, FL: Lewis Publishers.
- WEF. 1998. Urban Runoff Quality Management. Manual of Practice No. 87. Reston, VA: ASCE.
- Weiss, P. T., J. S. Gulliver, and A. J. Erickson. 2007. Cost and pollutant removal of stormwater treatment practices. *Journal of Water Resources Planning and Management* 133 (3): 218-229.
- Westholm, L. J. 2006. Substrates for phosphorus removal - potential benefits for on-site wastewater treatment? *Water Res.* 40 (1): 23-36.
- Wheeler, S. M., and T. Beatley. 2004. The Sustainable Urban Development Reader. New York, NY: Routledge.
- White, J. R., L. M. Gardner, M. Sees, and R. Corstanje. 2008. The short-term effects of prescribed burning on biomass removal and the release of nitrogen and phosphorus in a treatment wetland. *J. Environ. Qual.* 37: 2387-2391.
- Wilson, G. V., F. E. Rhoton, and H. M. Selim. 2004. Modeling the impact of ferrihydrite on adsorption-desorption of soil phosphorus. *Soil Science* 169 (4): 271-281.
- Winter, J. G., and H. C. Duthie. 2000. Export coefficient modeling to assess phosphorus loading in an urban watershed. *Journal of the American Water Resources Association* 36 (5): 1053-1061.
- Zeng, L., X. Li, and J. Liu. 2004. Adsorptive removal of phosphate from aqueous solutions using iron-oxide tailings. *Water Res.* 38 (5): 1318-1326.
- Zhang, J., and X. Huang. 2007. Relative importance of solid-phase phosphorus and iron on the sorption behavior of sediments. *Environ. Sci. Technol.* 41 (8): 2789-2795.

- Zhang, W., G. O. Brown, D. E. Storm, and H. Zhang. 2008. Fly-ash-amended sand as a filter media in bioretention cells to improve phosphorus removal. *Water Environ. Res.* 80 (6): 507-516.
- Zhang, W., J. W. Faulkner, S. K. Giri, L. D. Geohring, and T. S. Steenhuis. 2009. Evaluation of two langmuir models for phosphorus sorption of phosphorus-enriched soils in New York for environmental applications. *Soil Science* 174 (10): 523-530.
- Zhang, W., J. W. Faulkner, S. K. Giri, L. D. Geohring, and T. S. Steenhuis. 2010. Effect of soil reduction on phosphorus sorption of an organic-rich silt loam. *Soil Sci. Soc. Am. J.* 74 (1): 240-249.
- Zhang, Y., X. Lin, and W. Werner. 2003. The effect of soil flooding on the transformation of Fe oxides and the adsorption/desorption behavior of phosphate. *J. Plant Nutr. Soil Sci.* 166 (1): 68-75.
- Zhu, T., P. D. Jenssen, and T. Krogstad. 1997. Phosphorus sorption and chemical characteristics fo lightweight aggregates (LWA)-potential filter media in treatment wetlands *Water Sci. Technol.* 35 (5): 103-108.
- Zhu, T., T. Maehlum, P. D. Jenssen, and T. Krogstad. 2003. Phosphorus sorption characteristics of a light-weight aggregate. *Water Sci. Technol.* 48 (5): 93-100.

Appendix E: Project Photo Gallery

Field-Scale Study of Phosphorus Removal by Sorption: Comparison of Substrates and Residence Times

S.E. Rosenquist, S. Braman, C. Newbill, W.C. Hession, D.H. Vaughan



Newbill

Layout of the twelve experimental cells at the Price's Fork research complex



Newbill

Head tank



The three filtration substrates from front to back: control, calcium-based, and iron-based

Newbill



#57-stone base layer

Newbill



#8-stone layer

Newbill



Filtration substrate layer

Newbill



Housing for pump and battery

Newbill



Pump inside housing

Newbill



Newbill

Outlet Structure at the top of a cell



Newbill

Sieved substrates from left to right (iron-based, control, calcium-based)



Newbill

Sample preparation for hydraulic conductivity testing



Newbill

Double ball-valve flow control setup



Newbill

Manometer on an experimental cell



Rosenquist

Post-study view of iron-based substrate



Rosenquist

Post-study view of calcium-based substrate



Rosenquist

Post-study view of control substrate



Fouling on water inlet after completion of the study

Rosenquist



Experimental setup for hydraulic conductivity testing

Newbill & Braman



Location of the head tank atop the earthen embankment of the pond

Newbill & Braman



Taking a flow rate measurement on one of the experimental cells

Newbill & Braman



Bulk density testing on the various materials involved in this study

Newbill & Braman



Filtration setup used for analysis of dissolved phosphorus

Newbill & Braman



Photo spectrometer used for determination of phosphorus in samples

Newbill & Braman

Variability in Adsorptive Phosphorus Removal by Structural Stormwater Best Management Practices

