Developing a Stormwater Pond Filter to Capture Phosphorus and Other Pollutants

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Abstract

Excess nutrients, particularly phosphorus (P), significantly contribute to anthropogenic eutrophication, which negatively impacts ecosystems, human health, and the economy. Traditional Best Management Practices (BMPs) such as wet retention ponds prevent eutrophication by acting as a sink for nutrients, but can become a source of pollutants if not properly monitored and maintained. A proposed solution is a standalone, multi-stage filter system that can attach to BMPs with standing water for targeted removal of excess nutrients and with the potential to recycle the filter media. The studies in this dissertation seek to address the feasibility of this solution through the following tasks: 1.) develop a tool that can identify ponds and locations within ponds with high total phosphorus (TP) concentrations, 2.) evaluate filter media that can remove P and can be recycled along with captured P, and 3.) develop a filter system that can remove pollutants in separate stages for the option to recycle certain pollutants. The studies focused primarily on P because the nutrient has the potential to be recycled if captured within the filter. Models developed in the first task showed that TP concentrations in the water were correlated with the pond outlet, pH of the water, and iron concentrations. TP concentrations in the sediment were correlated with the pond's length-to-width ratio and the concentration of aluminum and copper. For the second task, a batch experiment and measurements of physicochemical properties were conducted on four biochars (corn stover pyrolized at 400°C , corn stover pyrolized at 600°C, mixed hardwood, and rice husk). Results indicated that mixed hardwood biochar could sorb dissolved phosphorus (DP) above a solution concentration of 2.9 mg P/L. The properties that could allow this biochar to sorb DP were a smaller negative surface charge, high surface area, smaller concentration of elemental P, and more water-extractable cations. A laboratory-scale test of a three-stage filter system was performed as part of the third task. The filter effectively separated nitrogen and P in different stages, but did not separate lead from P. Median water quality parameters (pH, conductivity, temperature, turbidity, dissolved oxygen, carbon, iron) met U.S. EPA recommended limits, but some parameters violated the recommended limits at a few time points. These studies demonstrate that excessive pollutant concentrations exist in current BMPs, which can benefit from a filter system. The filter system has the potential to collect pollutants separately provided that the correct media mix and configuration is identified such that P can be more completely isolated and water quality parameters are met.

Developing a Stormwater Pond Filter to Capture Phosphorus and Other Pollutants

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General Audience Abstract

Excess nutrients, particularly phosphorus (P), cause harmful algae blooms in the nation's water bodies, which negatively impacts ecosystems, human health, and the economy. Structures such as wet retention ponds detain these nutrients by storing them, but can become a source of pollutants if not properly monitored and maintained. A proposed solution is a standalone, multi-stage filter system that can attach to wet retention ponds for targeted removal of excess nutrients and with the potential to recycle the filter media. The studies in this dissertation seek to address the feasibility of this solution through the following tasks: 1.) develop a tool that can identify ponds and locations within ponds with high total phosphorus (TP) concentrations, 2.) evaluate filter media that can remove dissolved P (DP) and can be recycled along with captured DP, and 3.) develop a filter system that can remove pollutants in separate stages for the option to recycle certain pollutants. The studies focused primarily on P because the nutrient has the potential to be recycled if captured within the filter. Models developed in the first task showed that TP concentrations in the water were correlated with the pond outlet, pH of the water, and iron concentrations. TP concentrations in the sediment were correlated with the pond's length-to-width ratio and the concentration of aluminum and copper. For the second task, four biochars (corn stover pyrolized at 400°C, corn stover pyrolized at 600°C, mixed hardwood, and rice husk) were tested for their ability to collect DP. Only the mixed hardwood biochar was able to collect DP when the surrounding DP solution was higher than 2.9 mg P/L. A laboratory-scale test of a three-stage filter system was performed as part of the third task. The filter effectively separated nitrogen and P in different stages, but did not separate lead from P. Water quality parameters (pH, conductivity, temperature, turbidity, dissolved oxygen, carbon, iron) generally met U.S. EPA recommended limits, but some parameters violated the recommended limits at a few points in time. These studies demonstrate that excessive pollutant concentrations exist in current wet retention ponds, which can benefit from a filter system. The filter system has the potential to collect pollutants separately provided that the correct media mix and configuration is identified such that P can be more completely isolated and water quality parameters are met.

Dedication

To Brian, who was always there to tell me to look on the bright side of life.

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Author's Preface

This dissertation is comprised of an introductory chapter presenting the research goal and objectives, three chapters (Chapters 2 through 4) that describe the studies performed in support of the research goal and objectives, and a final concluding chapter that summarizes the efforts and provides recommendations for future work. The problem statement focuses on the issue of excess nutrients in surface water bodies and the goal of developing a cost-effective, standalone filtration system that removes these nutrients from the water with the intent of recycling specific elements.

To justify whether such a filtration system would be useful, Chapter 2 demonstrates that sufficient phosphorus concentrations exist in water bodies, specifically in wet retention ponds, to require remediation, and identifies likely locations where phosphorus is concentrated. The results showed that total phosphorus concentrations for all studied ponds exceeded U.S. EPA recommended limits and tended to be higher for urban ponds and where pH and iron concentrations are high. Within ponds, higher phosphorus concentrations were most likely to be found near the middle and outlet of the pond rather than at the inlet. This evidence will help inform where a filtration system could be installed on pond. In addition to this analysis, four models are supplied in Chapter 2 that can predict total phosphorus concentrations in the water column and in the sediment. One set of models (for both water and sediment) provides the highest correlation between pond characteristics and total phosphorus concentration. The second set of models would be used to provide quick, on-site assessments in lieu of costly and time-consuming sample testing.

Chapter 3 addresses the type of media that can be used in the filtration system with the intent of recycling the media along with trapped phosphorus as fertilizer. This study found that only the mixed hardwood biochar out of the four biochars tested could sorb dissolved phosphorus (DP), and only when solution concentration is higher than 2.9 mg P/L, which is higher than typical DP concentrations in stormwater. This study also found that the characteristics that potentially allowed the mixed hardwood biochar to sorb DP were a smaller negative surface charge, high surface area, smaller concentration of elemental P, and more water-extractable cations.

Given the results found in Chapter 3, biochar was used instead in a denitrifying stage in a prototype of a filtration system whose performance is described in Chapter 4. This study showed that nitrogen and phosphorus can be removed separately, but the media tested in the study did not sufficiently separate lead from the phosphorus removal stage. A mixture of biochar and woodchips was comparable to woodchips only in removing nitrate and total nitrogen, and an iron/sand mix removed a significantly greater amount of dissolved phosphorus and total phosphorus than sand alone.

Final concluding remarks provide suggestions for future work given the results found in Chapters 2 through 4.

Attribution

Assessment of Phosphorus and Other Pollutants in Five Shallow Retention Ponds in Montgomery County, VA
by Houston, S. C., Easton, Z. M., and Hession, W. C.

Physicochemical Properties and Phosphate Sorption of Corn Stover, Mixed Hardwood, and Rice Husk Biochars
by Houston, S. C., Eick, M. J., Easton, Z. M., and Hession, W. C.

Stormwater Pollutant Removal in a Laboratory-Scale Three-Stage Filter Using Biochar and Iron
by Houston, S. C., Eick, M. J., Easton, Z. M., and Hession, W. C.

1. Introduction

Impacts of Eutrophication and Nonpoint Source Pollution

Cultural eutrophication caused by human activity causes widespread degradation of water quality, which negatively impacts ecosystems, economic systems, and human health. Eutrophication is the enrichment of a water body with nutrients and is typically a natural process (Raven & Berg, 2006). However, human influence has increased the rate at which a water body is enriched with nutrients, causing plant growth and algal blooms that deplete dissolved oxygen in the water and establishing an unhealthy environment for aquatic life and human use (Brady & Weil, 2008). Impacts of cultural eutrophication include fish kills, reduced aquatic vegetation and organisms in the water body, and toxins and odor problems in the water (Brady & Weil, 2008; Carpenter et al., 1998).

Nonpoint source pollution (NPS) contributes significantly to cultural eutrophication in water bodies and is difficult to manage due to its diffuse nature and unpredictability (Novotny, 2003). These sources of pollutants come from agricultural and urban contributions such as application of fertilizers and runoff from construction sites (Carpenter et al., 1998). Among these pollutants that contribute to eutrophication are phosphorus (P) and nitrogen (N), specifically dissolved phosphrous (DP) and nitrate (NO_3). NO_3 tends to be the limiting nutrient for coastal waterways, whereas DP is typically the limiting nutrient for freshwater bodies (Brady & Weil, 2008; Fisher, Peele, Ammerman, & Harding, 1992). Both nutrients contribute to excess plant growth and algal blooms that deplete oxygen in the water bodies (Carpenter et al., 1998).

In addition to excess nutrients that cause eutrophication, other NPS pollutants can decrease water quality. Toxic metals such as lead persist in surface water bodies and when ingested, can cause adverse health effects such as mental impairment (Abadin et al., 2007; Raven & Berg, 2006). Depending on the type of metal, amounts as much as 470 μg/L (nickel) to as little as 1.4 μg/L (mercury) in the water can harm aquatic life (U.S. Environmental Protection Agency (USEPA), 2000). Therefore, although nutrients are a leading contributor of compromised water bodies, other pollutants also negatively impact water quality and should also be considered when developing a solution in improving water quality.

Best Management Practices: Solutions and Limitations

Best management practices (BMPs) have been employed to control NPS pollutants, as well as attenuate excess flows, in both agricultural and urban environments. Typical solutions include retention ponds, which improve water quality by allowing sediment to settle (Wong et al, 1999). This BMP is generally more efficient at removing a combination of total phosphorus (TP), dissolved phosphorus (DP), total nitrogen (TN), and nitrate (NO_3) when compared to other BMPs such as dry ponds, bioretention areas, and open channels (Leisenring et al., 2012; Center for Watershed Protection, 2007).

However, limitations exist for retention ponds. Retention ponds are susceptible to developing anoxic conditions, which releases phosphorus bound to sediments, and are not effective in settling very fine particles (Wong et al., 1999). Wet ponds also typically require sufficient space to be effective, and certain locations such as highly developed areas may not allow for such a footprint (U.S. Environmental Protection Agency (USEPA), 1999). Finally, wet retention ponds require regular maintenance to prevent sediment accumulation a resulting decrease in performance (U.S. Environmental Protection Agency (USEPA), 1999).

Wet retention ponds, as well as other traditional BMPs, also do not have a means to recycle any collected nutrients, which would increase the sustainability of natural resources. The ability for a BMP to be able to capture nutrients for potential reuse can provide economic incentive to install these BMPs, resulting in improved water quality.

Research Focus

Given the current limitations of traditional BMPs, the focus of this research is to develop a stand-alone system that complements these traditional BMPs in a compact, easily manageable unit that can also recycle collected nutrients. The research is further narrowed to focus on P. The reason for concentrating on this particular pollutant is twofold: 1.) P is a common pollutant that significantly contributes to eutrophication of freshwater bodies, and 2.) P is a limited natural resource. Finding a solution for these problems would both significantly reduce the negative impact of P to surface waters and increase the sustainability of a natural resource. P is the limiting nutrient in freshwater bodies (Brady & Weil, 2008; Carpenter et al., 1998; Fisher et al., 1998) and, unlike nitrogen, does not have a natural process by which P can be removed from water bodies (i.e., denitrification) (Davis et al., 2006). At the same time, P is a valuable and limited natural resource that can be depleted within 80 to 400 years (Cordell et al., 2009; Dawson & Hilton, 2011).

The duality of these issues requires a unique solution so that P is not only removed from a water body but is also retained for additional use. The goal of this research is to address both of these issues. Filtering of additional pollutants is also considered under this research project but is not the primary pollutant of concern.

Goals and Objectives

The ultimate goal of this research is to develop a standalone filtration system that primarily filters phosphorus from a surface water body and for which the used media has the potential to be recycled as fertilizer. This process will increase the nutrient-capturing capability of retention ponds, require a smaller land footprint than some BMPs such as wetlands, and act as a means to recycle P. Furthermore, this process will provide an economic incentive rather than a mandated requirement for entities to install stormwater BMPs.

To achieve this goal, three focus areas were identified, and objectives were defined within the focus areas. The three focus areas were as follows: 1.) determine whether there is sufficient P concentrations in surface water bodies, specifically ponds, for a filter to be effective; 2.) determine whether a recyclable media such as biochar can sorb P; and 3.) determine the feasibility of a filtration system that can remove pollutants separately.

Objectives were defined for each focus area. The first focus area concentrated on determining the amount and location of P in ponds. Objectives to achieve this goal were as follows: 1) determine the concentration and spatial distribution of P in a range of pond types, and 2) develop models to correlate P concentrations with pond attributes.

The second focus area concentrated on characterizing four biochars for their ability to sorb dissolved phosphorus (DP). Objectives to achieve this goal were: 1.) characterize the physical and chemical properties of four types of biochars (corn stover pyrolized at 400°C and 600°C, mixed hardwood, and rice husk), and 2.) determine the DP sorption capacity of the biochars.

The final focus area involved developing and testing a three-stage filter. Objectives for this area were as follows: 1.) assess the ability of different media to remove DP, NO_3,TP, TN, and lead in separate stages for potential reuse, and 2.) determine filter media's effects on water quality parameters.

In obtaining these objectives, the feasibility of a standalone filter system can be determined. Such a filter system can then be placed at strategic locations around wet retention ponds to remove pollutants without pond-wide maintenance efforts, and nutrients captured on the media can potentially be reused. The system would thus be a more sustainable pollutant removal solution.

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2. Assessment of Phosphorus and Other Pollutants in Five Shallow Retention Ponds in Montgomery County, VA

Abstract

Wet retention ponds can contribute nutrients to a downstream water body rather than prevent this occurrence if not properly maintained, exacerbating problems of eutrophication. Targeted monitoring and maintenance can be a more cost effective solution than a pond-wide effort but requires specific knowledge of the concentration and spatial distribution of pollutants in the pond. The objectives of this study were to determine the concentration and spatial distribution of total phosphorus (TP) and develop models to correlate TP concentration with pond characteristics. Water samples, sediment samples, and in-situ measurements were collected at different locations and depths from five shallow ponds (<2 m) of varying land uses in Montgomery County, VA. Samples were tested for dissolved P, total P (TP), nitrate, and metals. Four models were developed to correlate pond characteristics to TP in the water and TP in the sediment. Two of these models tested the feasibility of a “rapid assessment” tool using easily obtained pond data for quick estimates of TP concentrations in ponds. The outlet of the pond and iron concentration were significantly correlated with water TP concentrations, and length-to-width ratio, aluminum concentration, and copper concentration were significantly correlated with sediment TP concentrations. Models for water and sediment TP concentrations were able to explain 0.8 and 0.83 of the variation in the observations. The “rapid assessment” models could only explain 0.57 and 0.71 of the variation in the data in the water and sediment respectively. The results of this study can aid in prioritizing monitoring and maintenance of retention ponds, as well as target maintenance efforts at specific locations within ponds that are prone to pollutant release.

Introduction

Excess nutrients in urban and agricultural runoff contribute significantly to anthropogenic eutrophication in the nation’s water bodies (Carpenter et al., 1998; Chislock et al., 2013; Dubrovsky & Hamilton, 2010; Paul & Meyer, 2001; U.S. Environmental Protection Agency (USEPA), 2009a) and can negatively impact biological systems, economic systems, and human health (Chislock et al., 2013). Best Management Practices (BMPs) seek to prevent these pollutants from reaching major water bodies through a variety of mechanisms. Wet retention ponds are a common BMP used across the United States (Smith et al., 2002) that can help reduce pollutant loads to water bodies by reducing peak runoff flows and volumes, as well as act as traps for pollutants (U.S. Environmental Protection Agency (USEPA), 1999).

However, pond removal efficiencies are highly variable. Removal efficiencies for total phosphorus (TP) can range from 12% to 91%, and soluble nutrients can range from 40% to 80% (Center for Watershed Protection, 2007; Comings et al., 2000; U.S. Environmental Protection Agency (USEPA), 1999). In addition to mixed performance, retention ponds can act as a pollutant source rather than a sink under certain circumstances and if not properly maintained. Nutrients can be released if the pond becomes saturated with nutrients, anoxic conditions are established, or a storm event flushes the pond (Novotny, 2003; Wong et al., 1999). Studies also indicate that phosphorus (P) stored in sediment can be released back into the water column either through sediment resuspension or biological activity (Ogdahl et al., 2014; Olila et al., 1995; Palmer-Felgate et al., 2011; Shinohara et al., 2016).

The physical features and surrounding landscape of a pond can exacerbate pollutant release, particularly for P. The positioning of inlets and outlets can result in less-than-optimal retention time for sediment-attached nutrients such as P to settle (Mallin et al., 2002). Both shallow and deep ponds can be susceptible to internal P loading. Deeper ponds can result in anoxic conditions, which release P back into the water column (U.S. Environmental Protection Agency (USEPA), 1999). Shallower ponds (2.6 m or less) can also release P from internal sediment through mechanisms that differ from deeper ponds, such as resuspension of nutrient-laden sediment due to wind perturbation and high pH due to high photosynthetic activity (Jensen & Andersen, 1992; Kowalczewska-Madura & Gołdyn, 2012; Lake Simcoe Region Conservation Authority, 2011; Serrano & DeLorenzo, 2008; Welch & Cooke, 2005). Land disturbance activities within the watershed of a pond can also affect the amount of pollutants received in the pond (Mallin et al., 2002).

To prevent pollutant release, monitoring and maintenance schedules are typically implemented. Establishing overarching monitoring guidelines such as sampling location within a pond can be a challenge given the individuality of ponds and the surrounding landscape. P release can vary spatially within a water body (Ogdahl et al., 2014), due to different organic composition and biological activity (Kowalczewska-Madura & Gołdyn, 2012). Datry et al. (2003) found varying solute concentrations at different locations in a stormwater infiltration basin and noted that the location of a sample is an important factor in determining the representative concentration of pollutants. Sampling at multiple locations for one pond can be costly.

Ponds should also be maintained regularly to prevent retention ponds from contributing pollutants to downstream water bodies. Dredging is a typical solution for removing nutrient-rich sediment from ponds, but can be expensive due to permitting and the need to hire professional engineers, particularly if there may be hazardous elements in the sediment (Center for Watershed Protection, 2004; Welch & Cooke, 2005). Temporary solutions such as alum can be used to inactivate P through sorption. However, these solutions may be as costly as dredging given the frequency required to maintain clean pond conditions (Welch & Cooke, 2005), and may negatively impact biota if not properly applied (Pilgrim & Brezonik, 2005).

Given the variety of conditions by which wet retention ponds can release P, targeted monitoring and maintenance can be used to identify and capture pollutants released from these ponds. Such a tactic can reduce time and cost in maintaining ponds. A model that correlates pond characteristics with the concentration and spatial distribution of pollutants in a pond can aid in identifying ponds with high pollutant concentrations and where the pollutants tend to concentrate within the pond. Decisions for targeted monitoring and maintenance efforts can then be based off of these model assessments. The objectives of the study were therefore to: 1) determine the concentration and spatial distribution of P in a range of pond types, and 2) develop models to correlate P concentrations with pond attributes. The main focus of this study was on TP concentrations in the water column and sediment; nitrate and heavy metals were also evaluated. The results from this study can identify pond attributes associated with higher pollutant loads and potentially provide guidance for where targeted pond sampling and maintenance efforts would be most effective and.

Methods

Description of Ponds and Sampling Protocol

Five ponds in Montgomery County, VA, were chosen for this study. Two ponds were in agricultural lands on private property (designated as Ag1 and Ag2), and three ponds were in urban settings, one of which was located on a golf course (designated as Urb1, Urb2, and Urb3). All five ponds were less than 2 m deep. All sampled ponds except for Ag2 consisted of an upper pond and lower pond. The lower pond was sampled to obtain a representation of the water quality leaving the pond system. More details of each pond are provided in Table 2.1.

Samples from each pond were collected between June 30, 2014 and July 14, 2014 at similar times during the late morning. All water and sediment samples for a pond were taken on the same day and same sampling trip. Water and sediment samples were taken at the inlet, outlet, and middle of each pond at least 1 m away from the shore or inlet/outlet area. Water samples and water quality data were collected starting from 0.25 m below the surface of the water and continued at increments of 0.25 m until the bottom was reached, where a sample was taken approximately 0.05 m from the bottom. A multiparameter water quality sonde (Model 6920 V2-2, YSI Incorporated, Yellow Springs, OH) and 2.2-L horizontal Van Dorn sampler (Beta Plus model, Wildco, Yulee, FL) were submerged simultaneously to collect water samples and water quality data. Data obtained from the sonde included temperature, pH, dissolved oxygen (DO), turbidity, and conductivity. Once in-situ water quality data were recorded, a water sample was collected using the Van Dorn sampler and stored in a 1-L and a 250-mL acid-washed polypropylene container to be analyzed for dissolved nutrients plus metals and total nutrients respectively. Equipment, field, and trip blanks as defined by the U.S. EPA (U.S. Environmental Protection Agency (USEPA), 2009b) were also taken at each sampling site. Sediment cores were obtained at the inlet, outlet, and middle of each pond after collecting water samples. Samples were collected using a K-B corer (WildCo, Yulee, FL) and were taken within 1 m of the water samples.

Water samples were placed in a cooler and transported to the laboratory for processing immediately after sampling. The 250-mL sample bottle was placed in a freezer until analysis for total nutrients. Oxidation reduction potential (ORP) measurements were taken using an Orion Versa Star advanced electrochemistry meter (Thermo Fisher Scientific, Waltham, MA) on the 1-L sample. This sample was then filtered through a 0.45-μm filter using a peristaltic pump and frozen until analysis.

Sediment samples were immediately frozen until processing for sediment tests. The inlet sediment sample for pond Ag1 was misplaced during transport; therefore, nutrient and heavy metal information for this sample could not be processed. Prior to testing the sediment, the cores were split into two sections: the top two centimeters (0-2 cm, called “surface”) and two centimeters to ten centimeters (2-10 cm, called “subsurface”). Since some core samples did not extend beyond these depths, any remaining sample below 10 cm was not analyzed. The surface and subsurface core sections were freeze dried to remove all moisture and prepare the sample for digestion.

Water and Sediment Analyses

Water samples were tested for dissolved P (DP_{wat}), TP in the water (TP_{wat}), sulfate, dissolved organic carbon (DOC), nitrate (NO_3), total nitrogen (TN), and dissolved metals. DP_{wat}, TP_{wat}, and TN were measured using a SEAL AutoAnalyzer3, Multitest MT18 (Mequon, WI), which used Method 4500-P F. to determine orthosphosphate concentrations (Standard Methods for the Examination of Water and Wastewater, 2012). Samples that were analyzed for TP_{wat} and TN were digested with persulfate and autoclaved to oxidize the samples prior to analysis on the SEAL. NO_3 was also measured using the SEAL Autoanalyzer using Method 4500-NH_3^- F. (Rice et al., 2012). Sulfate was measured using a Dionex ICS-3000 Ion Chromatography System, which used Method 4110B to analyze anions (Standard Methods for the Examination of Water and Wastewater, 2012). DOC was measured using a Shimadzu TOC-V_{cph} Total Organic Carbon Analyzer (Shimadzu, Tokyo, Japan). Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Spectro ARCOS ICP Model FHS16, Mahwah, NJ).

Sediment samples were tested for P and metals. Each sediment core segment was digested using EPA Method 3050B. The digestate was analyzed using ICP-AES for the following elements: Al, Cd, Cr, Cu, Fe, Hg, Ni, P (denoted as P_{sed}), Pb, and Zn.

Statistics and Modeling

Data were analyzed in order to relate pond characteristics (e.g., pond surface area, sampling depth, pH) to pollutant concentrations (water and sediment). Pond water quality data collected at the pond were included in statistical analysis and modeling. Pond and watershed dimensions were estimated using Google Earth. Pond age estimates were obtained via interviews with the landowner, facilities manager, or reviewing historical Google Earth imagery.

Analysis of variances (ANOVAs) were performed to determine significance of sampling locations and depths across all ponds. This analysis was performed for both TP_{wat} and TP_{sed} concentrations and heavy metal concentrations using R Studio (version 1.1.442; Boston, MA) and R statistical software (version 3.2.3; Vienna, Austria). A significance level of $p<0.05$ was used to determine significance.

Four models were developed to correlate pond characteristics with TP_{wat} and TP_{sed}. Two models were developed with the purpose of finding explanatory variables that achieved the highest correlation with TP_{wat} and TP_{sed} respectively (referred to as “highest correlation” models). However, achieving the “highest correlation” models required variables that needed to be collected at the pond and measured in a lab with specialized instruments (e.g., iron concentration). Two additional models were therefore developed with the purpose of determining whether TP_{wat} and TP_{sed} can be estimated using explanatory variables that can be collected without additional sample processing (referred to as “rapid assessment” models). The “highest correlation” models were labeled Water Model A and Sediment Model A, and the “rapid assessment” models were labeled Water Model B and Sediment Model B.

Linear mixed effects models were used to develop the four models. The pond site was used as the random variable for all models. Interactions between pond site and other explanatory variables could not be included due to insufficient number of data points. The dependent variable was TP_{wat} for modeling P concentration in water, and P_{sed} for modeling P concentration in sediment. A list of explanatory variables tested for correlation with TP_{wat} and TP_{sed} is provided in Table 2.2. Variables that were nonlinear, such as P_{sed} concentration, pH, Al, and Cu, were linearized by either taking the natural log or squaring so that they could be used in a linear model. R statistical software (RStudio version 1.0.136) was used with the addition of the “lmerTest” package (Kuznetsova et al., 2015) for mixed effects model tools and “piecewiseSEM” package (Lefcheck, 2016) for goodness-of-fit statistics for mixed effects models. The R package “ggplot2” (Wickham, 2009) was used to generate graphs.

Results

Water Analysis

TP_{wat} concentrations were higher than nationally recommended levels (US EPA, 1986). DP_{wat} levels ranged from 0.003 mg/L to 0.13 mg/L; however, DP_{wat} concentrations in sample blanks ranged from 0.001 mg/L to 0.10 mg/L, suggesting either contamination of the blanks or unreliable DP_{wat} results from pond samples. The low DP_{wat} concentration is unsurprising since DP_{wat} quickly sorbs to sediment to become particulate P (Boyd, 1971; Corell, 1998), which would be measured as TP_{wat}. Therefore, no conclusions can be made regarding patterns seen in DP_{wat} from the water samples.

TP_{wat} concentrations ranged from 0.041 mg/L to 1.4 mg/L across the ponds, with maximum concentrations generally found at the outlets of ponds and in the top 0.25 m of the water column. A comparison of TP_{wat} concentrations across sampling locations and depths across ponds is provided in Figure 2.1(a). ANOVA results revealed that sampling location was significant, but sampling depth was not. The highest TP_{wat} concentration was found in Urb3, a pond within a research center.

NO_3 and dissolved heavy metal concentrations were either below the levels recommended by the US EPA (US EPA, 2016; US EPA, 1986) or below instrument detection limits. The maximum NO_3 concentration found was 0.94 mg/L, which was well below the limits that are protective of warm water fish (5 mg/L) and drinking water level requirements (10 mg/L) (US EPA, 1986). Cd, Cr, Cu, Hg, Ni, and Pb were all below detection limits on the ICP-AES (0.0004, 0.0002, 0.0025, 0.0022, 0.0036, and 0.0088 mg/L respectively). Fe and Zn maximum concentrations were 0.14 mg/L and 0.040 mg/L respectively over all ponds, which were lower than nationally recommended levels for freshwater criterion maximum concentrations (CMC) of 7439 mg/L and 7441 mg/L, respectively (US EPA, 2016).

Sediment Analysis

Sediment samples had significant concentrations of heavy metals and P trapped in sediment, most often in the surface sediment and located in the middle or outlet of the pond. Median and variance of TP_{sed} concentrations across ponds are shown in Figure 2.1b. Average TPsed concentrations across all ponds ranged from 240 mg/kg to 900 mg/kg with Ag1 having the lowest mean concentration and Urb1 the highest. The maximum TP_{sed} was 1100 mg/kg in Urb1, which is equivalent to 10.6 mg/L in solution, seven times the highest concentration found in the water column and four hundred times the nationally recommended limit for TP in lakes and reservoirs (U.S. Environmental Protection Agency (USEPA), 1986). Concentrations and the spatial distribution of TP_{sed} for each pond are provided in Figure 2.3. ANOVA results showed that sampling location was significant for TP_{sed} concentrations, and depth was not significant.

Cu, Fe, Hg, Ni, Pb, and Zn concentrations exceeded the ecological screening levels for freshwater sediment in at least one sediment sample in each pond. Maximum concentrations of each listed metal within each study pond and the corresponding location and depth are provided in Table 2.3. At least one sample from each pond exceeded the U.S. EPA Region 3 risk level for Fe concentration (20000 mg/kg) and Hg concentration (0.18 mg/kg) for freshwater sediment (U.S. Environmental Protection Agency (USEPA), 2006). Ni concentrations in Urb2 exceeded the U.S. EPA Region 3 risk level (22 mg/kg) and was significantly higher ($p<0.05$) than other ponds. ANOVA results indicated that different sampling locations and different sampling depths were not significantly different from each other for all metals.

Model

Coefficients, levels of significance, and goodness-of-fit are provided for all models in Table 2.4 (water models) and Table 2.5 (sediment models). The R^2 for the "rapid assessment" models, Water Model B and Sediment Model B, were 0.57 and 0.71 respectively, while the "highest correlation" models, Water Model A and Sediment Model A, yielded R^2 of 0.8 and 0.83 respectively. Although the "field application" models could provide rapid assessment of TP concentrations in pond water and sediment, the compromise in accuracy is significant.

Variables that contributed to the best goodness-of-fit over these models were pond type (urban/agricultural/golf), sampling location (inlet/middle/outlet), pH, temperature, length-to-width ratio, and various metal concentrations. Except for Water Model A, the marginal R^2 and conditional R^2 for all other models differed by >0.07, indicating that there existed features unique to each pond that could explain the variability in the data but were not identified in the regressions. All coefficients for the explanatory variables were positive except for temperature in Sediment Model B. These trends indicate that an increase in these variables correlated with an increase in TP_{wat} and TP_{sed} concentration except for temperature, which was inversely proportional to TP_{sed} concentration.

Discussion

Results indicate that P and certain metals are at levels that exceed environmental recommendations and can have major impacts on the pond and its environment should they be released. All water samples exceeded national recommendations at which TP_{wat} may promote nuisance algae. Median and variance in TP_{wat} concentrations across all ponds are compared in Figure 2.1(a). All samples exceeded the national water quality recommendation of 0.025 mg/L for lakes and reservoirs as noted in Figure 2.1a (US EPA, 1986) and the US EPA Ecoregion XI recommendation of 0.008 mg/L for lakes and reservoirs (US EPA, 2000). Such high TP_{wat} concentrations can result in eutrophication of the water body, which can disrupt the local ecology and potentially impact recreational activity (Chislock et al., 2013).

All ponds except Ag1 contained high TP_{sed} concentrations, averaging approximately 695 mg/kg. Given its current state, TP_{sed} is unavailable to plant and animal life, but multiple studies have demonstrated that this form of P can be released back into the water column by various mechanisms, including sediment resuspension, anoxic conditions along the sediment-water interface, and decomposition of organic matter that have settled along with the sediment (Datry et al., 2003; Søndergaard et al., 2001; Welch & Cooke, 2005; Wong et al., 1999). A review on P retention in streams and wetlands notes that high pollutant concentrations in the sediment in particular are more prone to dissolve back into the water (Reddy et al., 1999), resulting in biological degradation.

Finding high heavy metal concentrations across all ponds is unsurprising given the surrounding landscape, and the metals can potentially have negative impacts to the pond and downstream ecosystems. Multiple studies have found high concentrations of heavy metals in pond sediment (Datry et al., 2003; Kemp et al., 2005; Marsalek et al., 1997; Petticrew & Arocena, 2001; Spears et al., 2007). These studies also warned of the potential for these metals to be released under certain conditions such as changes in pH or during anoxic conditions, and released into the water column or percolate downwards (Datry et al., 2003; Kemp et al., 2005; Marsalek et al., 1997; Petticrew & Arocena, 2001; Spears et al., 2007).

A more detailed discussion of pollutant concentrations in context of pond characteristics and model results provides explanations as to how and why P is distributed across the ponds. Understanding these relationships can aid in discovering better predictive models and adjusting monitoring and maintenance activities accordingly.

Water Modeling and Analysis

The results of the “field applications” model, Water Model B, demonstrate that, although a few select variables can explain a significant amount of variability of TP_{wat} concentrations across all ponds, more model accuracy would require water testing or more specific details about the individual pond.

Water Model A (“best accuracy” model) yielded a marginal and conditional R^2 of 0.8 when including the variables pH and Fe concentration. pH at extreme levels (<4 and >9) can result in P release from sediments due to uncharged phosphates at lower pH and competing OH- ions at higher pH (Pratt et al., 2007). In this study, TP_{wat} concentrations generally appeared to increase with pH < 7.23 and pH > 9.31, which roughly coincides with the levels from the literature. Increased P concentrations at pH close to neutral imply that other factors are correlated with P concentrations. However, adding these factors to the model (e.g., DO, ORP, temperature, and DOC) did not improve its accuracy, most likely because their effects were subsumed by other explanatory variables. P is well known to sorb to Fe (Boyd, 1971; Brady & Weil, 2008; Reddy et al., 1999), which would explain why Fe concentration was the dominant factor that explained the most variability of P in the water column.

The fact that the marginal and conditional R^2 for Water Model A are the same indicates that the fixed effects variables accurately capture the common attributes across all ponds, leaving no random effects unique to each pond. However, submitting laboratory samples to measure Fe concentrations would be similar to submitting tests for P concentration. Therefore, developing a model without Fe concentration as a predictor would be ideal.

Water Model B was developed for the purpose of predicting TP concentrations and distributions without extensive lab testing and for ease of use. This model achieved a marginal R^2 of only 0.57

with a conditional R^2 of 0.64 suggesting that 0.07 of the model is explained by properties unique to each pond that has not been explained by the included explanatory variables. Further examination of the explanatory variables in Water Models A and B provided more understanding of P distribution within ponds and can possibly elucidate which variables could replace highly predictive variables such as Fe concentration.

In Water Model B, higher length-to-width ratios (LWratio) tended to correlate with higher TP_{wat} concentrations because this ratio was generally positively correlated with detention time (Mallin et al., 2002). Larger detention times would allow TP_{wat} to settle, keeping TP_{wat} in the pond rather than flushing out of the pond and therefore reflecting a higher concentration.

Sampling locations, specifically the middle and outlet locations, were significant in both Water Models A and B, indicating a positive correlation between these sampling sites and high TP_{wat} concentrations. Higher TP_{wat} concentrations at the outlet and middle of the ponds were most likely due to a higher distribution of finer sediment in these locations. Smaller particles have higher settling times, as well as larger surface areas on which more P can sorb (Marsalek et al., 1997; Wu et al., 1996). The model and collected data therefore suggest a high concentration of finer sediment with adsorbed phosphorus, which can potentially be released from the pond given the location of these high concentrations. The middle sampling location may also be significant because maximum TP_{wat} concentrations of Urb1 were found in the middle of the pond, most likely due to two islands located at this sampling location. These islands would reduce water velocities, thereby promoting sediment deposition.

One exception where maximum TP_{wat} concentration was not found at the middle or outlet was at Ag2. This was likely because the inlet to Ag2 TP_{wat} was extremely shallow and livestock (and related nutrient-rich fecal matter) tended to concentrate at this location. This exception highlights the unique features of each pond and that a site visit or more in-depth data collection of the pond would provide a more accurate characterization of pond water quality.

An urban pond type was significant in explaining an increase in TP_{wat} concentrations. While it was unsurprising that the urban pond type positively correlated with TP_{wat} concentration due to the presence of finer sediment runoff (Hubbart, 2012), the results maybe be overly influenced by one pond. Urb3 appeared to have an unusually high TP_{wat} concentration, which would significantly influence model results. Urb3 was the newest pond out of the study ponds. Young ponds typically have a larger P retention capacity because they have not received significant nutrient-rich stormwater yet (Sonderup, Egemose, Hoffmann, Reitzel, & Flindt, 2014). However, newly constructed ponds may initially have a large concentration of TP_{wat} if the existing soils and vegetation within the new pond are high in P (Boyd, 1971). The study area was historically an agricultural area, which has been proven to be rich in nutrients like P (Ludwig et al., 2016). This detail, combined with construction in the area adjacent to the pond, would explain a major influx of nutrients and heavy metals into this pond. This exception again highlights the complications of modeling ponds given their individual histories and environment.

Other variables that were included in the water models but were not significant included sampling depth. Both deep and shallow ponds can develop anoxic conditions either through the development of an anoxic hypolimnion layer for deeper ponds or through other mechanisms such as accumulation of biogenic P, sediment resuspension, or wind perturbation (Jensen & Andersen, 1992; Lake Simcoe Region Conservation Authority, 2011; Nürnberg, 1987; Ogdahl et al., 2014; Shinohara et al., 2016; Welch & Cooke, 2005). The end result is that sediment P is released into the water column (Jensen & Andersen, 1992; Lake Simcoe Region Conservation Authority, 2011; Nürnberg, 1987; Ogdahl et al., 2014; Shinohara et al., 2016; Welch & Cooke, 2005). In this study, only one pond, Urb1, generally appeared to have increased TP_{wat} concentrations at depths >0.75 (see Figure 2.2), which may suggest the development of a hypolimnion layer. This trend was not significant, however, when an ANOVA was applied. Maximum TP_{wat} concentrations were found towards the surface of the pond in three out of the five study ponds rather than at depth. The individual characteristics of the ponds could again explain why there is not a consistent pattern in the data. For Ag2, high TP_{wat} concentrations occurred in the shallow inlet area, which was explained in previous paragraphs. Urb2 and Urb3 may have higher TP_{wat} concentrations because urban sites tend to accumulate finer sediment due to increased imperviousness associated with this land type (Hubbart, 2012). Factors other than depth appear to have more influence or are more highly correlated to TP_{wat} concentrations.

Variables such as depth and pond location were used to attempt to predict P concentrations because they not only could predict the location of high P concentrations, but they can also easily be applied in a field setting. These variables most likely subsumed other potential explanatory variables; for example, the outlet variable most likely also represents particle size. More variables will need to be identified, however, in order to replace the high correlation between Fe concentration and P concentration since no combination of explanatory variables used for the “field application” model could achieve the high correlation of Fe with P in the “best accuracy” model. Despite this disparity, the above observations can still help inform monitoring and maintenance activities by providing likely locations for sampling or filtering systems.

Sediment Modeling and Analysis

Sediment model results reveal that the unique traits of each pond are even more prevalent when attempting to predict P_{sed} concentrations than for the water models. The difference between marginal and conditional R^2 values for Sediment Models A and B were 0.075 and 0.14, indicating that variations in data are explained by random effects unique to the ponds even more so than in the water models. The most significant variable for Sediment Model A was Al concentration, while the most significant variable for Sediment Model B was temperature. Both of these variables are known to impact P_{sed} concentration. Al, Ca, and Fe are react with P through either a sorption (Al and Fe) or precipitation (Ca) reaction (Boyd, 1971). Mineralization of organic-bound P occurs when temperature increases, resulting in a release of P into the water column and therefore a P loss from the sediment (Jensen & Andersen, 1992).

Other explanatory variables that were significant most likely coincided with the characteristics of one pond that dominated over other ponds and also coincided with high P_{sed} concentrations. Cu was significant in Sediment Model A most likely because Urb1 contained Cu concentrations that were four to seventeen times higher than other ponds. Cu has been a component of algaecides to treat algal blooms (U.S. Environmental Protection Agency (USEPA), 2018), which would therefore indicate a pond that has had issues with excess nutrients and would therefore positively correlate with P concentration. The golf dummy variable was also an explanatory variable that had significant impact on P_{sed} prediction for Sediment Model B although no obvious explanation can be found for this relationship.

Visual trends could be seen between P_{sed} concentration and sampling location and depth but were not significant in the models. However, other factors unique to the ponds appeared to dominate the sediment models. Maximum P_{sed} concentrations were found in the middle of three ponds and at the outlet of two ponds. These trends suggest that metals were in fine, particulate form, which take longer to settle (Wu et al., 1996) and which would mean that accumulation occured closer to the middle or outlet of the pond. Maximum P_{sed} concentrations were found in the surface layer of all but one of the study ponds, indicating recent additions of P_{sed} to most of these ponds. Any released P_{sed} from this surface sediment layer would immediately enter the water column, possibly causing algal blooms (Chislock et al., 2013). It is also interesting to note that for Urb2 and Ag2, the minimum and maximum P concentrations are at the same sampling location but different sediment layers. These results demonstrate that nutrient concentrations change over time, and prove that regular monitoring is needed in order to prevent nutrient saturation and therefore potential release. These trends also demonstrate that, although these variables are not statistically significant, observations of the pond's characteristics and surrounding landscape can provide explanations for why P_{sed} concentrations are high in certain locations.

Conclusion

Models created to predict P concentrations in the water column and sediment demonstrated that metal concentrations were significantly associated with high P concentrations. In particular, Fe concentrations were significantly correlated with TP_{wat} concentrations, and Al and Cu were significant factors in predicting P_{sed} concentrations. Sampling location proved significant in predicting TP concentrations in the water but was not significant for predicting sediment P. "Field application" models could not achieve as high a precision as the "best accuracy" models, which require sample testing. However, given the uniqueness of each pond sampled, the variables that were significant in these models demonstrate obvious indicators of P concentration. Sampling of additional ponds would provide a more accurate predictive model and further confirm the significance of the correlation between these particular pond features and P concentrations.

This study also revealed in all ponds sufficiently high concentrations of P in the water and sediment, and sufficiently high concentrations of certain metals in the sediment, that can cause potential ecological harm. General trends in spatial location of high phosphorus concentrations in the water column could be observed. Initial conclusions are that taking a surface sample near the outlet may not necessarily yield the highest concentration that can be found in a pond, but neither is it an unlikely location to find high TP_{wat} concentrations. If sampling opportunity is limited due to time or budget constraints, a surface grab sample towards the pond outlet has a likely chance of representing a high TP_{wat} concentration for the pond.

The highest concentrations of P in the sediment were towards the middle of ponds, although high concentrations were also located at the outlet of some ponds. A study on sediment particle size distribution over these ponds could explain this distribution of high P concentration as different-sized particles would settle at different rates (Brady & Weil, 2008). Sediment-bound P was generally located in the top surface layer of sediment, indicating recent inputs of P and therefore that nutrient input into the ponds is still an issue.

Although more data are needed to support the trends found in this study, the results of the data analysis and modeling effort provide insight into which pond features may have a significant impact on P concentrations. The “field application” model can aid pond owners and maintenance workers in determining which ponds require immediate monitoring and maintenance by providing a rough estimate of P concentrations in the pond. Understanding where P concentrations are the highest in a pond can provide a more targeted approach to monitoring and maintenance, particularly given any financial or time constraints in monitoring or maintenance efforts. Such targeted efforts would remove the optimal level of pollutants from ponds while providing cost savings. Finally, this information can be used to install a filtration system in a location that would best optimize P removal.

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Tables

Table 2.1. Details of study ponds located in Montgomery County, VA.

Pond ID	Pond Type	Pond System	Built	Last Dredged	Watershed Area (m^2)	Pond Volume (m^3)	Land Use	Other Features	Mean Depth	Max Depth
Urb1	Urban	2 ponds	1937	1986	7,100,000	14,000	96% urban 2% ag 2% forest	Primarily commercial, residential	0.82	1.63
Urb2	Urban/golf course	2 ponds	1960's	N/A	210,000	1,000	43% urban 57% forest	Golf course, local road, residential	0.58	1.25
Urb3	Urban	2 ponds	2011	N/A	89,000	1,200	20% urban 80% urban/ag	Commercial, fields, highway	0.58	1.00
Ag1	Agricultural	1 pond	1960's	1996	27,000	1,600	100% ag	1 local road, minimal ag use	0.70	1.25
Ag2	Agricultural	2 ponds	1960's	2001	200,000	630	28% urban 72% ag	2 local roads, some residential, active ag use	0.48	1.00

Table 2.2. Explanatory variables considered in linear mixed effects models for water and sediment phosphorus.

Water Models	Sediment Models
Pond type dummy (“d_{urban}”, “d_{golf}”, and “$d_{agricultural}$”)	Pond type dummy (“d_{urban}”, “d_{golf}”, and “$d_{agricultural}$”)
Pond sampling location (“d_{outlet}”, “d_{inlet}”, and “d_{middle}”)	Pond sampling location (“d_{outlet}”, “d_{inlet}”, and “d_{middle}”)
Sampling location	Sampling location
Water sampling depth	Sediment sampling depth
Pond length	Pond length
Pond width	Pond width
Pond length-to-width ratio	Pond length-to-width ratio
Pond surface area	Pond surface area
Pond volume	Pond volume
Pond age	Pond age
Watershed area	Watershed area
Water temperature	Water temperature at lowest depth
Conductivity	Conductivity at lowest depth
pH	pH at lowest depth
Percent dissolved oxygen	Percent dissolved oxygen at lowest depth
Turbidity	Turbidity at lowest depth
Redox value	Redox value at lowest depth
Sulfate	Metals in sediment (Al, Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn)

Table 2.3. Maximum heavy metal concentrations by pond, location, and depth. Concentrations that exceeded the US EPA Ecoregion 3 recommended levels for freshwater sediment are in bold.