S.E. Rosenquist, W.C. Hession, M.J. Eick, D.A. Vaughan



Constant head tank with associated plumbing

Julian



Setup showing several of the experimental cells

Julian



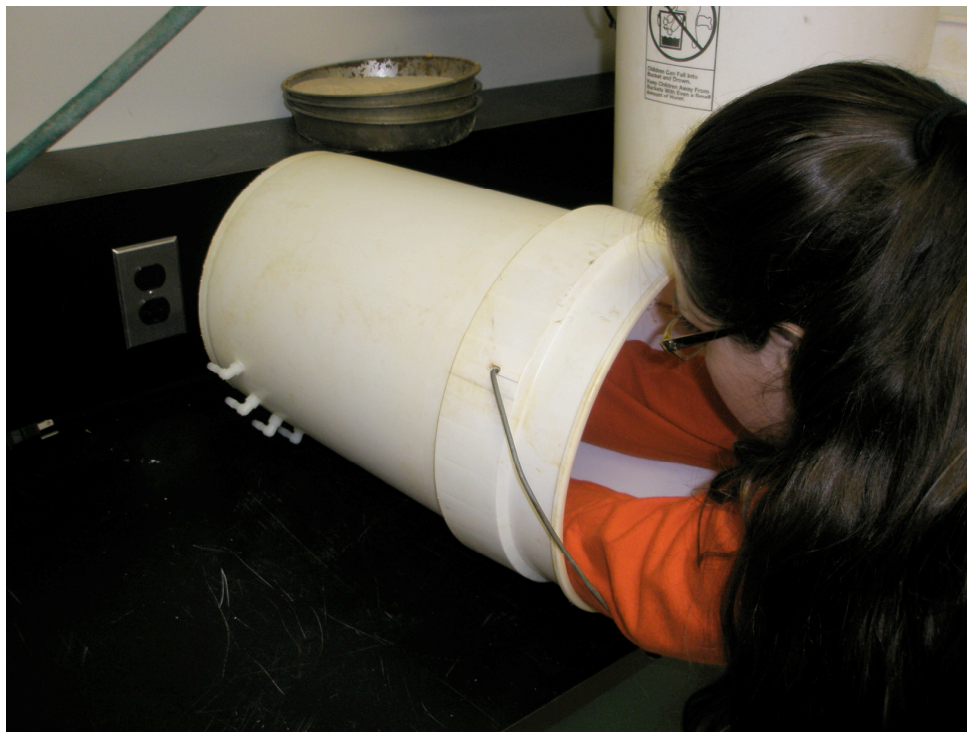
Julian

Holding tank



Rosenquist

Measuring head relative to the experimental cells to set the correct height for the Hudson flow control valve



Sealing the fittings to connect the constant head tank to the experimental cells

Rosenquist



Fittings and tubing used to connect cells to the constant head tank and back to the holding tank

Julian



Completed fittings on the constant head tank

Julian



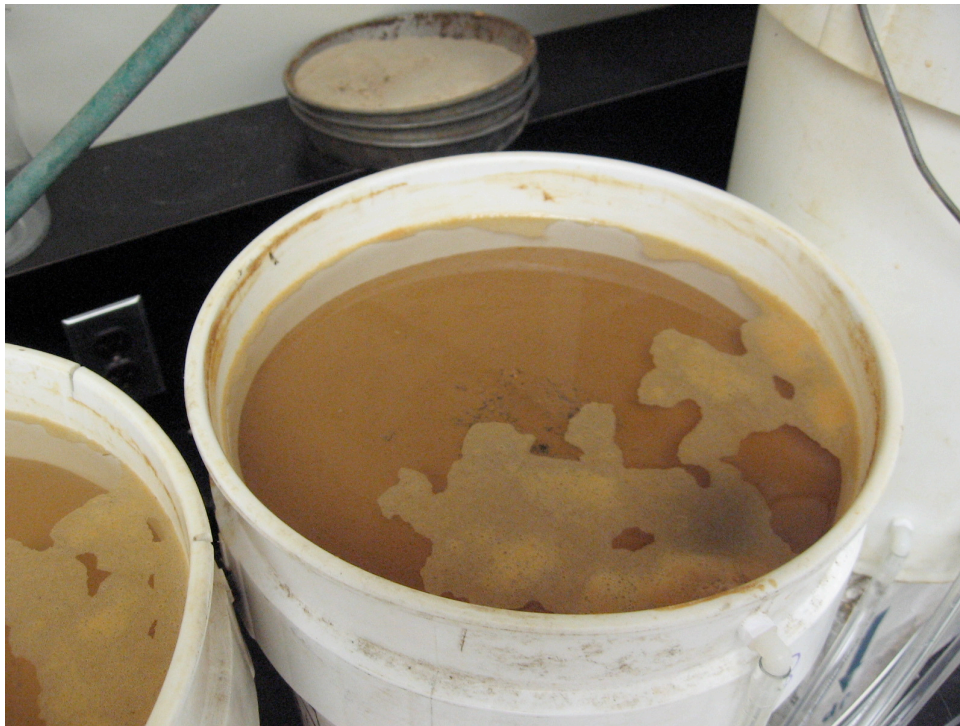
Gravel layer in the bottom of each experimental cell where the inlet was located

Rosenquist



Bulk density testing on substrate

Rosenquist



Experimental cell completed and ready for runs

Rosenquist



Completed setup being tested for flow rate before transitioning to single cell flow back to the holding tank including a view of the recirculation system which continuously mixed the tank water

Facilitated Iron Reduction as a Means of Rejuvenating Phosphorus Removal Performance of Filtration Substrates

S.E. Rosenquist, C.L. Levy, S.T. Sell, W.C. Hession, M.J. Eick, D.H. Vaughan



Rosenquist

Possible oxidized and reduced iron forms in top and bottom, respectively, of a rejuvenation cell



Rosenquist

Over months of reduction, the water in the cells developed a dark amber color



Sell and Levy

Treatment cells with carbon-source addition



Sell and Levy

Control cell with no carbon-source addition

Field-Scale Study of Phosphorus Removal by Sorption: Substrate and Residence Time Study Follow-up

S.E. Rosenquist, W.C. Hession, D.H. Vaughan



Sell

Experimental setup modified for follow-up study including raised concrete-block pedestals and head tank located below the pond with cells



Rosenquist

Cell arrangement with supply lines operating a siphon from the pond located to the left of the photo



Rosenquist

Valve setup including a Hudson Valve™ that regulated flow to maintain a constant head



Rosenquist

Cells were elevated on concrete and in some cases wooden blocks to set their desired relative elevation in an attempt to control flow rates while the 90° elbows were an attempt at finer control



A sand substrate cell

Rosenquist



A gravel substrate cell

Rosenquist

The Urban Wetland Filter: Field Results in the Development of a Renewable Practice for Managing Phosphorus in Stormwater Runoff from High Land-Value Areas

S. E. Rosenquist, W.C. Hession, M.J. Eick, D.H. Vaughan



Retention pond used in this study

Rosenquist



Rosenquist

Pond inlet during a storm event with turbid flow from an upstream construction site