	Urb1	Urb2	Urb3	Ag1	Ag2
Cu (mg/kg)	**108.7**	**39.6**	20.8	21.8	18.7
Location	Outlet	Inlet	Inlet	Middle	Middle
Depth	Subsurface	Subsurface	Surface/Subsurface	Subsurface	Surface
Fe (mg/kg)	**27192**	**22544**	**27314**	**23764**	**37103**
Location	Outlet	Middle	Inlet	Outlet	Outlet
Depth	Subsurface	Surface	Surface	Subsurface	Surface
Hg (mg/kg)	**0.9**	**0.9**	**0.9**	**1.1**	**1.1**
Location	Outlet	Outlet	Outlet	Outlet	Middle
Depth (m)	Surface	Surface	Subsurface	Subsurface	Surface
Ni (mg/kg)	22.4	**30.3**	17.8	15.1	18.5
Location	Outlet	Middle	Inlet	Middle	Middle
Depth (m)	Subsurface	Subsurface	Surface	Surface	Surface
Pb (mg/kg)	**137.7**	16.9	**86.1**	14.2	19.1
Location	Inlet	Middle	Outlet	Outlet	Outlet
Depth	Surface	Surface	Surface	Subsurface	Surface
Zn (mg/kg)	**420.9**	111.1	107.3	37.2	42.2
Location	Outlet	Inlet	Inlet	Middle	Middle
Depth	Subsurface	Subsurface	Surface	Subsurface	Surface

Table 2.4. Fixed effects for Water Model A (“best accuracy” model) and Water Model B (“rapid assessment” model).

Water Model A

Explanatory Variable	Coefficient
Intercept	-8.49***
d_{urban}	1.66***
d_{outlet}	1.22***
d_{middle}	0.548**
pH^2	0.0671***
Fe_concentration	11.2***
marginal R^2=0.799	conditional R^2=0.799

***0 **0.001

Water Model B

Explanatory Variable	Coefficient
Intercept	-4.86***
LWratio	0.769**
d_{outlet}	0.953***
d_{middle}	0.519*
marginal R^2=0.567	conditional R^2=0.642

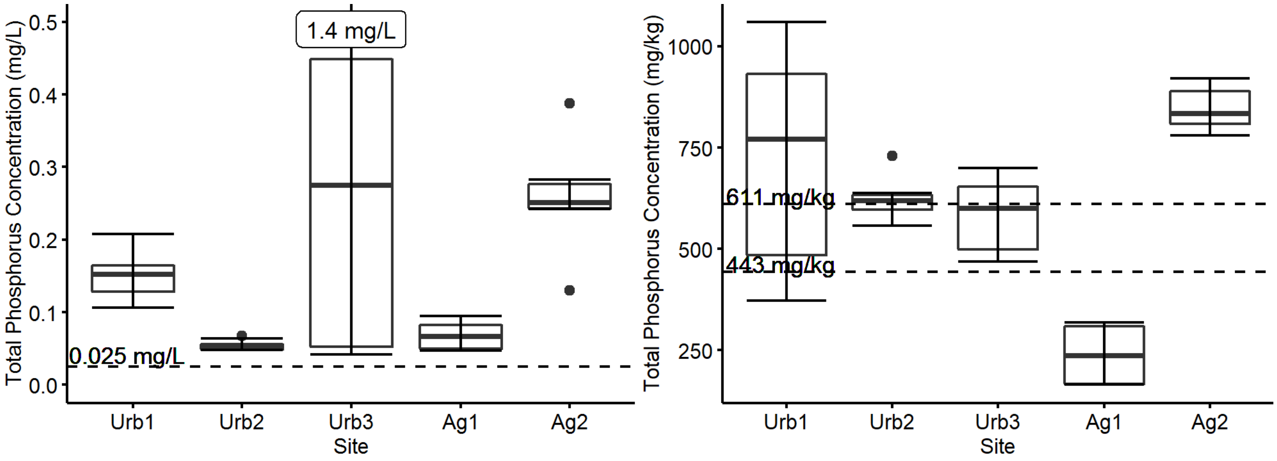
***0% **0.001 *0.01

Table 2.5. Fixed effects for Sediment Model A (“best accuracy” model) and Sediment Model B (“rapid assessment” model).

Sediment Model A	
Explanatory Variable	Coefficient
Intercept	-2500***
LWratio	225**
ln(Al)	231***
ln(Cu)	99.2*
marginal R^2=0.829	conditional R^2=0.904
***0 **0.001 *0.01	

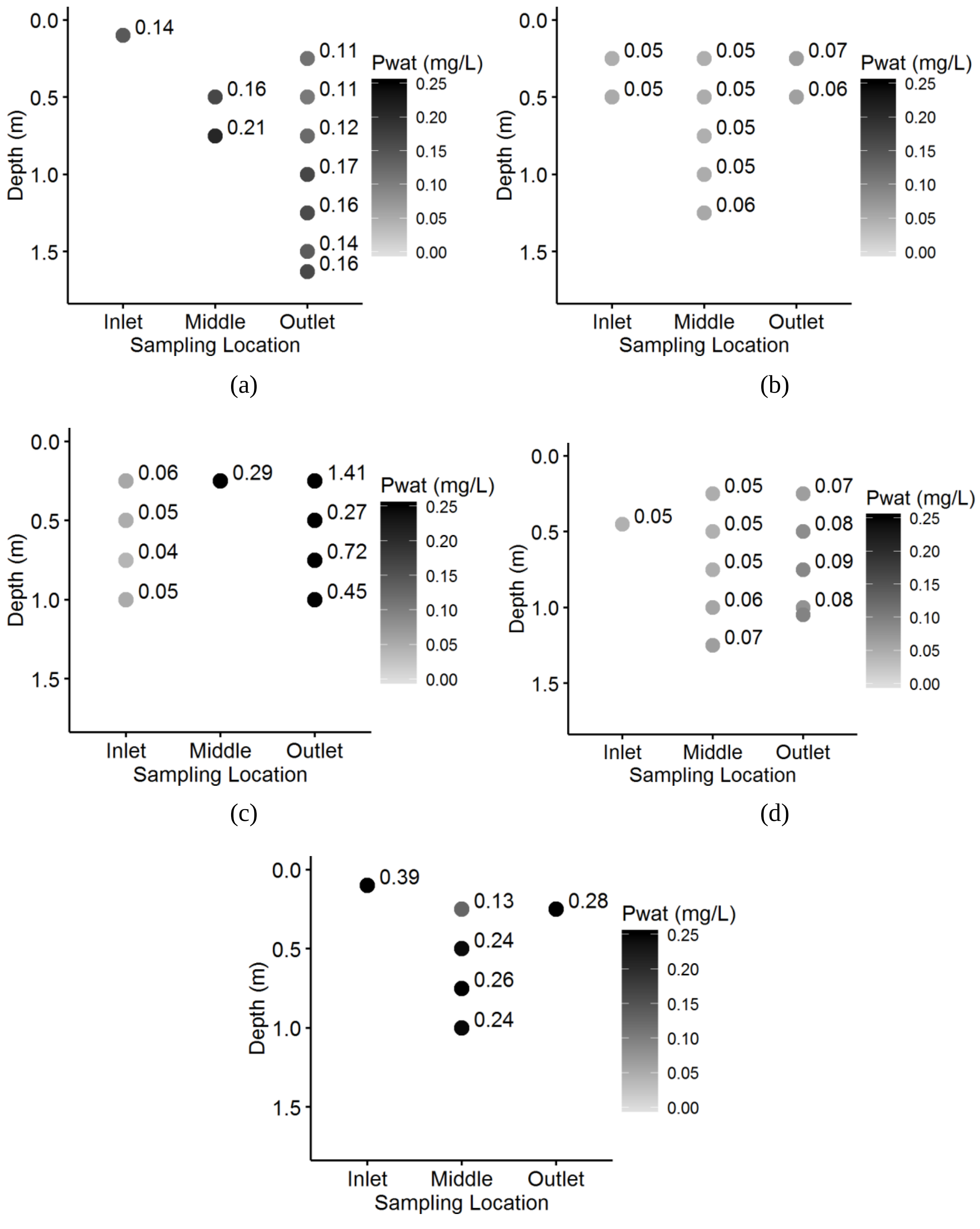
Sediment Model B	
Explanatory Variable	Coefficient
Intercept	4090***
temperature	-139***
d_{golf}	405*
marginal R^2=0.707	conditional R^2=0.850
***0 **0.001 *0.01	

Figures



(a) (b)

Figure 2.1. Comparison of total phosphorus concentrations across study ponds in (a) water samples, and (b) sediment samples. Dashed line for water samples indicate U.S. EPA recommended limit for total phosphorus in the water to prevent nuisance algae (U.S. Environmental Protection Agency (USEPA), 1986). Dashed lines for sediment samples indicate potential range for mesotrophic lakes (Dong, Yang, & Liu, 2011).



(a)

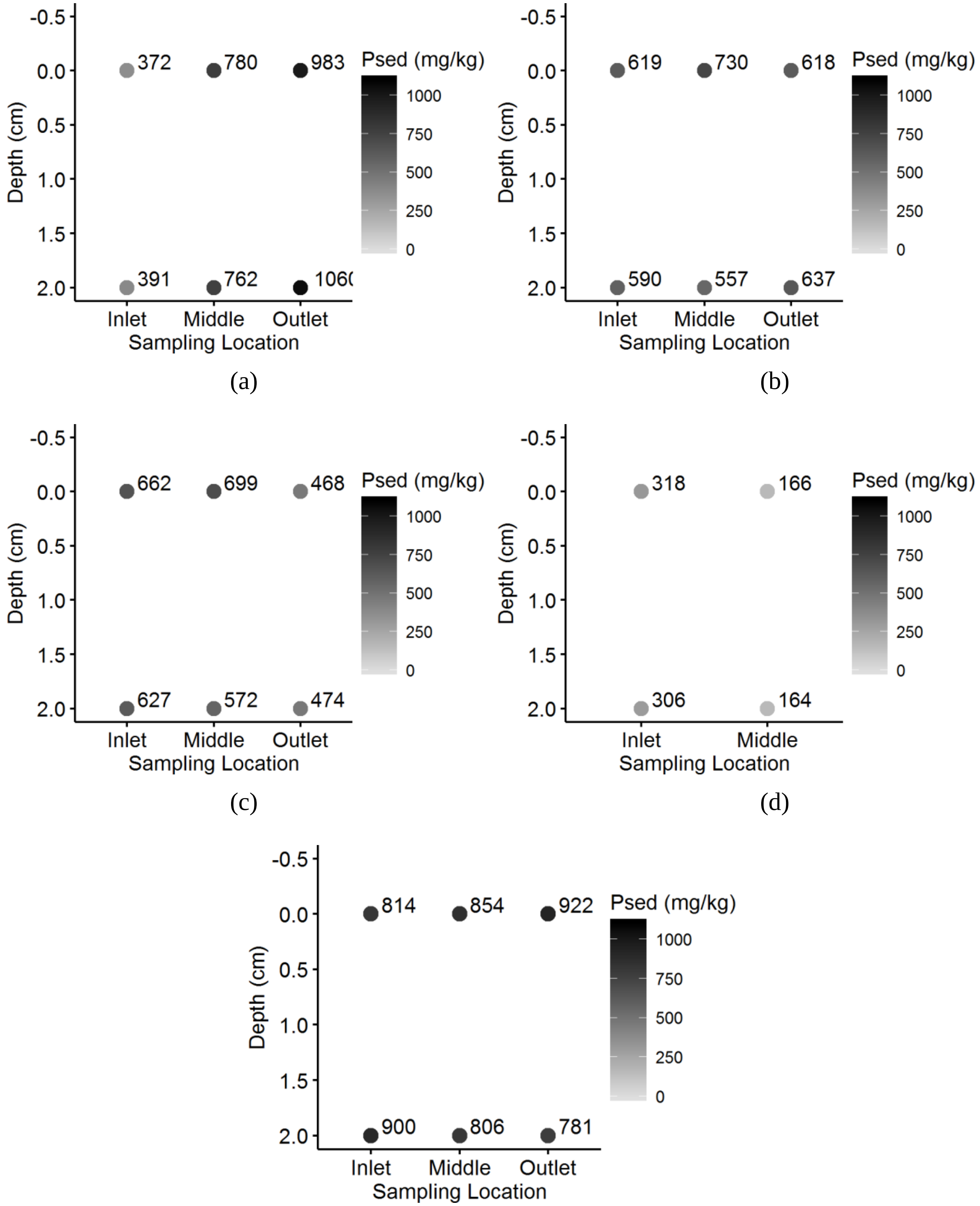
(b)

(c)

(d)

(e)

Figure 2.2. Comparison of total phosphorus in the water (TP_{wat}) concentrations by sampling location and sampling depth across study ponds: (a) Urb1, (b) Urb2, (c) Urb3, (d) Ag1, and (e) Ag2



(a) (b) (c) (d) (e)

Figure 2.3. Comparison of total phosphorus in the sediment (TP_{sed}) concentrations by sampling location and sampling depth across study ponds: (a) Urb1, (b) Urb2, (c) Urb3, (d) Ag1, and (e) Ag2

3. Physicochemical Properties and Phosphate Sorption of Corn Stover, Mixed Hardwood, and Rice Husk Biochars

Abstract

Traditional Best Management Practices (BMPs) can be effective at removing multiple pollutants, particularly in urban areas. However, removal efficiencies of certain pollutants can be less than 30%, BMP structures can require a substantial amount of space, and they can result in costly maintenance regimes, especially if saturated with pollutants. One alternative solution would be to develop a stand-alone filtration system that has a small footprint and easily removable and recyclable filter media. Biochar was considered for this study as a possible filter media that can remove phosphate from stormwater. The objectives of this study were to characterize the physicochemical properties of four biochars, and to determine its sorption capacity for phosphate. The four biochars tested were corn stover biochar pyrolized at 400°C (CS400), corn stover biochar pyrolized at 600°C (CS600), mixed hardwood biochar pyrolized at 600°C (MH), and rice husk biochar pyrolized at up to 750°C (RH). Tests performed to characterize biochar properties included surface area analysis, zeta potential measurement, measurement of water-extractable elements including phosphorus, and elemental analysis including carbon and nitrogen content as well as Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, and Zn concentrations in the biochar. Sorption results indicated that all four biochars released phosphate into the water up to a solution concentration of 2.9 mg P/L. At concentrations higher than this value, MH was able to sorb phosphate. Based on the measured properties of the biochars and sorption results, the most likely mechanism by which MH could sorb phosphate was through sorption onto variable-charge functional groups.

Introduction

Excess phosphorus (P) from urban and agricultural locations contributes significantly to cultural (i.e., anthropogenic) eutrophication in the nation’s water bodies and can negatively impact biological systems, economic systems, and human health (Carpenter et al., 1998; Chislock et al., 2013; Dubrovsky & Hamilton, 2010; Paul & Meyer, 2001; U.S. Environmental Protection Agency (USEPA), 1999). Regulations have reduced P input into waterways, but target values have not been achieved (Chesapeake Progress, 2017). Ironically, as excess P is escaping into the nation’s water bodies, mined P resources are decreasing – P reserve estimates indicate that the natural resource may be exhausted within 80 to 400 years (Cordell et al., 2009; Dawson & Hilton, 2011; Steen, 1998).

Traditional Best Management Practices (BMPs), such as retention ponds and wetlands, trap pollutants such as P that originate from agricultural and urban areas, but these systems have limitations. Common limitations include insufficient stormwater detention time, limited land area for the BMP, and conditions within the BMP that result in pollutant release (e.g., saturation, anoxic conditions) (U.S. Environmental Protection Agency (USEPA), 1999; Weiss et al., 2007; Wong et al., 1999). Improper design or insufficient maintenance of the BMP can also result in sediment or contaminant release (U.S. Environmental Protection Agency (USEPA), 1999; Weiss et al., 2007). Finally, BMP performance can vary significantly (Weiss et al., 2007), decreasing the reliability of the BMP.

One solution that can complement traditional BMPs and reduce the probability of contaminant release is a standalone filtration system. A filtration system can be attached to existing BMPs holding surface water, such as wet retention ponds, and provide additional filtering of stormwater, thereby extending the life of traditional BMPs and reducing or preventing pollutant release. Such a filtration system would require a media that sorbs contaminants. Biochar can be one such media. Biochar is biomass that has been heated in the absence of oxygen in a process called pyrolysis, and has properties similar to organic matter (Coumaravel et al., 2011). A review by Xie et al. (2014) listed the range of conditions and feedstocks that are possible for biochar – pyrolysis temperatures can vary from 220°C to 1040°C, and feedstock for biochar can range from agricultural residue (e.g., corn stalks, rice straw) to animal waste. The properties of biochar, including surface area, pH, and ability to sorb different pollutants, can vary considerably depending on the feedstock used and the pyrolysis process and temperature.

Multiple advantages exist in using biochar as a recycle media. Biochar can be generated from waste products, which will not compete with other food or natural sources. It can also potentially be used as an enriched fertilizer after its use in the filtration system; once saturated with nutrients from the filter, the biochar can be applied to fields as a slow-release fertilizer. In addition, multiple studies have demonstrated that biochar itself is an effective soil amendment with properties such as increasing cation exchange capacity within the soil and high water retention (Chintala et al., 2013; Coumaravel et al., 2011; Lehmann, 2007; Yao et al., 2011a).

Biochar has been investigated for its ability to sorb various contaminants and for its use in environmental remediation. Because of its many potential uses and variations, biochar has been studied extensively. Multiple studies have demonstrated that biochar can sorb dissolved phosphorus (DP) along with other contaminants including organic pollutants, total suspended solids (TSS), nitrate (NO_3), ammonium, and pharmaceuticals (Chen et al., 2011; Chintala et al., 2013; Jung et al., 2013; Reddy et al. , 2014b; Sarkhot et al., 2013; Streubel et al., 2012; Yao et al., 2011b). Studies that have used biochar to capture excess DP have focused mainly on reducing DP in wastewater though and therefore use higher DP concentrations than what is typically found in stormwater (Cao & Harris, 2010; Chen et al., 2011; Fang et al., 2014; Reddy et al., 2014b; Sarkhot et al., 2013; Streubel et al., 2012; Yao et al., 2011b). Studies that use biochar as a stormwater filter tend to focus on contaminants other than DP, such as ammonium, trace organic contaminants, and heavy metals (Reddy et al., 2014b; Tian et al., 2016; Ulrich et al., 2015).

Some studies have applied biochar as a stormwater filter specifically for P and demonstrated its efficacy. Beck et al. (2011) demonstrated that biochar decreased the release of DP and total P (TP) from soils in a simulated rainfall by as much as 43% and 52% respectively when applied as a soil amendment to a greenroof, indicating that biochar can retain P. Reddy et al. demonstrated that biochar can reduce DP, TSS, and NO_3 levels in synthetic stormwater by 47%, 86%, and 86% respectively (Reddy et al., 2014b). Bock et al. (2015) also showed in a lab-scale column experiment that as much as 67% of DP can be removed with bioreactor media that included woody biochar.

In contrast, some studies have found that biochar not only retains a minimal amount of DP but actually releases DP. Hollister et al. (2013) found that oak biochar pyrolized at 350°C and 550°C resulted in minimal sorption and corn stover biochars pyrolized at those same temperatures sorbed virtually zero DP. Soinne et al. (2014) found that adding mixed spruce and pine biochar pyrolized at 550-600°C to different types of soils found that biochar did not increase DP affinity to the soil, and in fact decreased DP affinity for sandy soils. Pratiwi et al. (2016) noted in a batch sorption experiment of rice husk biochar pyrolized at >600°C that DP was released from the char at concentrations lower than 60 mg P/L.

The feedstock and pyrolysis process of biochar can vary significantly, which can explain differences in DP sorption. Morales et al. (2013) found that a pyrolysis temperature greater than 600°C led to more DP release from biochar. Ahmad et al. (2014) noted in a review of biochar studies that surface area tended to increase with increasing pyrolysis temperature. Ahmad et al. (2014) also noted that the amount of nitrogen (N) found in biochars is typically dependent on the feedstock, which can affect the biochar's ability to sorb DP due to competition between the anions for sorption sites.

Given that few studies have applied biochar to stormwater filtration and the limited types of biochar feedstock that have been used in those studies, the goal of this study is to evaluate selected biochars as a stormwater filter and to add to the body of knowledge of biochar properties. Within this context, the objectives for this study are the following: 1.) characterize the physical and chemical properties of four types of biochars (corn stover pyrolized at 400°C and 600°C, mixed hardwood, and rice husk), and 2.) determine the DP sorption capacity of the biochars.

Methods

Biochars

Four biochars from three different feedstocks were chosen for this study. The biochars used were corn stover pyrolized at 400°C (CS400), corn stover pyrolized at 600°C (CS600), mixed hardwood biochar (MH), and rice husk biochar (RH). CS400 and CS600 were sourced from ARTi (artichar.com; Prairie City, IA). MH was sourced from Biochar Now (Berthoud, CO) and created using a slow pyrolysis process in computer-controlled kilns for 8-12 hours and with a temperature between 550-600°C. RH was sourced from Carolina Soil Company (Kinston, NC) and was burned in a stack furnace whose temperature could reach up to 750°C. These biochars were chosen because they were derived from waste products and would therefore not compete with natural resources. They were also chosen based on literature describing biochar traits that would most likely sorb DP, such as high surface area and high base cation concentrations (Chintala et al., 2013; Yao et al., 2011b). Prior to performing any tests on the biochars, they were spread in a thin layer to air dry at approximately 23°C for at least two days. The biochars were then filtered through a 2mm sieve to homogenize particle sizes so that results of filtration experiments would be a reflection of chemical properties and not simply particle size.

Physicochemical Properties

All four biochars were analyzed for carbon and nitrogen content, zeta potential, surface area, pH, conductivity, water-extractable elements, and elemental composition. Carbon and nitrogen content were analyzed using a Costech 4010 elemental analyzer (Costech Analytical Technologies, Inc; Valencia, CA). The zeta potential (ZP) of the four biochars was measured to determine the net charge on the biochar surface. A sample of biochar was mixed with DI water, measured for pH, and injected into a Zetasizer 3000 HSa Particle Sizer (Mavern Instruments; Westborough, MA).