Rosenquist

Surface runoff entering the pond form the nearby dairy farm



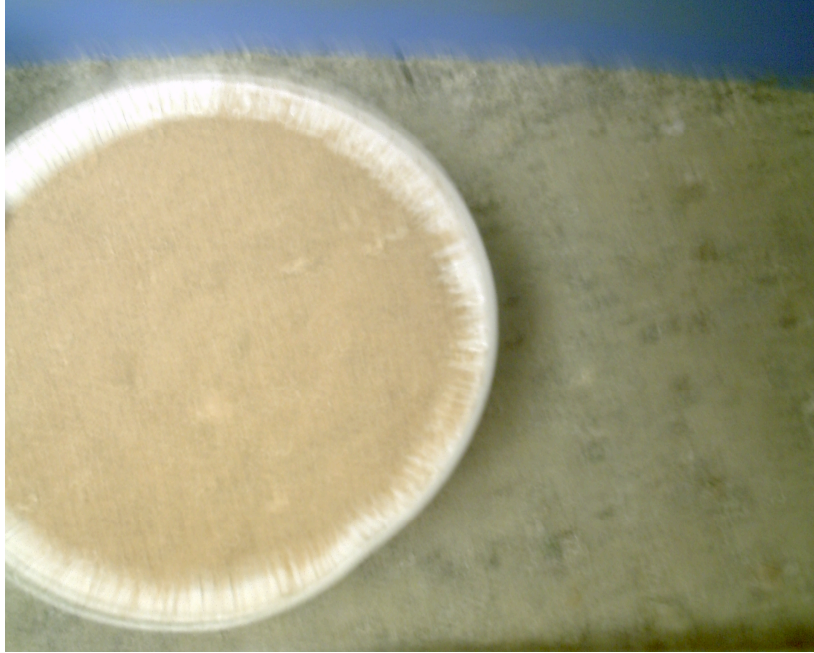
Another view of the pond inlet

Rosenquist



Filtration setup at the retention pond with two experimental cells, inlet structure, and automated samplers

Rosenquist

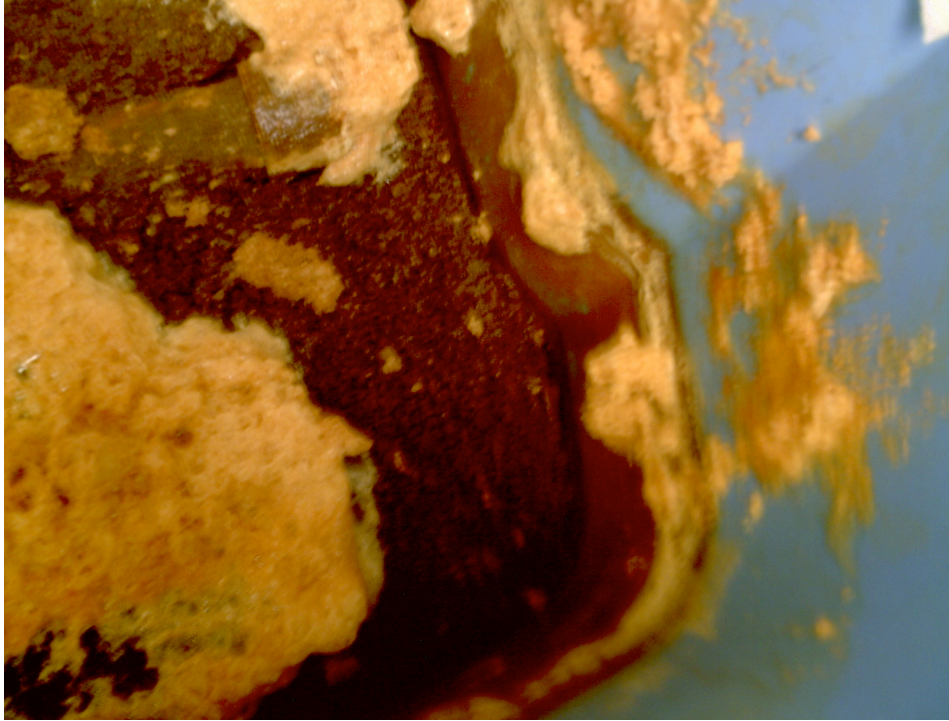


Rosenquist
Gleyed matrix in sand-only cells after rejuvenation compared to un-rejuvenated substrate



Another view of the gleyed matrix

Rosenquist



Rosenquist

Post-rejuvenation iron/sand substrate retains a red color throughout



Rosenquist

Foam present in iron/sand cells during rejuvenation



Sand-only cells produced little or no foam

Rosenquist



Iron and sand from this experiment with weights (g) listed for the containers shown

Rosenquist



Rosenquist

Experimental cells in storage during the rejuvenation cycle



Rosenquist

Samples collected from experimental cells during rejuvenation



Rosenquist

Draining process after completion of the rejuvenation cycle



Rosenquist

Water drained from one of the experimental cells at the end of the rejuvenation cycle



Iron/sand (left) and Sand-only (right) substrate layers in containers

Rosenquist



Incomplete bottom gravel layer showing outlet structure

Rosenquist



Complete bottom gravel layer with outlet structure covered

Rosenquist



Adding the filtration substrate layer over the gravel layer

Rosenquist



Finished filtration substrate layer

Rosenquist



Mixing the Iron/sand substrate (1:2 volume ratio)

Rosenquist

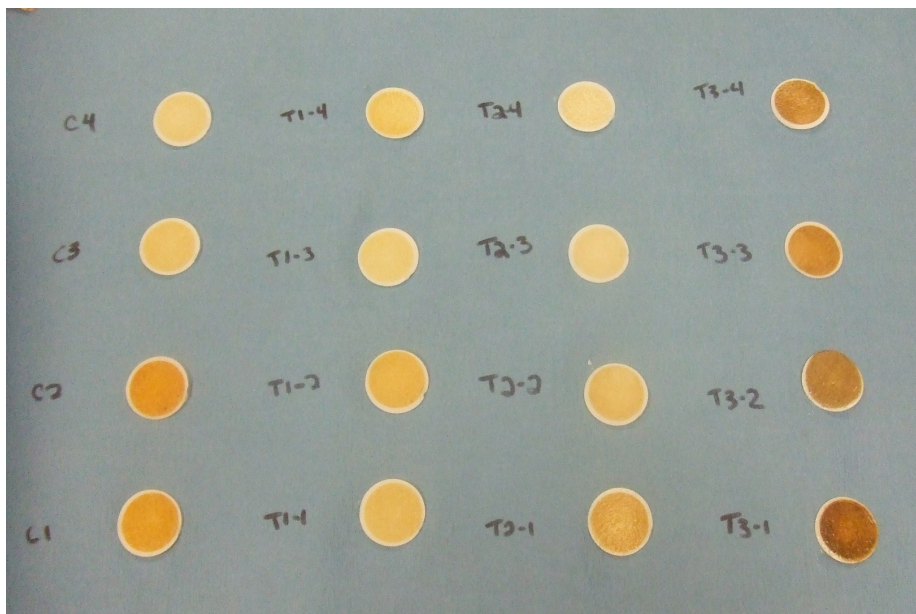
Effect of Humic Acid on Microbial Reduction of Iron and Release of Phosphorus from Wetland Substrates

S.E. Rosenquist, A. Egner, J. Pennington, M. J. Eick, D. H. Vaughan



Egner and Pennington

Experimental cells in incubator during the reduction process



Egner and Pennington

Filters with labels corresponding to treatment group, level, then replication



Egner and Pennington

Sample collection from experimental cells

Appendix F: Copyright Information

Chapter 1

The use of information in Table 1.1 and Table 1.2 is permitted based on public domain as this material is from US government documents and therefore not eligible for copyright.

Chapter 2

Ecological Engineering, a publication of Elsevier, has accepted the material of this chapter for publication, citation below. The publisher has a written policy to grant to the author permission to duplicate the published work "in full or in part, in a thesis or dissertation" (<http://www.elsevier.com/wps/find/authorsview.authors/copyright#whatrights>). Specific permission to reprint as a copyright agreement between the author and the publisher is provided below. Citation of the available version of this article is also available as a footnote on the first page of the chapter.

Rosenquist, S. E., W. C. Hession, M. J. Eick, and D. H. Vaughan. In Press. Variability in adsorptive phosphorus removal by structural stormwater best management practices. *Ecol. Eng.* <http://dx.doi.org/10.1016/j.ecoleng.2009.12.008>

**ELSEVIER LICENSE
TERMS AND CONDITIONS**

Mar 15, 2010

This is a License Agreement between Shawn E Rosenquist ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Shawn E Rosenquist
Customer address	200 Seitz Hall Blacksburg, VA 24061
License Number	2390251178729
License date	Mar 15, 2010
Licensed content publisher	Elsevier
Licensed content publication	Ecological Engineering
Licensed content title	Variability in adsorptive phosphorus removal by structural stormwater best management practices
Licensed content author	Shawn E. Rosenquist, W. Cully Hession, Matthew J. Eick, David H. Vaughan
Licensed content date	25 January 2010
Volume number	n/a
Issue number	n/a
Pages	1
Type of Use	Thesis / Dissertation
Portion	Full article
Format	Electronic
You are an author of the Elsevier article	Yes
Are you translating?	No
Order Reference Number	001
Expected publication date	
Elsevier VAT number	GB 494 6272 12

Permissions price	0.00 USD
Value added tax 0.0%	0.00 USD
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. **Website:** The following terms and conditions apply to electronic reserve and author websites:

Electronic reserve: If licensed material is to be posted to website, the web site is to be password-protected and made available only to bona fide students registered on a relevant course if:

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting,

All content posted to the web site must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com> , and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. **Author website** for journals with the following additional clauses:

All content posted to the web site must maintain the copyright information line on the bottom of each image, and

he permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version,

A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> , As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

18. **Author website** for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.