Surface area analysis was performed using N_2 gas on a Quantachrome Instruments Autosorb-1 surface area analyzer (Quantachrome Instruments, Boynton Beach, FL). Prior to analysis, biochars were further filtered through a 0.5mm sieve, and the fraction greater than 0.5mm was kept. Surface area was measured using N_2 gas and an adsorbate gas temperature of 77.3 K. Each biochar sample was outgassed for 19 hours at 200°C. An 11-point Brunauer-Emmett-Teller (BET) curve was collected; for the MH biochar, the three points corresponding to the lowest P/P_0 were removed as they appeared to be anomalies.

pH, conductivity, and water-extractable Al, Ca, Fe, K, Mg, P, and Zn were measured for all four biochars and one control sample of deionized (DI) water. Three grams of biochar were mixed with 75 g DI water in a 125-mL glass Erlenmeyer flask, hand swirled for one minute, and measured for pH and conductivity with an Oakton pH/CON 510 Series benchtop meter (Oakton Instruments, Vernon Hills, IL, USA). After measuring pH and conductivity, the biochars and control were placed in an Excella E24 orbital shaker (New Brunswick Scientific Co., Enfield, CT) and shaken for one hour at 200 RPMs and at a temperature of 23°C in the dark. The biochars were allowed to settle for 0.5 hr before pH and conductivity were measured again. The biochar and control solutions were filtered through 0.45-μm glass filter paper using a vacuum filter system, and the filtrate was analyzed for Al, Ca, Fe, K, Mg, P, and Zn on a Spectro ARCOS ICP Model FHS16 with CETAC Autosampler (Spectro Analytical Instruments, Inc; Mahwah, NJ).

Biochar solids were analyzed for multiple elements to characterize the chemical composition of the biochars and assess the potential for the biochars to release contaminants to the environment. The biochars were digested using US EPA Method 3050B (U.S. Environmental Protection Agency (USEPA), 1996) and then analyzed on a Spectro ARCOS ICP Model FHS16 with CETAC Autosampler (Spectro Analytical Instruments, Inc; Mahwah, NJ). Elements measured included the following: Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, and Zn.

Sorption Experiment

CS600, MH, and RH were tested for their sorptive abilities. Four grams of biochar were placed in a 125-mL Erlenmeyer flask along with 100 mL of Type 2 water, 0.01M NaCl (Fisher Scientific, Hampton, NH), K_2HPO_4 (Fisher Scientific, Hampton, NH), and 40 mg/L mercuric chloride (Fisher Scientific, Hampton, NH) as a microbial inhibitor. The amounts of K_2HPO_4 added corresponded to the following P concentrations that were tested: 0, 0.05, 0.1, 0.5, 1, 2, 5, 10, 15 mg P/L. Solutions were prepared for each biochar plus one control with no K_2HPO_4 added, and each P concentration and biochar type was made in triplicate. Prior to placing the samples into the shaker, pH was measured. The samples were then placed into an Excella E24 orbital shaker (New Brunswick Scientific Co., Enfield, CT) and shaken for 24 hours at 200 RPMs and at a temperature of 23°C in the dark. Reddy et al. indicates that a shaking period of 24 hours is sufficient to achieve equilibrium (Reddy et al., 2014c).

After shaking, the samples were allowed to settle for 10 minutes before pH was measured again. The samples were then filtered through a vacuum system using 0.45-µm nylon membrane filters (Sterlitech Corporation, Kent, WA) and the filtrate was frozen until analysis.

DP was measured using a SEAL AutoAnalyzer3, Multitest MT18 (Mequon, WI), which used Method 4500-P F. to determine orthosphosphate concentrations (Standard Methods for the Examination of Water and Wastewater, 2012).

Data and Statistical Analysis

DP concentration on the biochar was calculated by subtracting the final solution DP concentration with the DP concentration in the control. A one-way analysis of variance (ANOVA) followed by a Tukey Honest Significant Difference (HSD) test was applied to determine the effects of biochar type on DP sorption using R Studio (version 1.1.442; Boston, MA) and R statistical software (version 3.2.3; Vienna, Austria). A significance level of $p<0.05$ was used to determine significance.

Results

Physicochemical Properties

Physical and chemical properties measured from the four biochars are shown in Table 3.1, Table 3.2, and Table 3.3. Carbon content in all four biochars ranged from 39% (RH) to 77% (MH), which is within the range found by other studies (Chintala et al., 2013; Peterson et al., 2012) (see also Table 3.4). Nitrogen content was minimal with CS400 having the highest nitrogen content (0.83%). All biochars made the surrounding solution more alkaline with MH effecting the greatest change in pH after one hour of shaking (see Table 3.1). CS400 changed the pH of the surrounding solution the least, followed by RH, CS600, and MH; however, the change in pH from the control to the lowest pH change by CS400 was noticeable, from 7.8 to 8.7. Surface area varied from 424 m2/g (MH) to 79.8 (RH) (see Table 3.1). CS600 had a greater surface area than CS400, which is expected due to a higher pyrolysis temperature, which would break apart the biochar more completely (Ahmad et al., 2014).

Elemental P and cation concentrations in the four biochars were generally within range of biochars of similar feedstock as reported by other studies (see Table 3.4). Elemental P concentrations in the biochars' compositions (Table 3.3) were relatively high when compared to water-extractable P (Table 3.2), indicating that, despite having high concentrations of P, most of the P within the biochar remained in the biochar. RH had the highest P concentration, and MH had the lowest. Water-extractable P, however, ranged from 1.6 mg/L (MH) to 10.7 mg/L (CS400), which tends to be relatively high compared to typical stormwater concentrations (0.35 mg P/L) (Bratieres et al., 2008). Water-extractable P from all biochar except MH exceeded the range typically found in stormwater (0.01 to 7.3 mg/L) (Reddy et al., 2014b). Concentrations of cations including Ca, Mg, and Fe were three to eleven times as high as P concentrations. Reasons for differences in elemental composition between biochar of similar feedstock can be due to differing pyrolysis temperatures (e.g., higher pyrolysis temperatures result in more carbonized residual) or different growing conditions (Ahmad et al., 2014; Tan et al., 2015; Xie et al., 2014).

Some biochars contained heavy metal concentrations that, if released into the environment in their entirety, can pose an ecological risk. Both corn stover biochars (CS400 and CS600) contained enough zinc to exceed the US EPA Region 3 zinc concentration guideline for ecological risk (155.9 mg/kg and 132.4 mg/kg respectively compared to a limit of 121 mg/kg) (U.S. Environmental Protection Agency (USEPA), 2006). All other metal concentrations in biochars (Cr, Cu, Fe, Mn, Ni, and Pb) were below the risk guidelines. However, when looking at the water-extractable results, the amount of zinc released by CS400 and CS600 was 2.3 mg/kg and 1.6 mg/kg respectively, indicating that the likelihood that these biochars will release all its zinc contents is highly unlikely. All biochars should therefore be suitable for use in a filter media.

Sorption Experiment

Only MH was able to sorb P above a DP concentration of 2.9 mg P/L in solution. A graph of the concentration of DP sorbed onto biochars is shown in Figure 3.2. The equilibrium concentration of DP in solution for CS600 and RH was maintained consistently at 11.6 mg/L and 12.9 mg/L respectively, regardless of the initial DP solution concentration. These DP concentrations found in solution were slightly higher than water-extractable P from these biochars (Table 3.2) and total elemental P in the biochars (Table 3.3). These results coincide with studies that have also reported minimal P sorption or even P release from biochar (Hollister et al., 2013; Pratiwi et al., 2016; Soinne et al., 2014). Because DP desorption occurred, neither a Langmuir nor Freundlich model could be fit to the data. One-way ANOVA results followed by Tukey HSD test showed that DP sorption/desorption on the three biochars were significantly different from each other (see Figure 3.1).

Discussion

Four biochars were evaluated for a variety of physicochemical properties to both assess their suitability as a filter media and to evaluate any negative environmental impacts of their use. Because all biochars, including MH, released DP in solutions with DP concentrations less than 2.9 mg P/L, these biochars would not be suitable for stormwater treatment in areas where typical stormwater DP concentrations are less than 2.9 mg P/L. Stormwater TP concentrations can range from 0.01 mg/L to 7.3 mg/L (Reddy et al., 2014b), but typical concentrations appear to be closer to 0.33 mg/L and 0.6 mg/L (Bratieres et al., 2008; Davis et al., 2001). Therefore, the biochars used in this study would most likely release DP under typical stormwater pollutant concentrations.

Measured physicochemical properties suggested that DP would not sorb to the biochars. Zeta potential measurements indicated that all biochars were negatively charged at near neutral pH values (see Table 3.1), which would make DP less likely to sorb to the biochar. Biochars consist primarily of organic matter, which tends to be negatively charged at pH>3 (Sparks, 2003). Studies have demonstrated that biochars with negative surface charges can sorb DP (Lehmann, 2007; Yao et al., 2011b) and suggest mechanisms by which DP would be sorbed, such as through divalent cation bridging (ternary complex) or excess metal oxides (Mukherjee et al., 2011; Yao et al., 2011b). The current study results indicate that negative surface charges on CS600 and RH biochars, combined with other factors such as a high solution pH, would not promote these mechanisms.

Based on the observed properties of the biochars, particularly for CS400, CS600, and RH, the lack of P sorption is most likely due to competition with OH^- ions coupled with excess P in the biochar relative to the surrounding solution. Other sources support this conclusion, stating that biochars tend to make its surrounding solution basic, which could promote competition between OH^- and DP ions (McBride, 1994; Pratt et al., 2007). Studies have proposed that P can potentially have an affinity with biochar either through ligand exchange with functional groups on Fe- and Al-oxides and hydroxides, ternary complexes, and adsorption or precipitation with Ca and Mg (Novak et al., 2009; Yao et al., 2011b). In this study, ligand exchange with P would be unlikely given the negative surface charge of the biochar coupled with a high pH solution. Given the low concentration of water-extractable cations relative to water-extractable P, sorption or precipitation with cations would also be unlikely.

MH was the only biochar that sorbed DP at concentrations above 2.9 mg P/L. The properties that could allow it to sorb DP over the other biochars were a smaller negative surface charge, less P in its composition, more water-extractable cations, and a large surface area (see Table 3.1, Table 3.2, and Table 3.3). One exception was MH, which had a higher pH than other biochars during the zeta potential measurement, suggesting that, at a neutral pH, MH would be less negatively charged than other biochars. MH would therefore be the most likely biochar out of the study biochars to sorb DP based on surface charge. MH contained two to three times less total P concentration than the other biochars, and the water-extractable fraction of P relative to total P in the biochar was smaller than other biochars. MH also contained a higher amount of water-extractable cations, which may form precipitates or coprecipiates with DP. Finally, MH had the largest surface area of the biochars, which corresponds to smaller particle sizes and therefore more sorption sites. Given these attributes, MH had the greatest likelihood to sorb P over the other biochars.

Finally, the biochars were tested to determine whether they would contribute pollutants to the environment. One of the concerns for using biochar as a filtration media is its high carbon and P concentrations. A high carbon content can result in release of dissolved organic carbon as surface water passes through the filtrations system, which can cause increased biological activity or metal concentrations in downstream waters (Evans et al., 2005). Higher pyrolysis temperatures and wood feedstock generally have higher fixed carbon content but lower labile carbon content, and it is the labile carbon content in particular that can affect downstream water (Xie et al., 2014). In this study, MH had the highest percent of carbon over all biochars (77%), but due to high lignin content in woody materials (Xie et al., 2014), MH would mostly contain fixed carbons, which are less impactful on the environment. Regardless, biochars should be rinsed prior to use in a filtration system to prevent an efflux of carbon and P into the environment. Nitrogen content was non-detectable in MH and RH, indicating that these biochars would not release excessive concentrations of nitrogen if they were to be used as filter media. Toxic metals release from biochars is not a concern as they were all below the U.S. EPA Ecoregion III freshwater screening benchmarks, which delineate the level at which risks to the ecosystem could occur. CS600 had the highest Cr concentration (5.2 mg/kg), RH had the highest Mg concentration (372 mg/kg), and CS400 had the highest Pb concentration (3.6 mg/kg), all of which are below the U.S. EPA screening levels (43.4 mg/kg for Cr, 460 mg/kg for Mn, and 35.8 mg/kg for lead) (U.S. EPA, 2006).

Conclusion

Given negative zeta potential values, the tendency for biochar to make surrounding water basic, and DP release rather than sorption below 2.9 mg P/L, all biochars included in this study were not suitable for sorbing DP in stormwater. MH could potentially sorb DP because it has less P in its composition than other study biochars, it has more soluble cations, and it has a higher surface area. However, the concentration at which MH can sorb DP is significantly higher than typical DP concentrations found in stormwater. Future work can be to pre-wash the biochar prior to use or to test these biochars in removing other pollutants such as nitrate and heavy metals.

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Tables

Table 3.1. Results for pH, zeta potential, C/N analysis, and surface area. Tested biochars were corn stover pyrolized at 400°C (CS400), corn stover pyrolized at 600°C (CS600), mixed hardwood (MH), and rice husk (RH).

	pH	Zeta Potential			%C		%N		Surface Area (m^2/g)
		Average (mV)	STD (mV)	pH	Average	STD	Average	STD	
CS400	8.74	-28.9	2.5	7.5	52.9	0.0	0.8	0.0	128
CS600	9.42	-32.3	6.2	7.5	62.2	0.0	0.7	0.0	260
MH	9.66	-26.6	0.9	8.9	77.4	0.1	0.0	0.0	424
RH	9.08	-45.7	4.9	7.8	39.1	0.0	0.0	0.0	79.8

Table 3.2. Results for water-extractable elements of biochars in mg/kg. Tested biochars were corn stover pyrolized at 400°C (CS400), corn stover pyrolized at 600°C (CS600), mixed hardwood (MH), and rice husk (RH).

Analyte (mg/kg)	Al	Ca	Fe	K	Mg	P	Zn
Control	0.2	2.9					0.6
C400	3.0	61.3	3.9	6742.9	48.8	267.6	2.3
C600	2.8	49.4	5.2	5903.6	25.5	205.1	1.6
MH	28.2	171.8	0.4	3083.3	70.7	40.7	0.9
RH	0.5	19.9	0.7	2362.1	44.5	231.1	1.0

Table 3.3. Results of elemental analysis of biochars in mg/kg. Tested biochars were corn stover pyrolized at 400°C (CS400), corn stover pyrolized at 600°C (CS600), mixed hardwood (MH), and rice husk (RH).

	Analyte (mg/kg)										
	Al	Ca	Cr	Cu	Fe	K	Mg	Mn	Ni	P	Pb	Zn
CS400	1681	11439	4.3	16.2	5292	17522	5395	124.4	3.6	1007	3.6	155.9
CS600	2319	15834	5.2	16.2	7569	16015	6353	162.3	4.8	1138	2.1	132.4
MH	683.4	5621	2.6	9.6	937.3	5332	1065	214.9	3.4	589.5	<1.6	13.6
RH	98.6	1479	<0.5	3.1	180	8713	777.2	372.2	<0.5	1559	<1.6	35.8

Table 3.4. Comparison of biochar characteristics with other literature. Tested biochars were corn stover pyrolized at 400°C (CS400), corn stover pyrolized at 600°C (CS600), mixed hardwood (MH), and rice husk (RH).

	Pyrolysis Temperature			Elemental Composition (mg/kg)					Reference
	(C)	%C	%N	Ca	Fe	K	P	Mg	
Corn stover (CS400)	400	52.9	0.83	11400	5290	17500	1010	5390	this study
Corn stover (CS600)	600	62.2	0.72	15800	7570	16000	1140	6350	this study
Corn stover	350			2440			8040	3720	Hollister et al., 2013
Corn stover	550			2710			11300	8890	Hollister et al., 2013
Corn stover	500	57.3	1.47	3250	2.35	4.44	2150	2340	Mullen et al., 2010
Corn stover	650	74	1.23	7510		21.4	2000	5340	Chintala et al., 2013
Mixed Hardwood (MH)	600	77.4	0	5620	937	5330	590	1060	this study
Oak	350			14			52	665	Hollister et al., 2013
Hardwood	450	53.4	0.07	27	9.33	32.95	1	4.42	Chen et al., 2011
Oak	550			38			53	976	Hollister et al., 2013
Ponderosa pine	650	83.3	0.35	2570		1.96	360	620	Chintala et al., 2013
Rice husk (RH)	<750	39.1	0	1480	180	8710	1560	777	this study
Rice husk	>600	41.0	0.47						Pratiwi et al., 2016
Rice husk	350	38.6	0.43	5700	900	12200	2600	2100	Xu et al., 2013

Figures

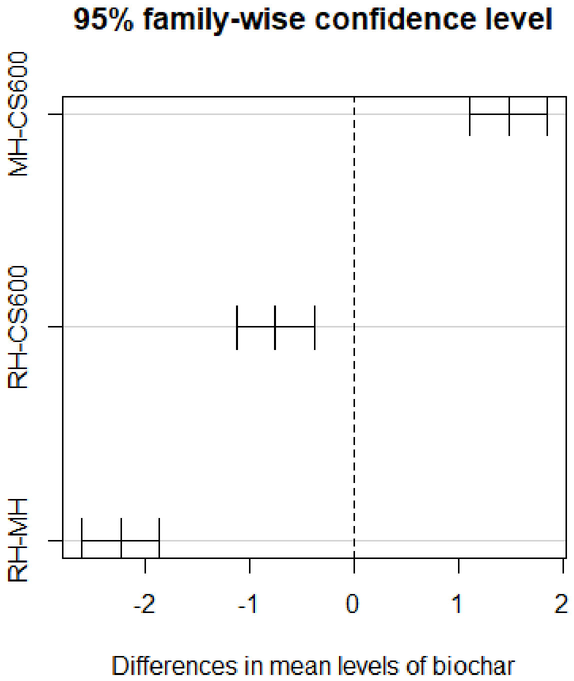

Figure 3.1. Tukey HSD plot comparing corn stover pyrolized at 600°C (CS600), mixed hardwood (MH), and rice husk (RH).

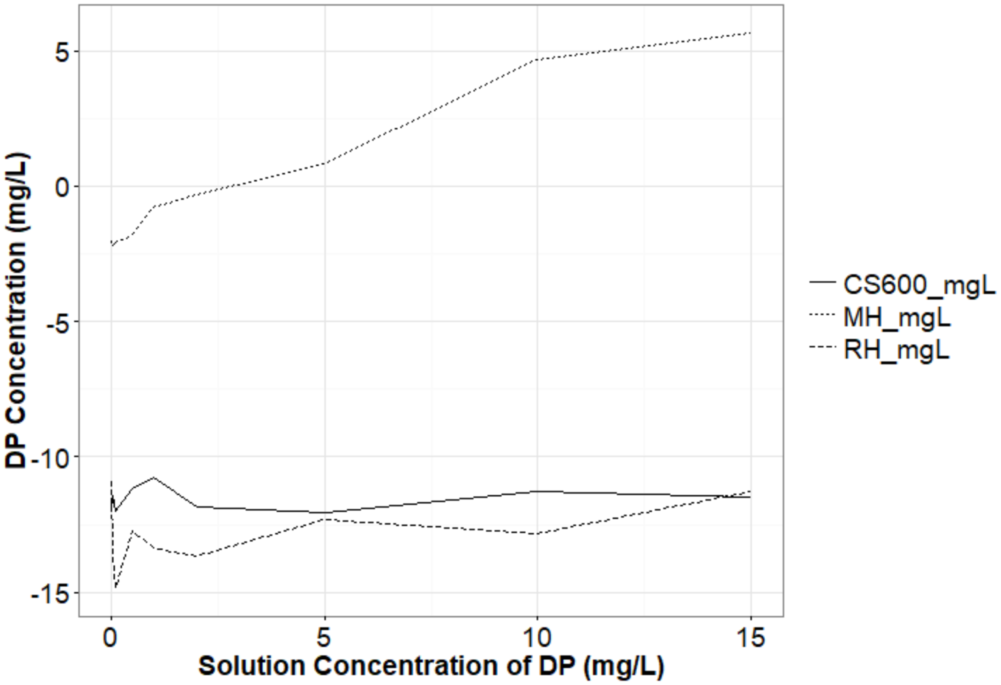

Figure 3.2. Concentration of dissolved phosphorus (DP) sorbed onto biochar as a function of DP concentration in solution. Tested biochars were corn stover pyrolized at 600°C (CS600), mixed hardwood (MH), and rice husk (RH).

4. Stormwater Pollutant Removal in a Laboratory-Scale Three-Stage Filter Using Biochar and Iron

Abstract

Wet retention ponds attempt to prevent excess nutrients from contributing to eutrophication in natural water bodies but can cause nutrient pollution as well if not properly maintained. A stand-alone filtration system designed to attach to BMPs such as wet retention ponds can provide targeted maintenance and monitoring and be more cost effective. Such a system can also be configured to remove pollutants separately so that nutrients such as phosphorus can be reused. This study evaluated the feasibility of a three-stage filtration to separately remove multiple pollutants from retention ponds, including phosphorus for the purposes of recycling. Biochar+woodchips mix, woodchips-only, iron+sand mix, and sand-only were subjected to a high and low concentration of stormwater consisting of dissolved phosphorus (DP), total phosphorus (TP), nitrate (NO_3), total nitrogen (TN), lead (Pb), and sediment. Iron+sand removed up to 95% dissolved phosphorus, 85% total phosphorus, and 75% lead. Biochar/woodchips and woodchips-only removed up to 95% nitrate and 57% total nitrogen. The filtration system removed primarily NO_3 and TN in Stage 2 and DP and TP in Stage 3. Pb was primarily removed in Stage 3 and was therefore not separated from DP. Water quality values generally met U.S. EPA recommended limits for aquatic life. This study demonstrated that removing pollutants separately is feasible, but media mix and configurations must be revised to retain only phosphorus in one stage and to ascertain that all recommended water quality limits are always met.

Introduction

Excess nutrients and heavy metals in urban and agricultural runoff contribute to eutrophication in the nation's water bodies and can negatively impact biological systems, economic systems, and health (Chislock et al., 2013; Dubrovsky & Hamilton, 2010). At the same time, certain pollutants such as phosphorus (P) are a valuable and limited natural resource that can be depleted within 100 to 400 years (Dawson & Hilton, 2011).

Current Best Management Practices (BMPs) such as wet retention ponds are only partially successful at removing pollutants and can become saturated with pollutants, resulting in costly maintenance actions such as dredging the entire pond (Novotny, 2003; U.S. Environmental Protection Agency (USEPA), 1999; Welch & Cooke, 2005). These BMP structures remove pollutants through physical sedimentation, biological uptake via microorganisms and phytoplankton living in the water, and pollutant transformation through adsorption, or pollutant storage. However, all of these mechanisms can result in the release of pollutants, such as reducing conditions, insufficient settling time, or insufficient volume for storage (Wong et al., 1999). Some studies also indicate that such BMPs can only remove pollutants to a minimum level called the irreducible pollutant concentration. Schueler (2000) indicated that the irreducible stormwater concentrations for total phosphorus (TP), total nitrogen (TN), and nitrate-nitrogen (NO_3) are 0.15 mg/L, 1.9 mg/L, and 0.7 mg/L respectively based on mean outflow concentrations found at structures such a wetlands and retention ponds. Some of these values are still above the recommended concentrations for healthy aquatic life; for example, the maximum limit for total phosphorus recommended by the U.S. EPA to prevent algae blooms is 0.025 mg/L.

Additional filtering will therefore be required in order to further reduce the pollutant concentrations to recommended levels.

A BMP that acts as a filter rather than container for pollutants could resolve some of the above issues. A more recent BMP that acts more as a filter are bioretention cells, which filter pollutants utilizing various media and vegetation. Bioretention cells can be aesthetically pleasing and require smaller areas than retention ponds and wetlands (Hunt et al., 2003). However, depending on the pollutant, media, and performance characteristics of the bioretention structure, these BMPs also have mixed results in removing pollutants. Traditional bioretention cells are generally effective at removing P, sediment, and heavy metals (Bratieres et al., 2008; Davis et al., 2006; Trowsdale & Simcock, 2011). However, removal of nitrogen (N), particularly NO_3, has been mixed to poor (Bratieres et al., 2008; Davis et al., 2006; Hatt et al., 2008). Vegetation has been used to remove nitrate with mixed results (-630% to 96% removal rate) depending on the vegetation (Bratieres et al., 2008; Lucas & Greenway, 2008).

Denitrifying bioreactors are similar to bioretention cells but establish an anaerobic zone so that NO_3 can be removed as well. Heterotrophic bacteria within the media reduce NO_3 to N_2 gas by utilizing organic matter as a food source (Lassiter & Easton, 2013). This type of BMP also has achieved mixed results in removing certain pollutants. Hunt et al. (2003) found that anaerobic bioreactors were not significantly different than traditional bioreactors in removing nitrate. Bock et al. (2015) achieved NO_3 removal efficiencies of up to 97% in a study of denitrifying bioreactors that included biochar in the media.

One of the underpinnings to the effectiveness of bioretention cells or any filtration BMP is the media used. Numerous studies have been performed to test the efficacy of various media to remove specific pollutants. The materials that have been evaluated in these studies include iron filings, drinking water treatment residuals, aluminum, fly ash, and zeolite to name a few (Leader et al., 2008; Penn et al., 2011; Reddy et al., 2014a; Rosenquist et al., 2011). Each of these media has their strengths and weaknesses. Davis et al. (2006) found in laboratory and field-scale experiments that bioretention cells could remove up to 85% P and 65% Total Kjeldahl Nitrogen (TKN) with most of the P removal occurring in the sand media and the TKN removal occurring in the mulch media. However, none of the media could remove a large portion of NO_3, and NO_3 was even released under certain conditions (Davis et al., 2006). Hsieh and Davis (2005) tested different sands, soils, and mulches and found that sand and soil media were most effective at removing lead (Pb), mulch did not effectively remove TP, and sand was ineffective at removing NO_3 whereas mulch was most effective at removing NO_3.

Given all of these considerations, the ability to remove multiple pollutants from polluted waters is complex. Competing media within a design can produce pollutants while removing others (Bratieres et al., 2008; Hatt, Fletcher, & Deletic, 2009; Hatt et al., 2008; Healy et al., 2015). Studies have attempted to resolve this issue by either having separate layers of media or separate stages through which the polluted water sequentially passes with some success (Hsieh & Davis, 2005; Seo et al., 2008). However, none of these designs consider reusing the media or extracting nutrients from the media for reuse. Experiments have been conducted to remove P from the media through a regeneration process (Genz et al., 2004; Rosenquist et al., 2011) but have not explored this concept in relation to a broader filter system for multi-pollutant removal.

In this study, a three-stage filter with different filtrates in each stage was examined to target different pollutants with the intent to recycle P. This filter system was designed to be a stand-alone, compact, aboveground filter that is attached to an existing BMP or water body such as a retention pond. These features allow it to be accessible, easily maneuvered, and require little space. A laboratory-scale experiment was designed to test the ability of such a filter to remove various pollutants in a flow-through configuration. The objectives of this study were as follows: 1) assess the ability of different media to remove dissolved phosphorus (DP), NO_3, TP, TN, and lead (Pb) in separate stages for potential reuse, and 2) determine filter media's effects on water quality parameters (conductivity, dissolved oxygen (DO), pH, water temperature, and turbidity).

Methods

Filter Design

An experimental filter system was designed with three stages. A diagram of the filter system is provided in Figure 4.1. The first and second stages of the system were contained in a polyethylene box with inner dimensions of 37.6 cm L x 31.6 cm W x 23.2 cm H. This box was divided into two sections with the first section (first stage) containing a sediment trap made of a poly filter pad, and the second section (second stage) containing filter media. The box was loosely capped to prevent media from escaping the box. The third stage of the system consisted of a PVC pipe open to the air and with inner dimensions of 10 cm D x 18.7 cm L. The two stages were connected with a 2.5-cm PVC pipe. Stormwater entered at the top of the filter system in the first stage and is filtered through the sediment trap. The stormwater passed under a divider and into the second stage filter media. The stormwater exited the second stage at the top of the container and flowed downward through the third stage column and out of the system. Three sampling ports were built into the filter systems to collect water samples across the system. The first sampling port (Sample 1) was located at the bottom of the first stage just before stormwater entered the first stage media. The second sampling port (Sample 2) was located in the PVC pipe connecting the second stage to the third stage. The third sampling site (Sample 3) was at the outlet of the third stage column.

Four filter treatments with different combinations of media at each stage were tested to assess the performance of each media, and diagrams of each are provided in Figure 4.2. The media tested in Stage 2 included woodchips only and woodchips plus 10% biochar by volume (biochar+woodchips). The media tested n Stage 3 included sand only and sand plus 5% iron by mass (Fe+sand). The four treatments were as follows: biochar+woodchips and Fe+sand (BF); nothing and Fe+sand (NF); nothing and sand only (NS); and woodchips only and sand only (WS).

Media

The media was chosen based primarily on their ability to remove NO_3 and DP from stormwater. Woodchips and biochar were chosen to remove NO_3 through denitrification. These media can also sorb heavy metals as organic matter is typically negatively charged (Brady & Weil, 2008). The woodchips consisted of mixed hardwood chips. The biochar was a mixed hardwood sourced from Biochar Now (Berthoud, CO) and created using a slow pyrolysis process in computer-controlled kilns for 8-12 hours and with a temperature between 550-600°C. Sand and iron filings were chosen to remove DP through adsorption. Washed play sand was purchased from a local hardware store. Iron filings were purchased through an online store selling iron filing waste. The iron filings were washed with phosphate-free soap and allowed to air dry to form rust prior to use in the filter systems to obtain an iron oxide with positive valence.

Stormwater

Two types of artificial stormwater were mixed for this experiment: a low and a high pollutant concentration. The pollutants in the stormwater included DP, NO_3, TP, TN, Pb, and Total Suspended Solids (TSS), and were chosen to test the ability of the different media to remove these pollutants at different stages of the filter system. These differing concentrations will be referred to as "low pollutant stormwater" and "high pollutant stormwater" throughout the paper. Target concentrations for the low and high concentration stormwaters as well as the actual average concentrations measured at the inlet source are listed in Table 4.1. Stormwater concentrations were chosen based on water samples from five urban and agricultural ponds in Montgomery County, VA (refer to Chapter 2), from literature describing typical concentrations found in urban and non-urban areas, particularly for ponds or lakes, and from literature descrbing similar laboratory experiments (Bratieres et al., 2008; Davis et al., 2001, 2006; Reddy et al., 2014b; Vollertsen et al., 2009; Wium-Andersen et al., 2012). Tap water was used as the base of the artificial stormwater. Because the tap water contained concentrations of NO_3 and DP higher than the lowest ranges of pollutant concentrations found in the literature, the low pollutant stormwater was set at the level found in the tap water. The high pollutant stormwater was determined based on the literature with regards to what can realistically be found in water bodies (Bratieres et al., 2008; Davis et al., 2001, 2006; Reddy et al., 2014b; Vollertsen et al., 2009; Wium-Andersen et al., 2012). Sediment used to represent TSS were collected from a construction site on the Virginia Tech campus and sieved to collect particles <0.5mm.

Experimental Setup

The twelve filtration systems were arranged as shown in Figure 4.3 in a climate-controlled room set at 21°C. Prior to the start of the experiment, the second stage of each filtration system was flushed with DI water twice to remove excess debris and nutrients. After flushing, the second stage was allowed to soak in DI water for eleven hours (the retention time allotted for the second stage), then drained to further release any excess constituents bound to the media. The third stage of each filtration system was flushed with approximately two pore volumes of DI water.

Stormwater was mixed in a 1230-L tank using a submersible pump and pumped to each filtration system using two peristaltic pumps (Cole-Parmer FH100M digital 4-channel pump Model No. 77724-04, Vernon Hills, IL; Cole-Parmer Masterflex L/S 8-channel pump, Model No. 7528-20, Vernon Hills, IL). Low pollutant stormwater was pumped for seven days through all filtration systems simultaneously. The media in each filtration system was then replaced, flushed with DI water as detailed in the previous paragraph, and high pollutant stormwater was pumped through all filtration systems simultaneously for an additional seven days.

Stormwater flow rate was adjusted to 25 mL/min in order to achieve a target hydraulic retention time (HRT) of 10 hours. This HRT was chosen in order to minimize the time to achieve anaerobic conditions while assuring that anaerobic conditions are established and undesired conditions are not established due to long retention times.

During the experiment, multiple variables were collected to determine the performance of the filters and the water quality of the effluent. Water samples were collected at time t=0, 2, 4, 8, 12, 24, 48, 72, 96, 120, 144 hr for both low pollutant and high pollutant stormwater tests. A water sample was taken at each of the sampling ports shown in Figure 4.1 in addition to a water sample taken at the source tank. Each water sample was measured for water temperature, conductivity, pH, dissolved oxygen (DO), and turbidity using an YSI Pro OBOD Probe (Yellow Springs, OH). Water samples were then divided into separate containers to be tested for the following constituents: DP, TP, NO_3, TN, dissolved organic carbon (DOC), Pb, and iron (Fe). DOC samples were collected over all sample locations for t=0 hr for the low pollutant stormwater. Thereafter, DOC samples were collected at Sample 3 for t= 0, 24, and 144 hr for low and high pollutant stormwater. Samples to be tested for Fe were collected over all sample locations for t=0 hr and only at Sample 3 for t=4, 24, and 144 hr for both high and low pollutant stormwater.

Sample Analysis

Water samples were prepared for laboratory tests according to the requirements of the elements being tested. Water samples to be tested for DP and NO_3 were filtered through a 0.45-μm filter prior to storing in 50-mL plastic centrifuge tubes, then frozen. Water samples to be tested for TP and TN were poured directly into 50-mL plastic centrifuge tubes and frozen. Water samples to be tested for DOC were stored in amber glass vials, refrigerated, and filtered prior to analysis. Water samples to be tested for Pb and Fe were poured into 20-mL plastic scint vials, acidified with 0.4 mL of nitric acid, and refrigerated.

Nutrient analysis was based on colorimetric methods and performed on a SEAL AutoAnalyzer 3, Multitest MT18 using Method 4500-P F. (Mequon, WI). Water samples from all treatments and from the Inlet, Sample 2, and Sample 3 were analyzed for DP, NO_3, TP, and TP using this method. DOC analysis was performed on a Shimadzu TOC-V carbon analyzer using oxidative combustion-infrared analysis. All water samples at t=0 hr for the low pollutant stormwater were analyzed for carbon, and water samples from the filter system outlets (Sample 3) were tested thereafter. Metals analysis was performed using inductively coupled plasma atomic emission spectroscopy on a Spectro ARCOS ICP Model FHS16 (Mahwah, NJ). Water samples from all treatments and locations were analyzed for Pb, and Fe samples from Sample 3 were measured.

Data and Statistical Analysis

Some turbidity data points were removed due to issues that developed during the experiment. Clogging in Stage 3 of BF and WS occurred starting at t=48 hr (i.e., 48 hours from the start of sample collection) for both low and high pollutant stormwaters. The columns were tapped so that samples could still be collected to be analyzed for pollutant constituents and other water quality parameters (e.g., pH). However, these data were not used to analyze turbidity due to heightened turbidity caused by the tapping. Two additional turbidity points at t=120 hr for the high pollutant concentration were removed from data for NF and NS due to clogging issues. All data points were kept for all other constituent analyses because an assessment of these data points did not show any noticeable change at $t \geq 48$ hr.

Stage 1 (sediment trap) was also removed from any data analysis because the samples collected from the Stage 1 sampling port appeared to be influenced by media in Stage 2. The effect of the sediment trap therefore could not be separated from influences by the Stage 2 media. Qualitative analysis is provided for some variables from Sample 1 data, but these data were removed from statistical analysis and calculations.

Descriptive statistics, piecewise linear regression, linear interpolation, and linear mixed effects model as a repeated measures ANOVA, and Tukey's Honest Significant Difference (HSD) test were used to analyze water quality and pollutant data using R Studio (version 1.1.442; Boston, MA) and R statistical software (version 3.2.3; Vienna, Austria). Descriptive statistics were used to describe changes in the effluent from the influent and to confirm that water quality parameters did not exceed recommended limits for aquatic life. Piecewise linear regression was used to evaluate trends and whether the treatment achieved steady state. A treatment was determined to have achieved steady state if the p-value for the slope was less than 0.05. Linear interpolation between time points was used to approximate hourly and total percent removal of DP, TP, NO_3, TP, and Pb for each treatment and pollutant concentration. Statistical significance at $p<0.05$ was determined using repeated measures ANOVA followed by Tukey's HSD test and using the statistical software JMP Pro 13 (version13.0.0; Cary, NC).

Percent removal of pollutants by treatment was calculated for Samples 2 and 3 for nutrients and lead. Total mass removed was calculated as follows:

$$TMR_m = \sum_{t=0}^{144} 0.06 * C_{m,j-i} * Q_{m,n} \qquad (1)$$

where m = treatment (BF, NF, NS, WS), n = pollutant concentration (high, low), i = previous sample (Inlet, Sample 2), j = subsequent sample (Sample 2, Sample 3), TMR_m = total mass removed (mg) by treatment m, C_{i-j} = the difference in pollutant concentration between Sample i and Sample j for treatment m (mg/L), $Q_{m,n}$ = average flow rate over time for treatment m and Storm n (mL/min), and t = time in hourly increments (h).

Percent removal was calculated as follows:

$$\%removal_m = \frac{TMR_{m.j}}{TM_{m,i}} * 100 \qquad (2)$$

where % $removal_m$ = percent pollutant removal for treatment m, $TMR_{m,j}$ = total mass removed (mg) by treatment m in Sample j, and $TM_{m,i}$ = total pollutant mass from treatment m and from previous Sample i.

Results

Experiment Performance

The actual measured HRT was approximately 10.75 hr and was measured from when influent began flowing into the first stage of the filter system and when the water flowed out of the second stage. Smaller HRTs allow for a smaller bioreactor, and guidelines suggest a HRT of four to eight hours with HRT's ideally achieving at least six hours in order to assure anaerobic conditions (National Resources Conservation Science, 2016). Studies indicate, however, that longer retention times allow for higher NO_3 removal rates and found HRTs for optimal NO_3 removal ranging from greater than 10 hours to 5 days (Christianson et al., 2011; Healy et al., 2015; Hoover et al., 2016; Lepine et al., 2016). Hoover et al. (2016) found however that the rate of nitrate removal decreases at a HRT of approximately 10.9 hours. In addition, various literature note that overly long retention times (e.g., 42+ hours) can result in conditions that produce undesired byproducts such as hydrogen sulfide that can harm aquatic life (Lepine et al., 2016; National Resources Conservation Science, 2016; Schipper et al., 2010).

Pollutant Removal

Nutrients

For both low and high pollutant concentrations, treatment effect on pollutant removal in Stage 2 was significantly different from zero for NO_3, TN, and TP but not DP. Treatment effect on pollutant removal in Stage 3 was significantly different from zero for DP, TP, and TN, but not NO_3. The statistical results of the mixed linear regressions are provided in Table 4.5 and Table 4.6 for Stages 2 and 3 respectively. Graphs of remaining pollutant masses after each stage and by treatment (Figure 4.4 for low pollutant concentrations and Figure 4.5 for high pollutant concentrations) show that NO_3 and TN were removed in Stage 2, while DP and TP are removed in Stage 3. These trends demonstrate that these pollutants can be removed separately.

In Stage 2, BF and WS removed >93% NO_3 in solution under low pollutant stormwater and were not significantly different from each other based on Tukey HSD test results (see Table 4.7). BF and WS were less effective at removing TN (56% and 38% respectively), but removal percentages were still significantly different from NF and NS. BF removed significantly more TN than WS. NO_3 removal rates in Stage 2 of BF reached steady state almost immediately upon the start of the experiment, whereas NO_3 removal decreased for WS after 84 hours. These trends can be seen in Figure 4.7, and levels of significance are provided in Table 4.9. TN removal rates for both BF and WS increased initially, then decreased after approximately 20 hours. TP concentration increased in Stage 2 of BF and WS with WS contributing significantly more than Treatment BF (25% versus 5%) (see Figure 4.4 and Table 4.7).

Under high pollutant stormwater, BF and WS still removed significantly more NO_3 and TN than NF and NS in Stage 2, but removal percentages were lower for NO_3 (see Table 4.7). NO_3 and TN removal rates achieved steady state for BF whereas TN removal increased for WS (see Table 4.9). BF significantly reduced the amount of TP in the high pollutant stormwater instead of contributing TP as it did under low pollutant stormwater (see Figure 4.5).

In Stage 3, BF and NF removed significantly more DP and TP than NS and WS under low pollutant stormwater and were not significantly different from each other (see Table 4.7). BF and NF removed >94% DP and >71% TP while NS and WS removed at most 41% DP and 19% TP. All treatments except for WS achieved steady state for DP removal, whereas TP removal rates for BF and WS decreased over time. These trends for phosphorus can be seen in Figure 4.6, and levels of significance are provided in Table 4.9. Removal percentages for NO_3 appeared high for BF and WS in Stage 3 (see Table 4.7); however, the total amount of NO_3 that entered Stage 3 was insignificant (<8 mg NO_3) compared to the inlet total mass (110 mg NO_3), which inflated the percentage removed (see Figure 4.4). BF and WS removed significantly more TN than NF and NS but did not remove as much as in Stage 2.

Under high pollutant stormwater, NF removed significantly more TP than BF (84% versus 38%), whereas DP removal was comparable between these treatments (see Table 4.7). All treatments under high pollutant stormwater achieved steady state for DP and TP removal with the exception of NS, whose TP removal rate decreased over time. Trends in NO_3 and TN removal for Stage 3 were the same as under low pollutant concentrations (see Figure 4.5).

Lead

Actual Pb concentrations for the low and high pollutant stormwaters were 0.03 and 0.06 mg Pb/L respectively. The high pollutant stormwater in particular was lower than the target concentration most likely due to Pb sorption to iron oxides in the sediment used to represent TSS.

From the remaining Pb in solution, NF and NS removed the most significant amount of Pb in Stage 3. NF and NS removed approximately 57% Pb in the low pollutant stormwater, and 75% and 52% respectively in the high pollutant stormwater (see Table 4.8). Stage 2 of BF and WS removed approximately 25% of Pb in both the low and high pollutant stormwater; however, the amount removed for the high pollutant stormwater was not significantly different from NF and NS. In general, time was not a significant factor, implying that Pb was adsorbed to filter materials near instantaneously for the duration of the experiment.

Water Quality

Median, minimum, and maximum values for temperature, conductivity, pH, DO, turbidity, carbon, and Fe are provided in Table 4.2, Table 4.3, and Table 4.4. Temperature never increased above the inlet temperature, and the greatest decrease in temperature was a difference of 6.1°C between inlet and outlet in the WS system.

Median conductivity measurements for high and low pollutant stormwater were 258 μS/cm and 201 μS/cm respectively with a maximum of 675 μS/cm at Sample 3 for BF. These values were within the range of the U.S. EPA's recommended values of 150 to 500 μS/cm for inland freshwater that also promotes mixed fisheries (U.S. Environmental Protection Agency (USEPA), 2012). Conductivity values increased for BF and WS in Sample 2 but reduced to levels comparable to NF and NS by 24 hours.

Median pH values for all treatments, locations, and pollutant concentrations were between 6.6 and 8.4. These values are within a range that would sustain freshwater aquatic life (6.5-9.0) (U.S. Environmental Protection Agency (USEPA), 1986). BF and WS had significantly lower pH's than NF and NS with a minimum of 5.51.

DO was lowest in Treatments BF and WS in the second stage of the filter system and increased in the third stage for these treatments. Median DO levels at the outlet were within the acceptable range for most stream animals (60-79% saturation) (Behar, 1997).

Median turbidity levels in the effluent of all treatments were lower than influent levels for the high pollutant stormwater but were comparable or higher than influent levels for the low pollutant stormwater. Turbidity increased after Stages 2 and 3 for Treatments BF and WS, and increased after Stage 3 for Treatments NF and NS. A review of state and federal guidelines for turbidity revealed that 10 NTU is the recommended limit for drinking water and cold water habitat, and 25 to 50 NTU for warm water lakes, rivers, and fisheries (U.S. Environmental

Protection Agency (USEPA), 1980). Except for three instances, all treatments were able to meet the standard of 25 NTU.

DOC levels for BF and WS reached levels above 30 mg/L for some filter stages during the first sample time period but decreased below 5 mg/L at the outlet of the filter system by the last sampling time. As a comparison, DOC concentrations in pristine streams range from 1 to 3 mg/L, and rivers and lakes can range from 2 to 10 mg/L with some lakes reaching concentrations of 34 mg/L depending on their trophic status (Rand, 1995).

Iron concentration for BF increased over time, whereas iron concentration for other treatments remained constant or decreased over time. Median iron concentrations at the outlet of BF for the low and high pollutant concentrations were 3.9 mg/L and 5.3 mg/L respectively, which is higher than the U.S. EPA recommended limit of 1.0 mg/L for freshwater aquatic life.

Discussion

Pollutant Removal

Media used in BF effectively removed NO_3 and TN in Stage 2 and DP and TP in Stage 3, demonstrating that separating pollutants within a filter is feasible for low and high pollutant stormwater (see Figure 4.4 and Figure 4.5). However, Pb was removed in Stage 3 rather than in Stage 2 (see Table 4.8). Since the intent of Stage 3 was to isolate DP and TP for potential reuse, additional types of media will need to be tested to remove Pb prior to Stage 3.

Nutrients

In Stage 2, biochar+woodchips (BF) and woodchips-only (WS) effectively removed NO_3, and to a lesser extent, TN. NO_3 was most likely removed through denitrification, which is supported by DO levels of approximately 45% in Stage 2 of BF and WS versus DO levels of 88+% for other treatments and the inlet. Because Stage 2 was primarily targeting NO_3 removal through denitrification, other forms of N would most likely not be removed except possibly through physical filtering, which was also a hypothesis made by Hatt et al. (2007). Other filtering mechanisms will need to be explored in order to capture N fractions besides NO_3.