A hyper-text must be included to the Elsevier homepage at <http://www.elsevier.com>

All content posted to the web site must maintain the copyright information line on the bottom of each image

You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the

material to be stored in a central repository such as that provided by Heron/XanEdu.

19. **Website** (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx>, or for books to the Elsevier homepage at <http://www.elsevier.com>

20. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. **Other Conditions**: None

v1.6

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK10750837.

Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006

If you find copyrighted material related to this license will not be used and wish to cancel, please contact us referencing this license number 2390251178729 and noting the reason for cancellation.

Questions? customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Chapter 3

Transactions of the ASABE, a publication of ASABE, has received the material of this chapter for review. While the publisher has not yet accepted the material for publication, the following copyright agreement was required along with submission. In agreement with this agreement, the copyright information pertinent to publications in this journal has been included as a footnote on the first page of the chapter.

Now—Submit your journal manuscript online at

<http://mc.manuscriptcentral.com/asabe>

ASABE Copyright Transfer and Page Charge Agreement

Please complete this form and return it to ASABE. You may:

- Add your electronic signature, or scan the signed form, and then upload it at asaejournals.manuscriptcentral.com in the same way you submit your manuscript or send it as an e-mail attachment to gillis@asabe.org, or
- Print, sign, and fax it to 269-429-3852 or mail it to ASABE Manuscript Coordinator, 2950 Niles Rd., St Joseph, MI 49085-9659 USA.

Corresponding Author's Name Shawn E. Rosenquist

Manuscript Title Facilitated Iron Reduction as a Means of Rejuvenating Phosphorus Removal Performance of Filtration Substrates

Manuscript ID number, if known (sent to you at submission) _____
 Presented as ASABE Meeting Paper No. _____ (if applicable)

Page Charges

I agree to pay, at publication, a page charge based on the number of published journal pages. The current charge is \$100 (non-members \$110) per 8.5 by 11 inch published page in *Transactions of the ASABE* and *Applied Engineering in Agriculture* and \$50 (non-members \$55) per 6 by 9 inch published page in the *Journal of Agricultural Safety and Health* or *Biological Engineering*.

Copyright Transfer

If my manuscript is accepted for publication by ASABE, I hereby assign and transfer to the American Society of Agricultural and Biological Engineers all right, title, and interest in and to the copyright in said manuscript.

The American Society of Agricultural and Biological Engineers in turn hereby grants to the Author and, in the case of a work made for hire, his employer, a nonexclusive, royalty-free license to use, reproduce, and distribute the article including the right to sublicense the copyright in the published article, provided that each copy shall include the copyright notice appearing on the published article.

No manuscript shall be published by ASABE unless the Society has received this transfer signed by at least one author who can represent the others. If the reported work is made for hire, this assignment should be signed by an authorized representative of the employer.

SIGN HERE (If you are a U.S. Government employee see below.)

Shawn E. Rosenquist _____ 12/10/09
 Corresponding Author Date

If submitting to the *Journal of Agricultural Safety and Health*. ALL other authors must sign.

 Author Date

OR SIGN HERE

The article cited was prepared by a U.S. Government employee as part of official duties and legally cannot be copyrighted.

 Author Date

American Society of Agricultural and Biological Engineers
www.asabe.org

Chapter 4

There is no additional copyright information for this section

Chapter 5

There is no additional copyright information for this section

Appendix A

The "fair use" of Figure A.4 was determined based on the following criteria provided by the Virginia Tech ETD Fair Use Analysis Tool (<http://etd.vt.edu/fairuse/analyzer/results.php>).

1. Consideration of the purpose and character of this use of the work weighs in favor of fair use
2. Consideration of the nature of the work weighs in favor of fair use
3. Consideration of the effect or potential effect on the market after use of this work weighs in favor of fair use

Appendix B

The "fair use" of Figure A.4 was determined based on the following criteria provided by the Virginia Tech ETD Fair Use Analysis Tool (<http://etd.vt.edu/fairuse/analyzer/results.php>).

1. Consideration of the purpose and character of this use of the work weighs in favor of fair use
2. Consideration of the nature of the work weighs in favor of fair use
3. Consideration of the effect or potential effect on the market after use of this work weighs in favor of fair use

Appendix C

There is no additional copyright information for this section

Appendix D

There is no additional copyright information for this section

Appendix E

There is no additional copyright information for this section