Piecewise linear regression results showed that removal rates for BF and WS tended to be proportional to the influent concentration and that steady state was achieved for BF but not WS. Literature has shown that N removal rates are dependent on influent N concentrations (Bock et al., 2016; Christianson et al., 2012), which appears to be corroborated by the data in this study. Initial removal rates for BF and WS (indicated by the intercept of the regression in Table 4.9) are higher in the high pollutant concentration than the low concentration. Piecewise regression results also show that BF appears to have achieved steady state in Stage 2 (see Table 4.9) for NO_3 and TN removal, whereas the rate of NO_3 and TN removal for WS decreased over time under low N concentrations and increased over time under high N concentrations. This observation may suggest that the ideal HRT was achieved for BF but was too long for WS at low N concentrations and not long enough at high N concentrations.

TP concentrations in Stage 2 for Treatments BF and WS increased at the low pollutant concentration most likely due to the organic matter in the biochar and woodchips. Organic matter typically contains P (Brady & Weil, 2008), which can be leached into the surrounding solution. The biochar used in Treatment BF in particular was known to leach P at solution concentrations of less than 2.9 mg P/L (previous study). However, the biochar+woodchips (BF) media was able to remove TP in Stage 2 at the high pollutant concentration most likely because the influent TP concentration was greater than 2.9 mg P/L. The biochar media in Stage 2 of Treatment BF was also comprised of small particles, which can act as a physical filter for TP. This potential for the filter media to release additional nutrients into the water exemplifies the need to account for other potential environmental issues introduced when attempting to rectify pollutant issues.

In Stage 3, the iron/sand media (BF, NF) was more effective at removing DP and TP than sand alone (NS, WS). This trend was not surprising as multiple experiments have confirmed the ability of materials containing iron to sorb P (Boyer et al., 2011; Genz et al., 2004; Leader et al., 2008; Rosenquist et al., 2010; Rosenquist et al., 2011; Stoner et al., 2011; Zeng et al., 2004). The Stage 3 media was used in conjunction with Stage 2 media to test the media's ability to remove pollutants separately and will be discussed in more detail in the analysis of Pb removal. NF removed more TP than Treatment BF, suggesting that media in Stage 2 of BF inhibited TP from being removed in Stage 3. TN removal was significant in Stage 3 as well although NO_3 removal was not significant. Physical filtration is most likely the explanation for significant decreases in TN but not NO_3 in Stage 3.

The behavior of DP and TP removal over time in Stage 3 demonstrate an initial rapid removal rate followed by a noticeable transition to a slower removal rate (see Figure 4.6). This trend has been noted in multiple studies (Arai & Sparks, 2007; Lai & Lam, 2009; Lopez et al., 1996; Ryden et al., 1977) and is attributed to an initial, physical sorption of P onto the mineral surface followed by chemisorption of P into the minerals as time lapses (Ryden et al., 1977). This behavior is particularly prevalent in the high pollutant stormwater scenario as seen in Figure 4.6 (c) and (d). There is an initial decrease in removal rate for both DP and TP, possibly indicating that physical sorption sites are rapidly becoming occupied, followed by a gradual increase in removal rate as the slower chemisorption process begins to occur.

Lead

The aim of the filter design was for Pb to be complexed with the organic matter in Stage 2 so that only P is sorbed in Stage 3 and can be recycled without concern for other toxic pollutants. However, Stage 3 media over all treatments were more effective at removing Pb in addition to P due to chemisorption of Pb onto metal oxides in this stage. The sand used in the study most likely contained other minerals besides quartz as quartz sand is typically white in color (Sepp, 1999), and the playground sand used was a tan in color. A representative chemical composition of this type of sand includes various oxides, including Fe_2O_3, Al_2O_3, TiO_2, CaO, and MgO (Herron, 2006). Iron oxides in particular are known to chemisorb lead (Bohn et al., 2011). Since all treatments removed Pb in Stage 3, iron oxides was most likely present in both media types. Considering that the aim of the study was to retain P in Stage 3 to the exclusion of toxic elements, a different media would need to be considered for Stage 3 that will sorb P but not Pb, or another media be considered in Stage 2 that is more effective at removing Pb.

Treatments NF and NS removed more Pb in Stage 3 than BF and WS most likely due to the presence of organic matter in Treatments BF and WS. A study by Ashworth and Alloway demonstrated that an increase in soluble organic matter could either increase the solubility of Pb or result in organo-metal complexes that are more mobile (Ashworth & Alloway, 2008). DOC was clearly present in the outflow of Treatments BF and WS, supporting the theory that increased soluble organic matter causes Pb to be more mobile. Competition between Pb and organic matter for available sorption sites on iron oxide could also explain why more Pb was released for Treatments BF and WS than Treatments NF and NS. Pb chemisorbs to iron oxides, and organic matter complexes to iron oxides (Gu et al., 1994; McBride, 1994; Wu et al., 2008), which means that both have the potential to bond with iron and therefore reduce the number of available sites for bonding.

Water Quality

The water quality parameters collected during the experiment can indicate potential stressors to the ecosystem if the filter were installed in the field. Results showed that median temperature, conductivity, and pH values were generally within the recommended limits and therefore would generally not have a negative impact on ecosystem health. However, all water quality parameters violated recommended limits in at least one sampling period. These values tended to occur within the first 24 hours of the experiment, which suggests that the media had not been sufficiently cleaned prior to use. Another option to prevent excessive values is to restrict the effluent flow rate such that significant changes in water quality can be attenuated by the receiving water body.

DOC was measured during the experiment to determine if the amount of DOC released from the filter would affect aquatic life. Excess DOC can affect water quality such as changing the acidity of the water (Eshleman & Hemond, 1985) and deoxygenating the water (Osmond et al., 1995). Treatments BF and WS naturally released the highest amounts of carbon since the media in Stage 2 is comprised of organic matter. Effluent samples showed that Stage 3 of the filter systems was able to mitigate the additional carbon from Stage 2 such that DOC never exceeded 12 mg/L at the outlet, and after 144 hours of run time, DOC effluent levels did not exceed 5 mg/L. To ensure that effluent DOC does not affect the receiving water body, the same solutions can be applied to DOC as to the water quality parameters.

A high median concentration of iron for Treatment BF indicates that effluent concentrations of iron remained high over the duration of the experiment. The reason for a continually high Fe concentration is most likely due to Fe solubilization because of a low oxygenated environment. Receiving waters low in oxygen from Stage 2, organic matter contributions from Stage 2, and the tendency for Stage 3 to be water-logged due to clogging all combine to create a low oxygen environment. Such an environment allows Fe to be reduced and therefore increases its solubility (Lindsay, 1991). Median DO percentages for Stages 2 and 3 are 46% and 65%, supporting the theory that a low oxygen environment existed. Given that the median iron concentration for Treatment BF is higher than the recommended limit, the filter design should be reconsidered. Solutions to resolve this problem include sizing Stage 3 so that clogging does not occur as quickly, and allowing the water to aerate more between Stage 2 and 3.

Conclusion

Based on the results from this experiment, the iron/sand media was significantly more effective at removing DP and TP than sand-only, whereas woodchips-only and biochar/woodchips media were comparable in performance. Filter systems BF and WS were able to separate a majority of

N and P between Stages 2 and 3, but did not successfully capture all Pb in Stage 2 as intended due to iron oxides in Stage 3 that sorbed Pb.

All treatments generally released effluent with water quality parameters within recommended limits for freshwater aquatic life except for iron. A thorough flushing of the media prior to installation can ensure that no water quality parameter is violated. Iron output from the iron/sand media was most likely due to reduced conditions and can pose a problem to aquatic life. The problem can be remedied by either slightly altering the filter system design so that aeration occurs prior to effluent release, or decreasing the filter effluent rate such that impact to the receiving waters is minimal.

Multiple improvements can be made to this experiment. Placement of the sampling port for Stage 1 should be placed such that impacts of the sediment trap can be more accurately estimated. An additional sediment trap may also be useful after Stage 2 to prevent clogging of Stage 3; Stage 3 can also be sized more appropriately to prevent clogs. A limited number of filter configurations were tested due to logistic constraints. Additional tests on different filter configurations would help confirm which filter configuration is optimal. For example, a filter configuration where Stage 2 is woodchips and Stage 3 is iron+sand may be the most effective and the most economical configuration. Additional tests for other constituents would also be beneficial. Tests for ammonium and nitrite would help determine the quantity of the other N fractions. Tests for sulfate and nitrite production will verify if alternative harmful pollutants are being produced. Finally, additional media can be tested to capture other forms of N and to more effectively remove Pb prior to P capture so that P can be isolated and potentially reused.

This study demonstrates that removing pollutants separately is possible with the discriminatory removal of N and P in the different stages. This study also demonstrated that the filter system can be implemented without negatively impacting the receiving waters given proper precautions prior to implementation, such as flushing the media thoroughly. The biggest challenge would be finding a media mixture that would completely prevent toxic metals from entering the stage in which nutrients will be recycled.

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Tables

Table 4.1. Target and Actual Pollutant Concentrations. Actual values provided are the median and the range in parenthesis.

Pollutant	Low Concentration (mg/L)		High Concentration (mg/L)	
	Target	Actual	Target	Actual
NO_3	0.56	0.51 (0.34 – 0.57)	4	4.1 (3.8 – 4.3)
PO4	0.39	0.26 (0.20 – 0.30)	3	3 (2.2 – 3.4)
Pb	0.05	0.03 (0.025 – 0.038)	0.3	0.06 (0.04 – 0.146)
TSS	10	10	150	150

Table 4.2. Summary of water quality parameters from low pollutant water. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

	Conductivity (µS/cm)			DO (%)			pH			Temperature (°C)			Turbidity (NTU)		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Inlet	195	199	201	89	91.8	94.7	7.42	7.74	7.83	21.5	23	24	-0.7	0.2	1.3
BF3	142	221	675	52.9	64.5	78.1	6.79	7.1	9.19	18.2	19.8	21.6	-0.4	5.3	112.0
NF3	183	197	201	54	68.2	73.1	7.01	7.64	8.03	19.0	19.6	21.6	-0.3	2.8	22.4
NS3	176	197	200	62.4	90.8	92.8	6.77	7.67	7.87	18	19	21.4	-1.3	-0.5	18.2
WS3	169	208	258	57	71.5	92.1	6.81	6.94	7.38	17.9	19.2	21.4	-0.8	2.8	1879

Table 4.3. Summary of water quality parameters from high pollutant stormwater. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

	Conductivity (µS/cm)			DO (%)			pH			Temperature (°C)			Turbidity (NTU)		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Inlet	255	258	263	90	92.8	93.8	7.32	7.73	7.85	22.3	22.7	23.1	14.5	21	28.5
BF3	114	268	340	59.6	65.5	75.5	6.39	7.23	7.45	18.1	19.4	20.3	-0.5	14.1	119.5
NF3	215	245	255	59.6	68.5	71.6	6.46	8.42	8.64	18.8	19.3	20.2	-1.3	0.1	13.8
NS3	230	252	262	89.4	91.3	94.0	6.47	7.69	7.91	18.4	19.0	19.5	-1.4	0.3	126.1
WS3	149	255	274	61.9	71.8	91.5	5.51	7.01	7.25	18.2	19.1	20.1	-0.5	7.8	82.0

Table 4.4. Summary of carbon and iron concentrations from the outlet for low and high pollutant stormwater. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

	Low Pollutant Concentration						High Pollutant Concentration					
	Carbon (mg/L)			Iron (mg/L)			Carbon (mg/L)			Iron (mg/L)		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Inlet	1.4	1.4	1.4	0.10	0.12	0.13	1.6	1.7	2.2	0.30	0.36	0.37
BF3	3.6	4.9	7.3	0.48	3.90	10.70	2.5	3.4	8.4	3.59	5.29	6.81
NF3	1.1	1.2	7.1	0.27	0.77	2.00	1.2	1.4	3.0	0.02	0.43	7.37
NS3	1.2	1.5	4.5	0.00	0.01	0.03	1.6	1.7	4.1	0.00	0.01	0.17
WS3	3.9	6.1	9.1	0.00	0.07	0.66	3.1	4.8	11.6	0.01	0.05	0.07

Table 4.5. Results of mixed linear regression at Sample 2. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

Pollutant Concentration	Form	Fixed Effect	DFnum	DFden	F Statistic	p-value
Low	Nitrate	Time	10	78.4	5.689	<0.0001*
		Treatment	3	8.1	678.74	<0.0001*
		Time*Treatment	30	78.3	4.072	<0.0001*
	Total Nitrogen	Time	10	80	35.578	<0.0001*
		Treatment	3	8	27.456	0.0001*
		Time*Treatment	30	80	6.886	<0.0001*
	Dissolved Phosphorus	Time	10	78.1	6.226	<0.0001*
		Treatment	3	8	3.498	0.0694
		Time*Treatment	30	78.1	2.075	0.0054*
	Total Phosphorus	Time	10	80	18.288	<0.0001*
		Treatment	3	8	31.065	<0.0001*
		Time*Treatment	30	80	3.267	<0.0001*
High	Nitrate	Time	10	80	2.272	0.0213*
		Treatment	3	8	309.968	<0.0001*
		Time*Treatment	30	80	4.354	<0.0001*
	Total Nitrogen	Time	10	80	9.299	<0.0001*
		Treatment	3	8	210.841	<0.0001*
		Time*Treatment	30	80	8.429	<0.0001*
	Dissolved Phosphorus	Time	10	80	15.668	<0.0001*
		Treatment	3	8	0.847	0.5157
		Time*Treatment	30	80	1.553	0.0621
	Total Phosphorus	Time	10	80	4.568	<0.0001*
		Treatment	3	8	14.777	0.0013*
		Time*Treatment	30	80	3.408	<0.0001*

Table 4.6. Results of mixed linear regression at Sample 3. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

Pollutant Concentration	Form	Fixed Effect	DFnum	DFden	F Statistic	p-value
Low	Nitrate	Time	10	76.1	1.549	0.1388
		Treatment	3	8.5	3.741	0.0568
		Time*Treatment	30	75.8	4.941	<0.0001*
	Total Nitrogen	Time	10	80	11.079	<0.0001*
		Treatment	3	8	17.386	0.0007*
		Time*Treatment	30	80	4.273	<0.0001*
	Dissolved Phosphorus	Time	10	75.9	33.773	<0.0001*
		Treatment	3	7.9	22.127	0.0003*
		Time*Treatment	30	75.9	9.482	<0.0001*
	Total Phosphorus	Time	10	80	34.352	<0.0001*
		Treatment	3	8	37.794	<0.0001*
		Time*Treatment	30	80	9.534	<0.0001*
High	Nitrate	Time	10	79.1	4.845	<0.0001*
		Treatment	3	8	2.077	0.1822
		Time*Treatment	30	79.1	4.282	<0.0001*
	Total Nitrogen	Time	10	80	3.074	0.0024*
		Treatment	3	8	9.74	0.0048*
		Time*Treatment	30	80	2.416	0.001*
	Dissolved Phosphorus	Time	10	79.1	19.04	<0.0001*
		Treatment	3	8.1	72.97	<0.0001*
		Time*Treatment	30	79.1	4.378	<0.0001*
	Total Phosphorus	Time	10	80	59.663	<0.0001*
		Treatment	3	8	218.061	<0.0001*
		Time*Treatment	30	80	6.825	<0.0001*

Table 4.7. Total inlet DP, TP, NO_3, and TN mass and percent pollutant removal by pollutant concentration, treatment, and stage. Treatments that are significantly different from each other for each pollutant type, pollutant concentration, and sample location are denoted by different superscript letters after removal percentages. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

			Pollutant Concentration				
			Low			High	
Pollutant	Treatment		2	3		2	3
DP	Inlet (mg)	56			635		
	BF		4%^{a}	95%^{a}		10%^{a}	76%^{a}
	NF		5%^{a}	96%^{a}		7%^{a}	82%^{a}
	NS		2%^{a}	18%^{b}		12%^{a}	-5%^{b}
	WS		-12%^{a}	41%^{b}		5%^{a}	-6%^{b}
NO_3	Inlet	110			881		
	BF		94%^{a}	27%^{a}		59%^{a}	21%^{a}
	NF		0%^{b}	2%^{a}		1%^{b}	0%^{a}
	NS		1%^{b}	1%^{a}		2%^{b}	-2%^{a}
	WS		95%^{a}	72%^{a}		71%^{a}	27%^{a}
TP	Inlet	57			707		
	BF		-5%^{a}	72%^{a}		10%^{a}	38%^{a}
	NF		8%^{b}	100%^{a}		5%^{b}	84%^{b}
	NS		8%^{b}	19%^{b}		9%^{b}	0%^{c}
	WS		-25%^{c}	18%^{b}		6%^{b}	9%^{c}
TN	Inlet	213			995		
	BF		56%^{a}	19%^{a}		53%^{a}	19%^{a}
	NF		6%^{b}	-11%^{b}		1%^{b}	1%^{bc}
	NS		3%^{b}	-2%^{b}		1%^{b}	0%^{b}
	WS		38%^{c}	7%^{a}		61%^{a}	18%^{ac}

Table 4.8. Total inlet Pb mass and percent pollutant removal by pollutant concentration, treatment, and stage. Treatments that are significantly different from each other for each pollutant type, pollutant concentration, and sample location are denoted by different superscript letters after removal percentages. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

		Pollutant Concentration				
		Low			High	
Treatment		2	3		2	3
Inlet (mg)	6.5			13		
BF		25%^{a}	19%^{a}		20%^{a}	24%^{a}
NF		9%^{b}	58%^{b}		-8%^{a}	76%^{b}
NS		3%^{b}	56%^{b}		7%^{a}	52%^{c}
WS		26%^{a}	19%^{a}		28%^{a}	26%^{a}

Table 4.9. Piecewise linear regression statistics. Asterisks (*) indicate significance at $p<0.05$. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

Nutrient	Pollutant Concentration	Form	Treatment	Intercept	1st Slope	2nd Slope	Breakpoint p-value
Sample 2	Low	Nitrate	BF	0.488*	0.001	-0.001	0.332
			NF	0.064*	-0.015	0.000	0.410
			NS	0.050*	-0.006	0.001	0.694
			WS	0.453	0.001	-0.002*	0.027*
		Total Nitrogen	BF	-0.278*	0.051*	-0.002*	0.000*
			NF	-0.059	0.009	-0.001	0.412
			NS	-0.139	0.029	-0.001	0.285
			WS	-0.483*	0.063*	-0.003*	0.000*
	High	Nitrate	BF	3.306*	-0.102	-0.001	0.172
			NF	0.071	0.0132	-0.002	0.958
			NS	0.012	0.004	-0.002	0.425
			WS	2.378*	-0.022	0.009*	0.848
		Total Nitrogen	BF	2.411*	0.012	-0.004	0.204
			NF	0.085	-0.001	-0.001	0.925
			NS	0.07	-0.002	0.000	1.000
			WS	1.449*	0.044*	0.007*	0.000*
Sample 3	Low	Dissolved Phosphorus	BF	0.306*	-0.006*	0.000	0.162
			NF	0.243*	0.001	0.000	0.607
			NS	0.266*	-0.009*	0.000	0.000*
			WS	0.345*	-0.021*	-0.001*	0.000*
		Total Phosphorus	BF	0.369*	-0.015	-0.001*	0.059
			NF	0.206*	0.01	0.000	0.822
			NS	0.263*	-0.001*	0.000	0.001*
			WS	0.475*	-0.039*	-0.001*	0.000*
	High	Dissolved Phosphorus	BF	2.121*	-0.01	0.002	0.851
			NF	2.872*	-0.06	-0.001	0.506
			NS	2.739*	-0.493*	-0.001	0.000*
			WS	2.581*	-0.376*	-0.003	0.000*
		Total Phosphorus	BF	2.470*	-0.107*	0.002	0.002*
			NF	3.148*	-0.031	0.001	0.452
			NS	3.225*	-0.569*	-0.004*	0.000*
			WS	2.774*	-0.404*	0.000	0.000*

Figures

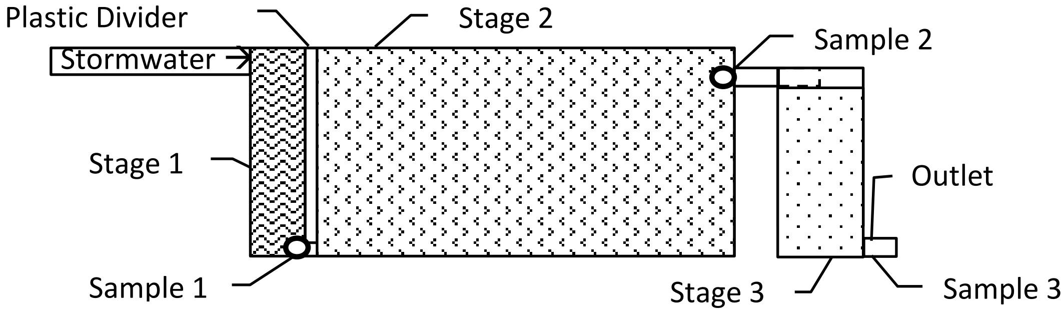


Figure 4.1. Side view of three-stage filter system.

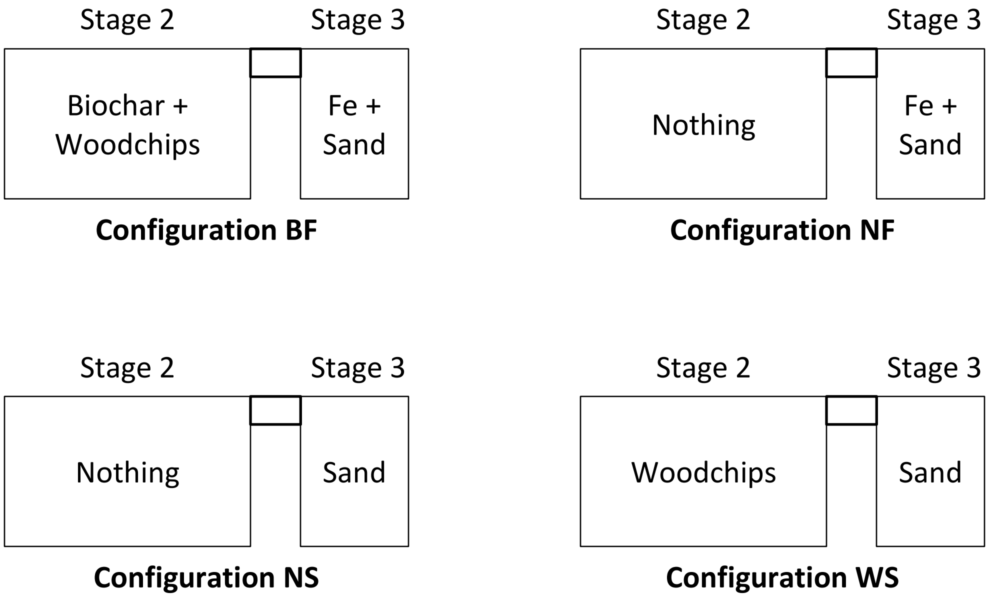


Figure 4.2. Four filter treatments. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS).

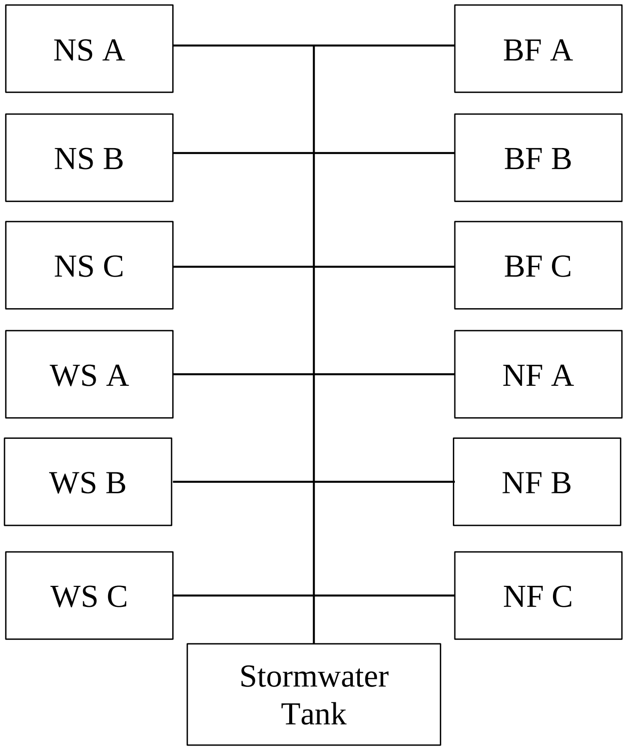
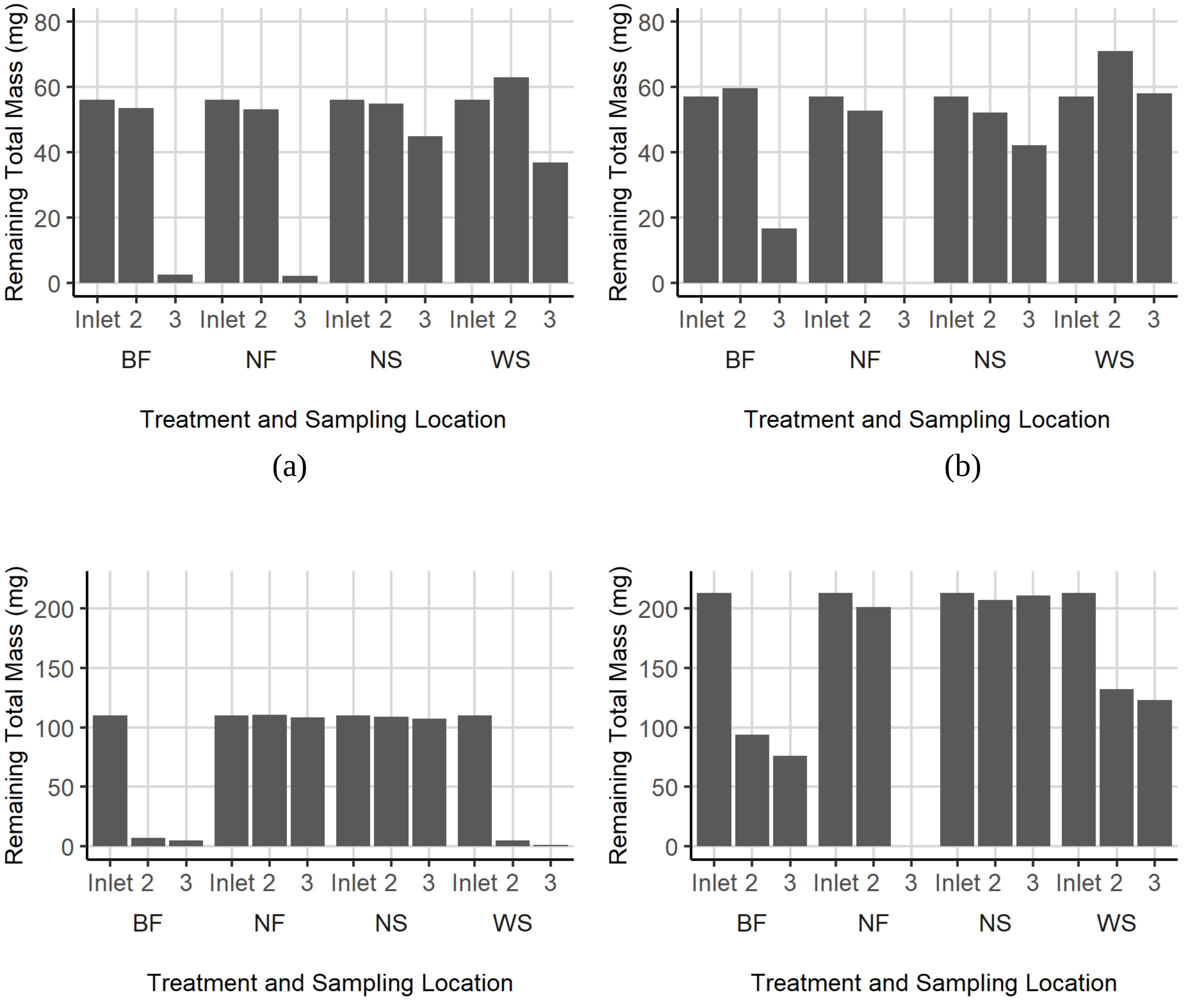


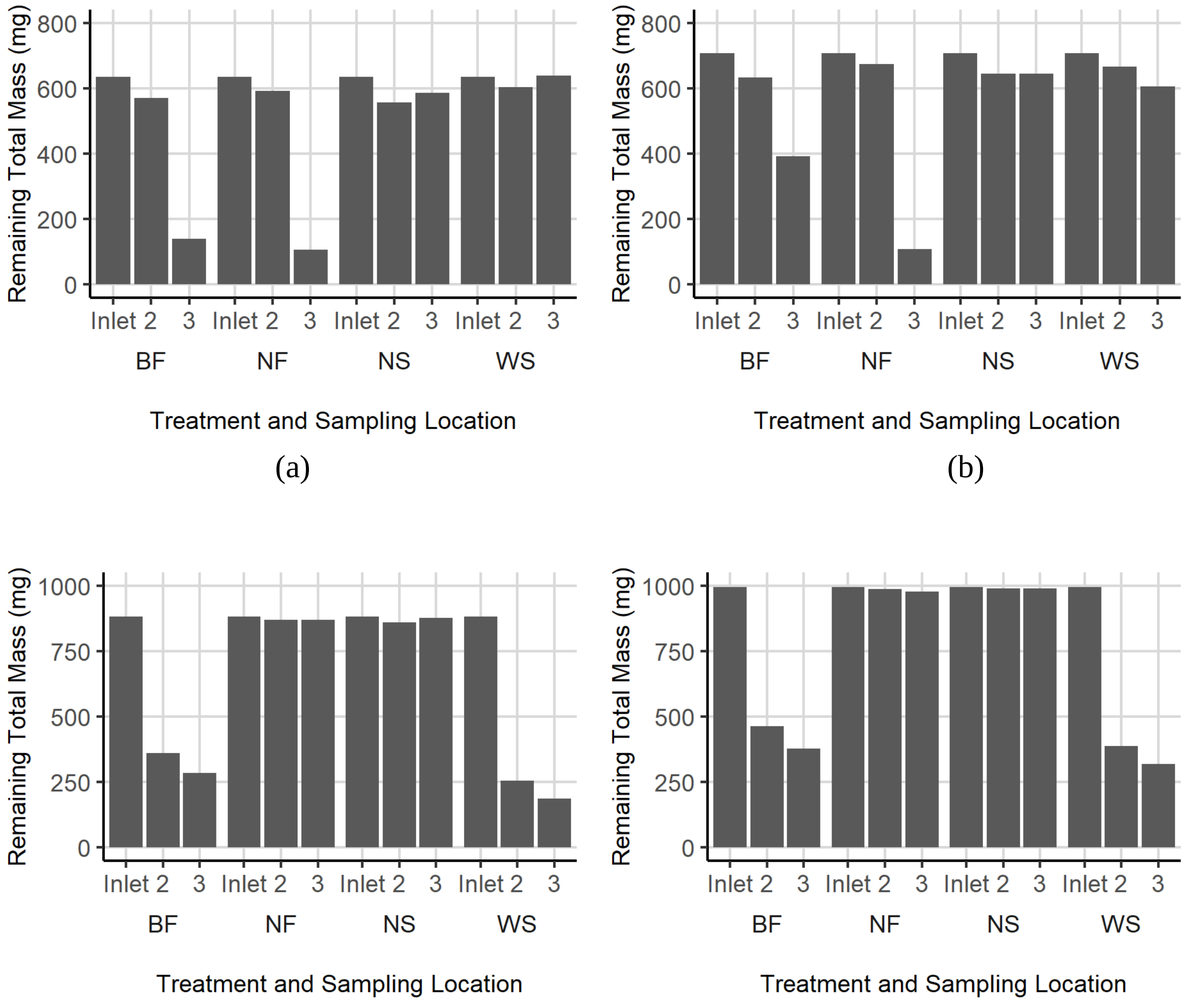
Figure 4.3. Top down view of experimental setup. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS). Letters A, B, and C denote replicates of the treatment.



(a) (b)

(c) (d)

Figure 4.4. Remaining total pollutant mass at sampling location by treatment and pollutant type for low pollutant concentration stormwater. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS). (a) dissolved phosphorus, (b) total phosphorus, (c) nitrate, (d) total nitrogen.



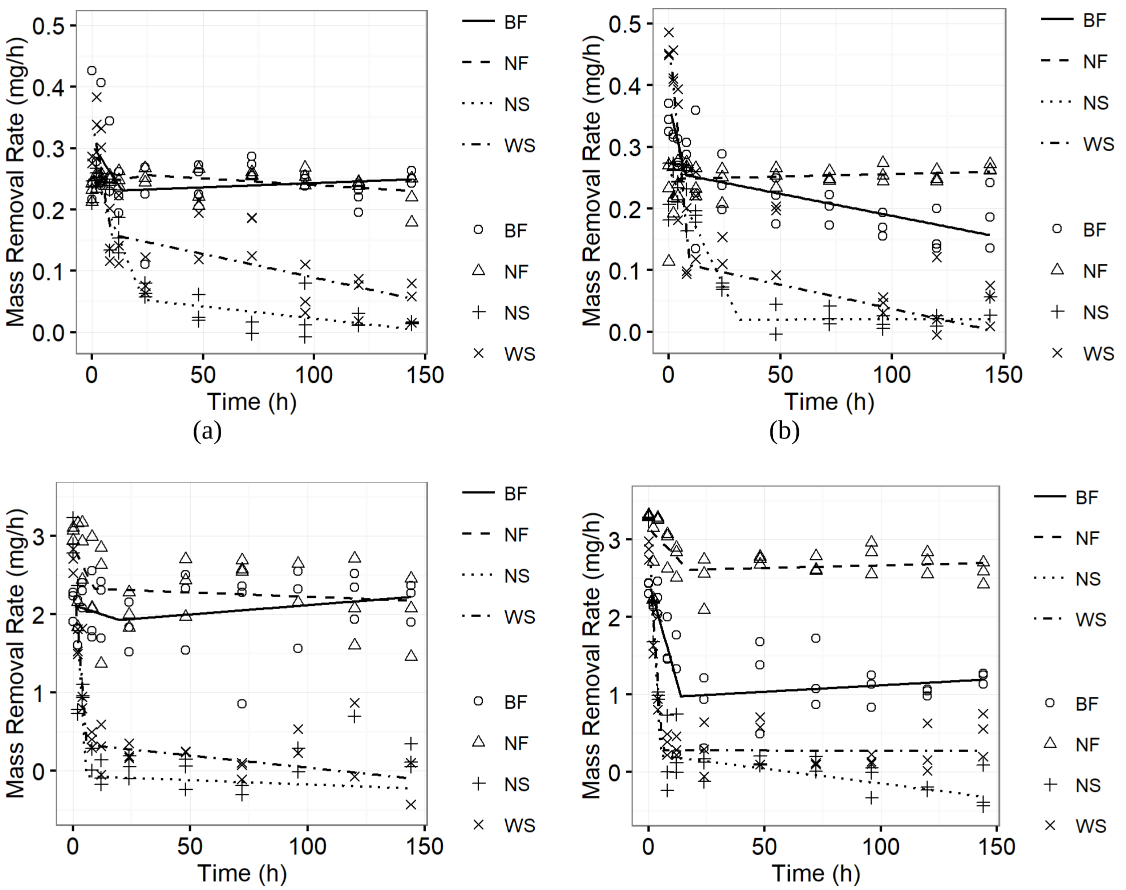
(a)

(b)

(c)

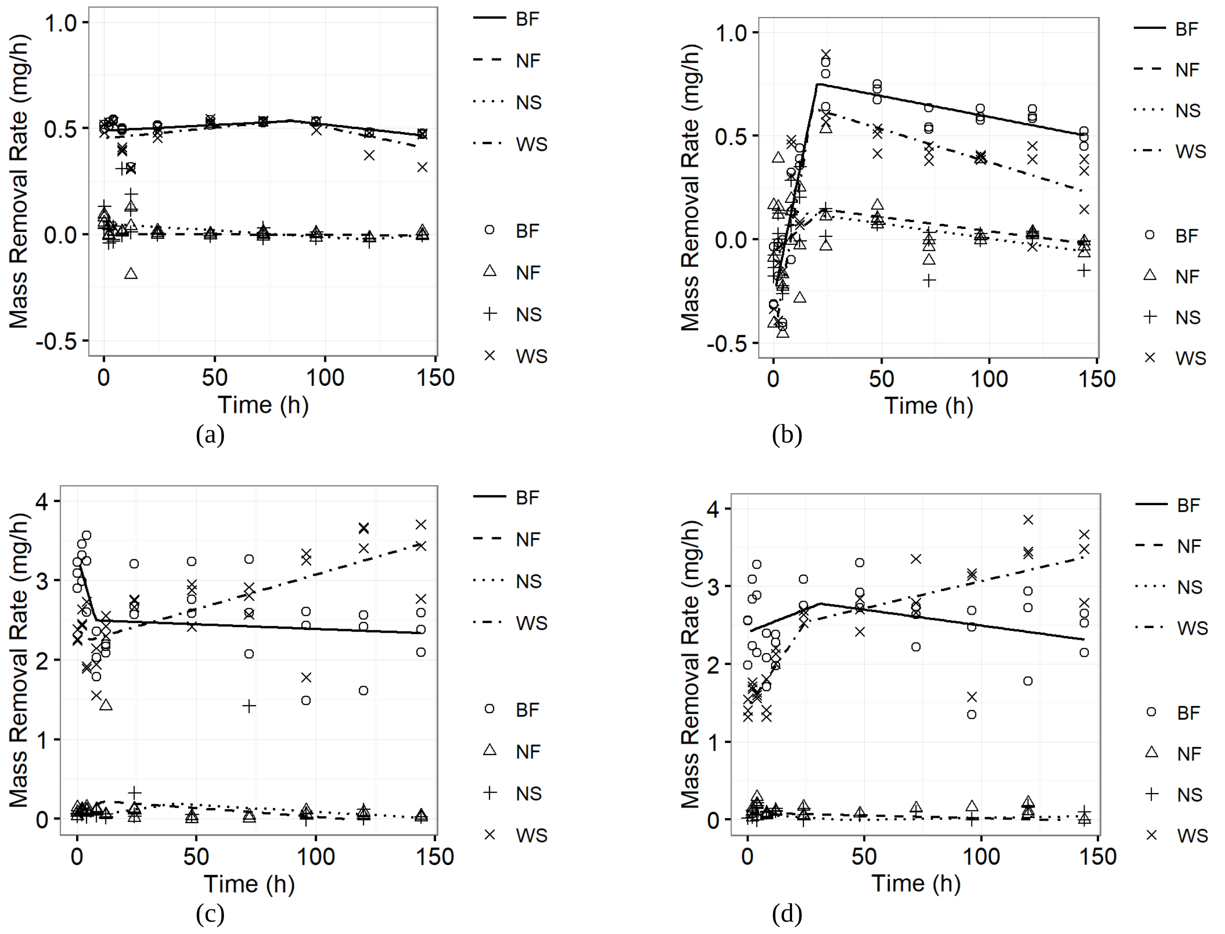
(d)

Figure 4.5. Remaining total pollutant mass at sampling location by treatment and pollutant type for high pollutant concentration stormwater. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS). (a) dissolved phosphorus, (b) total phosphorus, (c) nitrate, (d) total nitrogen.



(a) (b) (c) (d)

Figure 4.6. Piecewise linear regression of P removal rate over time with raw data. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS). Graphs shown are for Stage 3 and for the following conditions: (a) DP, low pollutant concentration, (b) TP, low pollutant concentration, (c) DP, high pollutant concentration, (d), TP, high pollutant concentration



(a) (b) (c) (d)

Figure 4.7. Piecewise linear regression of N removal rate over time with raw data. The treatments are biochar+woodchips in Stage 2 and iron+sand in Stage 3 (BF), nothing in Stage 2 and iron+sand in Stage 3 (NF), nothing in Stage 2 and sand in Stage 3 (NS), and woodchips in Stage 2 and sand in Stage 3 (WS). Graphs shown are for Stage 2 and for the following conditions: (a) NO_3, low pollutant concentration, (b) TN, low pollutant concentration, (c) NO_3, high pollutant concentration, (d), TN, high pollutant concentration.

5. Final Remarks and Suggested Future Research

Excess nutrients continue to be an issue affecting surface water ecosystems, and current Best Management Practices have limits on their capacity to ameliorate this issue (Chesapeake Bay Program, 2017; Wong et al., 1999). A proposed solution is a stand-alone filtration system that can be added to current wet retention ponds for a targeted monitoring and maintenance approach to avoid costly maintenance work across the entire pond. Furthermore, an additional aim of the filtration system is to capture certain nutrients like phosphorus (P) to be reused, thereby also sustaining a limited natural resource. The three studies in this dissertation worked towards this solution by estimating the most likely ponds and locations within ponds of high total phosphorus (TP) concentrations; testing four biochars to determine their efficacy at removing dissolved phosphorus (DP) from the water solution; and developing and testing a laboratory-scale prototype of a multi-stage filtration system for the purpose of removing and separating pollutants.

The results of these studies helped to inform the goal of developing a stand-alone filtration system with recyclable media. The first study found that TP concentrations tended to concentrate in the water column near the outlet and middle of ponds, in urban ponds, and when pH and Fe concentrations are high. Length-to-width ratio of the pond can also be a significant indicator of TP concentration if information on pH and Fe concentration is not available. This information can help find the optimal location for the filtration system and also inform targeted monitoring and maintenance activities in lieu of costly overhauls of the entire pond. The second study found that the tested biochars cannot sorb DP at typical stormwater concentrations due to large amounts of P in their composition, an insoluble base cation concentration, and a negative surface charge. The third study found that removing pollutants separately is possible, but improvements to the media used and configuration of the filtration system are required.

Given these outcomes, recommendations for future studies include the following:

1.) Perform additional laboratory-scale testing of the three-stage filter with different filter media and configurations
2.) Attempt to release phosphorus from the filter media to be recycled
3.) Implement and test the filtration system on a wet retention pond

Perform additional testing of the filtration system

The laboratory-scale study provided information on the efficacy of the particular filter configurations and media tested to remove nitrogen, phosphorus, and lead. Additional studies are recommended so that a multi-stage filter can optimally remove multiple pollutants and separate them such that phosphorus can be reused. Based on the results of this study, a combination of woodchips-only and iron/sand media may be the ideal combination that optimizes nutrient removal and decreases cost. Additional media should also be tested that specifically targets the removal of toxic metals such as lead so that media in subsequent stages can be recycled safely. Finally, a sediment trap and aeration area after any denitrifying stages with organic matter is recommended to avoid clogging and reducing conditions in subsequent stages.

Attempt to release phosphorus from the filter media to be recycled

One of the goals of the filtration system is to recycle collected nutrients such as phosphorus. Phosphorus attached to the media will therefore need to be released from the media to be reused. Such experiments have been conducted (Genz et al., 2004; S E Rosenquist et al., 2011), and testing is recommended for the specific media that will be used in this filtration system.

Implement and test the filtration system on a wet retention pond

Once a filter configuration and media combination have been successfully tested on the laboratory scale, the next step is to implement it in the field. Considering laboratory conditions are often controlled, results from any field-scale tests may yield different outcomes. The recommendation is to construct a field-scale version of the filtration system to be connected and tested on a functioning wet retention pond.

These recommendations will further advance the development of a filtration system that can both remove excess pollutants from retention ponds, therefore lengthening their useful life, and retain specific nutrients like phosphorus for recycling.

APPENDIX A: STATISTICAL CODE

Pond Analysis

```
# Stephanie Houston  9/28/2015
# Analysis for trends in pond data collected Summer 2014
# -- cleaned for LISA 2/1/2017


############# SETTING WORKING DIRECTORY AND READING IN FILES
###############

# open libraries
library("lmerTest", lib.loc="~/R/win-library/3.2")
library("piecewiseSEM", lib.loc="~/R/win-library/3.2")
library("plot3D", lib.loc="~/R/win-library/3.2")
library(plyr) # need this package to do rename factors
library("ggplot2", lib.loc="~/R/win-library/3.2")
library("scales", lib.loc="~/R/win-library/3.2") # need this with ggplot2 for
scale_colour_gradient

# package citations
citation(package="lmerTest")
citation(package="piecewiseSEM")
citation(package="ggplot2")
citation(package="scales")

# set working directory
setwd("~/VT/Research/Data/Ponds")

# read in pond data
water_raw<-read.csv("Rdata_water161013.csv")
sed_raw<-read.csv("Rdata_sediment170120.csv")
ssamples <- sed_raw  # duplicate raw dataset; want a copy that doesn't get manipulated with


############# VARIABLE PREPARATIONS ###################################


# filter variables
wsamples <- subset(water_raw, BottleID!="EB" & BottleID!="FB" & BottleID!="TB" &
SiteID!="NM" & (PondLocation=="I" | PondLocation=="M" | PondLocation=="O"))
wblanks <- subset(water_raw, BottleID=="EB" | BottleID=="FB" | BottleID=="TB")
wsamples$SiteID <- factor(wsamples$SiteID)
wsamples$PondLocation<-factor(wsamples$PondLocation)
```

```
wsamples$PondLocationNum <-
ifelse(wsamples$PondLocation=="I",1,ifelse(wsamples$PondLocation=="M",2,3))
wsamples$TP_mgLround <- round(wsamples$TP_mgL, digits=2)
ssamples <- subset(ssamples, Pond.ID!="NM")  # remove "NM" from sediment Pond ID
ssamples$Pond.ID <- factor(ssamples$Pond.ID) # applying factor again to update factors
because won't work otherwise for some reason - see "HelpfulRCommands.R" for URL
ssamples$Pmgkground <- round(ssamples$Pmgkg, digits=0)
ssamples$DepthValue <- ifelse(ssamples$Depth.Dummy==1,0,2)
DPvals <- subset(wsamples, SiteID=="DP")
GPvals <- subset(wsamples, SiteID=="GP")
IDvals <- subset(wsamples, SiteID=="ID")
JWvals <- subset(wsamples, SiteID=="JW")
LPvals <- subset(wsamples, SiteID=="LP")
DPvals_sed <- subset(ssamples, Pond.ID=="DP")
GPvals_sed <- subset(ssamples, Pond.ID=="GP")
IDvals_sed <- subset(ssamples, Pond.ID=="ID")
JWvals_sed <- subset(ssamples, Pond.ID=="JW")
LPvals_sed <- subset(ssamples, Pond.ID=="LP")


#### add variables to dataframe "wsamples"
wsamples$lnTP <- log(wsamples$TP_mgL)
wsamples$pH2 <- wsamples$pH^2
# dummy variables
wsamples$dagricultural <- as.numeric(wsamples$PondType=="ag")
wsamples$durban <- as.numeric(wsamples$PondType=="urb")
wsamples$durban2 <- as.numeric(wsamples$PondType=="urb" | wsamples$PondType=="golf")
wsamples$dgolf <- as.numeric(wsamples$PondType=="golf")
wsamples$doutlet <- as.numeric(wsamples$PondLocation=="O")
wsamples$dinlet <- as.numeric(wsamples$PondLocation=="I")
wsamples$dmiddle <- as.numeric(wsamples$PondLocation=="M")
wsamples$dummy_constr <- as.numeric(wsamples$SiteID=="ID")
wsamples$ln_DOperc <- wsamples$DO_perc
wsamples$pHhighlow <- as.numeric(wsamples$pH<7.3 | wsamples$pH>8.5)
wsamples$pHsqrt <- sqrt(wsamples$pH)
# adding pond built date and laste dredged date
DP <- wsamples$SiteID=='DP'
GP <- wsamples$SiteID=='GP'
ID <- wsamples$SiteID=='ID'
JW <- wsamples$SiteID=='JW'
LP <- wsamples$SiteID=='LP'
wsamples[DP,"DateBuilt"] <- 1937
wsamples[GP,"DateBuilt"] <- 1965
wsamples[ID,"DateBuilt"] <- 2011
wsamples[JW,"DateBuilt"] <- 1965
wsamples[LP,"DateBuilt"] <- 1965
```

```
wsamples[DP,"DateDredged"] <- 1986
wsamples[GP,"DateDredged"] <- 2003
wsamples[ID,"DateDredged"] <- 2011
wsamples[JW,"DateDredged"] <- 1996
wsamples[LP,"DateDredged"] <- 2011
wsamples[DP,"IOdistance"] <- 265
wsamples[GP,"IOdistance"] <- 4
wsamples[ID,"IOdistance"] <- 71
wsamples[JW,"IOdistance"] <- 48
wsamples[LP,"IOdistance"] <- 51
wsamples$pHbelow85 <- wsamples$pH[wsamples$pH<8.5]


#### add variables to dataframe "ssamples"
# add variable to normalize some metals
ssamples$lnCu <- log(ssamples$Cu)   # ln of Cu
ssamples$lnNi <- log(ssamples$Ni)   # ln of Ni
ssamples$lnCumgkg <- log(ssamples$Cu_mgkg)   # ln of Cu
ssamples$lnNimgkg <- log(ssamples$Ni_mgkg)   # ln of Ni
ssamples$lnAlmgkg <- log(ssamples$Al_mgkg)   # ln of Al
ssamples$lnFemgkg <- log(ssamples$Fe_mgkg)   # ln of Fe
ssamples$pH2 <- ssamples$pH^2
# dummy variables
ssamples$dagricultural <- as.numeric(ssamples$PondType=="ag")
ssamples$durban <- as.numeric(ssamples$PondType=="urb")
ssamples$dgolf <- as.numeric(ssamples$PondType=="golf")
ssamples$durban2 <- as.numeric(ssamples$PondType=="urb" | ssamples$PondType=="golf")
ssamples$doutlet <- as.numeric(ssamples$Location=="O")
ssamples$dinlet <- as.numeric(ssamples$Location=="I")
ssamples$dmiddle <- as.numeric(ssamples$Location=="M")
ssamples$dummy_constr <- as.numeric(ssamples$Pond.ID=="ID")

# rename factors to anonymize ponds - need these for graphs for paper
wsamples$SiteIDalt<-revalue(wsamples$SiteID, c("DP"="Urb1", "GP"="Urb2", "ID"="Urb3",
"JW"="Ag1", "LP"="Ag2"))
wsamples$PondTypealt<-revalue(wsamples$PondType, c("golf"="urb"))
ssamples$Pond.IDalt<-revalue(ssamples$Pond.ID, c("DP"="Urb1", "GP"="Urb2",
"ID"="Urb3", "JW"="Ag1", "LP"="Ag2"))
ssamples$PondTypealt<-revalue(ssamples$PondType, c("golf"="urb"))

################ ANOVA #################

# water: significance of sampling location and depth with interaction with pond site(Heather)
fit<-aov(lnTP~ SiteID + PondLocation + depth_m + SiteID:PondLocation + SiteID:depth_m +
         PondLocation:depth_m, data=wsamples)
summary(fit)
```

```
TukeyHSD(fit)

# sediment: significance of sampling location and depth with interaction with pond site(Heather)
sedfit<-aov(Pmgkg~ Pond.ID + Location + Depth.Dummy + Pond.ID:Location +
Pond.ID:Depth.Dummy +
        Location:Depth.Dummy, data=ssamples)
summary(sedfit)

# sediment: significance of Ni in ponds
sedNifit<-aov(Ni~ Pond.ID, data=ssamples)
summary(sedNifit)

DPvals_sedO <- subset(DPvals_sed, Location=="O")
DP_seddepthfit <- aov(Pmgkg~DepthValue, data=DPvals_sedO)
summary(DP_seddepthfit)

# ANOVAs for all metals - Location significance
sedCu_locfit <- aov(Cu ~ Location, data=ssamples)
summary(sedCu_locfit)

sedFe_locfit <- aov(Fe ~ Location, data=ssamples)
summary(sedFe_locfit)

sedHg_locfit <- aov(Hg ~ Location, data=ssamples)
summary(sedHg_locfit)

sedNi_locfit <- aov(Ni ~ Location, data=ssamples)
summary(sedNi_locfit)

sedPb_locfit <- aov(Pb ~ Location, data=ssamples)
summary(sedPb_locfit)

sedZn_locfit <- aov(Zn~ Location, data=ssamples)
summary(sedZn_locfit)


# ANOVAs for all metals - depth significance
sedCu_depthfit <- aov(Cu ~ DepthValue, data=ssamples)
summary(sedCu_depthfit)

sedFe_depthfit <- aov(Fe ~ DepthValue, data=ssamples)
summary(sedFe_depthfit)

sedHg_depthfit <- aov(Hg ~ DepthValue, data=ssamples)
summary(sedHg_depthfit)
```

```
sedNi_depthfit <- aov(Ni ~ DepthValue, data=ssamples)
summary(sedNi_depthfit)

sedPb_depthfit <- aov(Pb ~ DepthValue, data=ssamples)
summary(sedPb_depthfit)

sedZn_depthfit <- aov(Zn~ DepthValue, data=ssamples)
summary(sedZn_depthfit)


################# LINEAR MIXED MODELS
####################################################

# **** WATER MODELS ********

WaterModelA<-lmer(lnTP ~ d_urban + d_outlet + d_middle + pH + Fe_mgL + (1|SiteID),
data=wsamples, REML=FALSE) # FINAL - Water Model A
sem.model.fits(WaterModelA,aicc= TRUE)
summary(WaterModelA)

WaterModelB<-lmer(lnTP ~ LWratio + d_outlet + d_middle + (1|SiteID), data=wsamples,
REML=FALSE) # FINAL - Water Model B
sem.model.fits(WaterModelB,aicc= TRUE)
summary(WaterModelB)


# **** SEDIMENT MODELS ********

SedimentModelA <- lmer(P_mgkg ~ LWratio + lnAlmgkg + lnCumgkg + (1|Pond.IDalt),
data=ssamples, REML=FALSE) # FINAL
sem.model.fits(SedimentModelA,aicc= TRUE)
summary(SedimentModelA)

SedimentModelB <- lmer(P_mgkg ~ temp_C + d_golf + (1|Pond.IDalt) + (1|Depth.Dummy),
data=ssamples, REML=FALSE) #FINAL
sem.model.fits(SedimentModelB,aicc= TRUE)
summary(SedimentModelB)

######################## OLD GRAPH COMMANDS
#######################################
#
# # creating plot window of particular size:
http://stackoverflow.com/questions/2129952/creating-a-plot-window-of-a-particular-size
# #Example: plot(1:10); dev.new(width=5, height=4); plot(1:20)
# dev.new(width=5, height=4)
#
```

```
# # Pwat by site ID
# # thought "png" command allowed me to set size of graphic, but does not seem to work
# #png(file="BoxplotW_TPSiteIDAlt_sizetest.png",width=450,height=300,res=72)
# #dev.new(width=3.3, height=3.3)
# png("Pwat_boxplotSiteID.png", width=174, height=174, units="mm", res=600,
bg="transparent")
# par(font.axis=2, font.lab=2) # bolds axes labels
# boxplot(TP_mgL~SiteIDalt, data=wsamples, xlab="", ylab="Total Phosphorus (mg/L)",
ylim=c(0,0.5), cex.axis=1.5, cex.lab=1.5, col = "white", whisklwd=2, outlwd=2)
# #boxplot(TP_mgL~SiteIDalt, data=wsamples, xlab="", ylab="Total Phosphorus (mg/L)",
ylim=c(0,0.5), cex.axis=1.5, cex.lab=1.5, col =
c("greenyellow","green2","green4","sienna3","sienna4"), whisklwd=2, outlwd=2)
# abline(h=0.025, col="black", lty=5)
# # original code from URL to add text: text(-1.5, 0.1, "0.025 mg/L", col = "red")
# text(0.85, 0.05, "0.025 mg/L", col = "black")
# rect(2.5,0.48, 3.5, 0.515, col="white", border="white")
# text(3, 0.5, "1.4 mg/L", col = "black")
# dev.off()
#
# # Pwat by sampling location
# png("Pwat_boxplotPondLocation.png", width=174, height=174, units="mm", res=600,
bg="transparent")
# #dev.new(wwidth=174, height=174, units="mm", res=1200)
# #par(font.axis=2, font.lab=2)
# dev.new()
# boxplot(TP_mgL~PondLocation, data=wsamples, xlab="", ylab="Total Phosphorus (mg/L)",
ylim=c(0,0.5), cex.axis=1.5, cex.lab=1.5, col = "white", whisklwd=2, outlwd=2)
# dev.off()
#
#
#
#
# #############################################
#
#
#
#
# # total phosphorus in sediment
# par(font.axis=2, font.lab=2)
# boxplot(P_mgkg~Pond.IDalt, data=ssamples, xlab="", ylab="Total Phosphorus (mg/kg)",
cex.axis=1.5, cex.lab=1.5, col = "tan3", whisklwd=2, outlwd=2)
# abline(h=0.025, col=34, lty=5)


############### FINAL GRAPHS FOR PAPER
#####################################
```

```
### revised water boxplot using ggplot2
ggplot(wsamples, aes(x=SiteIDalt, y=TP_mgL))  +
  geom_boxplot() +
  stat_boxplot(geom='errorbar') +
  theme_classic(base_size=8) +
  coord_cartesian(ylim=c(0,0.5)) +
  xlab("Site") +
  ylab("Total Phosphorus Concentration (mg/L)") +
  geom_label(aes(x=3, y=0.49, label="1.4 mg/L"), fill="white", size=3) +
  geom_hline(aes(yintercept=0.025), linetype="dashed") +
  geom_text(aes(x=0.95, y=0.041, label="0.025 mg/L"), size=3) +
  theme(axis.text.x = element_text(size=8), axis.text.y = element_text(size=8)) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("boxplotW_TPvsSite.png", width=84, height=60, units="mm")

### revised water boxplot(sampling location) using ggplot2
ggplot(wsamples, aes(x=PondLocation, y=TP_mgL))  +
  geom_boxplot() +
  stat_boxplot(geom='errorbar') +
  theme_classic(base_size=8) +
  coord_cartesian(ylim=c(0,0.5)) +
  xlab("Site") +
  ylab("Total Phosphorus Concentration (mg/L)") +
  geom_label(aes(x=3, y=0.49, label="1.4 mg/L"), fill="white", size=3) +
  geom_hline(aes(yintercept=0.025), linetype="dashed") +
  geom_text(aes(x=0.95, y=0.041, label="0.025 mg/L"), size=3) +
  theme(axis.text.x = element_text(size=8), axis.text.y = element_text(size=8)) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("boxplotW_TPvsSite.png", width=84, height=60, units="mm")

### revised sediment boxplot using ggplot2
ggplot(ssamples, aes(x=Pond.IDalt, y=Pmgkg))  +
  geom_boxplot() +
  stat_boxplot(geom='errorbar') +
  theme_classic(base_size=8) +
  xlab("Site") +
  ylab("Total Phosphorus Concentration (mg/kg)") +
  theme(axis.text.x = element_text(size=8), axis.text.y = element_text(size=8)) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("boxplotS_TPvsSite.png", width=84, height=60, units="mm")

boxplot(P_mgkg~Pond.IDalt, data=ssamples, xlab="", ylab="Total Phosphorus (mg/kg)",
cex.axis=1.5, cex.lab=1.5, col = "tan3", whisklwd=2, outlwd=2)
```

```
# resources
# scaling graph without changing data: http://stackoverflow.com/questions/28198613/r-ggplot-boxplot-change-y-axis-limit


# useful websites
# changing plot and legend margins: http://stackoverflow.com/questions/12211890/the-space-above-and-below-the-legend-using-ggplot2
# change tick mark labels: http://www.sthda.com/english/wiki/ggplot2-axis-ticks-a-guide-to-customize-tick-marks-and-labels#change-tick-mark-labels
# set width and height of plot elements for PDF: http://stackoverflow.com/questions/21484999/r-scale-plot-elements-within-pdf-of-set-width-and-height


########### WATER PROFILE GRAPHS ##################

# DP sampling depth/location/TP_mgL plot
#png("Fig_DP.png", width=84, height=70, units="mm", res=100, bg="transparent")

ggplot(data = DPvals, mapping = aes(x = PondLocation, y = depth_m)) +
  geom_point(aes(colour = TP_mgL), shape = 19, size=3) +
  geom_text(aes(label=TP_mgLround), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE) +
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (m)") +
  scale_y_reverse(lim=c(1.75,0)) +
  scale_colour_gradient(name="Pwat (mg/L)", limits=c(0,0.25), low="gray87", high="gray0", oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_DP.png", width=84, height=60, units="mm")

# ggsave("ggplot_DP.png", width=84, height=60, units="mm", dpi=50)
#dev.off()

# GP sampling depth/location/TP_mgL plot
ggplot(data = GPvals, mapping = aes(x = PondLocation, y = depth_m)) +
  geom_point(aes(colour = TP_mgL), shape = 19, size=3) +
  geom_text(aes(label=TP_mgLround), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE) +
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (m)") +
```

```
  scale_y_reverse(lim=c(1.75,0)) +
  scale_colour_gradient(name="Pwat (mg/L)", limits=c(0,0.25), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_GP.png", width=84, height=60, units="mm")

# ID sampling depth/location/TP_mgL plot
ggplot(data = IDvals, mapping = aes(x = PondLocation, y = depth_m)) +
  geom_point(aes(colour = TP_mgL), shape = 19, size=3) +
  geom_text(aes(label=TP_mgLround), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE)
+
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (m)") +
  scale_y_reverse(lim=c(1.75,0)) +
  scale_colour_gradient(name="Pwat (mg/L)", limits=c(0,0.25), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_ID.png", width=84, height=60, units="mm")

# JW sampling depth/location/TP_mgL plot
ggplot(data = JWvals, mapping = aes(x = PondLocation, y = depth_m)) +
  geom_point(aes(colour = TP_mgL), shape = 19, size=3) +
  geom_text(aes(label=TP_mgLround), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE)
+
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (m)") +
  scale_y_reverse(lim=c(1.75,0)) +
  scale_colour_gradient(name="Pwat (mg/L)", limits=c(0,0.25), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_JW.png", width=84, height=60, units="mm")

# LP sampling depth/location/TP_mgL plot
ggplot(data = LPvals, mapping = aes(x = PondLocation, y = depth_m)) +
  geom_point(aes(colour = TP_mgL), shape = 19, size=3) +
```

```
  geom_text(aes(label=TP_mgLround), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE)
+
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (m)") +
  scale_y_reverse(lim=c(1.75,0)) +
  scale_colour_gradient(name="Pwat (mg/L)", limits=c(0,0.25), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_LP.png", width=84, height=60, units="mm")



########### SEDIMENT PROFILE GRAPHS #################
# DP sampling depth/location/Pmgkg sediment plot
ggplot(data = DPvals_sed, mapping = aes(x = Location, y = DepthValue)) +
  geom_point(aes(colour = Pmgkg), shape = 19, size=3) +
  geom_text(aes(label=Pmgkground), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE) +
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (cm)") +
  scale_y_reverse(lim=c(2,-0.5)) +
  scale_colour_gradient(name="Psed (mg/kg)", limits=c(0,1100), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_DPsed.png", width=84, height=60, units="mm")

ggplot(data = GPvals_sed, mapping = aes(x = Location, y = DepthValue)) +
  geom_point(aes(colour = Pmgkg), shape = 19, size=3) +
  geom_text(aes(label=Pmgkground), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE) +
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (cm)") +
  scale_y_reverse(lim=c(2,-0.5)) +
  scale_colour_gradient(name="Psed (mg/kg)", limits=c(0,1100), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
```

```
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_GPsed.png", width=84, height=60, units="mm")

ggplot(data = IDvals_sed, mapping = aes(x = Location, y = DepthValue)) +
  geom_point(aes(colour = Pmgkg), shape = 19, size=3) +
  geom_text(aes(label=Pmgkground), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE) +
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (cm)") +
  scale_y_reverse(lim=c(2,-0.5)) +
  scale_colour_gradient(name="Psed (mg/kg)", limits=c(0,1100), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_IDsed.png", width=84, height=60, units="mm")

ggplot(data = JWvals_sed, mapping = aes(x = Location, y = DepthValue)) +
  geom_point(aes(colour = Pmgkg), shape = 19, size=3) +
  geom_text(aes(label=Pmgkground), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE) +
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (cm)") +
  scale_y_reverse(lim=c(2,-0.5)) +
  scale_colour_gradient(name="Psed (mg/kg)", limits=c(0,1100), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
ggsave("ggplot_JWsed.png", width=84, height=60, units="mm")

ggplot(data = LPvals_sed, mapping = aes(x = Location, y = DepthValue)) +
  geom_point(aes(colour = Pmgkg), shape = 19, size=3) +
  geom_text(aes(label=Pmgkground), size=3.5, hjust=-0.3, vjust=-0.1, check_overlap=TRUE) +
  scale_x_discrete(labels=c("Inlet", "Middle", "Outlet")) +
  xlab("Sampling Location") +
  ylab("Depth (cm)") +
  scale_y_reverse(lim=c(2,-0.5)) +
  scale_colour_gradient(name="Psed (mg/kg)", limits=c(0,1100), low="gray87", high="gray0",
oob=squish) +
  theme_classic(base_size=10) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(legend.margin=unit(0,"mm")) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm"))
```

```
ggsave("ggplot_LPsed.png", width=84, height=60, units="mm")
```

Biochar Sorption

```
# Stephanie Houston, 7/21/2016
#
# graphs for biochar data


# open required packages
library("ggplot2", lib.loc="~/R/win-library/3.2")
library("reshape2", lib.loc="~/R/win-library/3.2")

# set working directory
setwd("~/VT/Research/Data/BiocharCharacterization")


# read in biochar data
WX<-read.csv("Rraw_WXdata170308.csv")
sorp_raw<-read.csv("Rraw_Sorpdata170330.csv")
sorp_long<-read.csv("SorptionDataLongFormat20180515.csv")

################### DATA
###############################################################
Cperc <- c(52.93, 62.22, 77.38, 39.14);
Cstd <- c(0.017, 0.027, 0.121, 0.026);
Nperc <- c(0.83, 0.72, 0, 0);
Nstd <- c(0.001, 0, 0, 0);
ZP <- c(-28.9, -32.3, -26.6, -45.7);
ZPstd <- c(2.5, 6.2, 0.9, 4.9);
ZP_pH1 <- c(7.11, 7.28, 8.81, 7.58);
ZP_pH2 <- c(7.48, 7.49, 8.87, 7.75);
SA <- c(128.476, 260.287, 423.768, 79.777);




# data manipulation
# pH variables
pHmean_tmp = aggregate(WX$pH_1hr, list(WX$Sample), mean)
pHstdev_tmp = aggregate(WX$pH_1hr, list(WX$Sample), sd)
WXpH<-data.frame(biochars = c("Control", "CS400", "CS600", "MH", "RH"),
pHmean=pHmean_tmp$x, pHstdev=pHstdev_tmp$x)
WXpH_nocontrol <- subset(WXpH, biochars!="Control")
# conductivity variables
condmean_tmp = aggregate(WX$cond_uS1hr, list(WX$Sample), mean)
condstdev_tmp = aggregate(WX$cond_uS1hr, list(WX$Sample), sd)
```

```
WXcond<-data.frame(biochars = c("Control", "CS400", "CS600", "MH", "RH"),
condmean=condmean_tmp$x, condstdev=condstdev_tmp$x)
WXcond_nocontrol <- subset(WXcond, biochars!="Control")


# manipulating "sorp_long" dataframe
sorp_longnocontrol<-sorp_long
sorp_longnocontrol<-sorp_longnocontrol[sorp_longnocontrol$biochar!="Control",]
sorp_longnocontrol$Bsorbed[sorp_longnocontrol$biochar=="Control"]<-NA
list15 <- rep(15,length(sorp_long$Bsorbed))
sorp_long$Bsorbedadd15<-sorp_long$Bsorbed+list15
sorp_long$lnbsorbedadd15<-log(sorp_long$Bsorbedadd15)

list15 <- rep(15,length(sorp_longnocontrol$Bsorbed))
sorp_longnocontrol$Bsorbedadd15<-sorp_longnocontrol$Bsorbed+list15
sorp_longnocontrol$lnbsorbedadd15<-log(sorp_longnocontrol$Bsorbedadd15)

#sorp_long$Bsorbedadd15<-sorp_long$Bsorbed+15 # doesn't seem to add to all rows

############ STATISTICS ###########################
pH_anova <- anova()


# testing statistical assumptions
qqnorm(sorp_long$Bsorbed)


# anova but residual plots iffy
fit_biochar <- aov(Bsorbed ~ biochar, data=sorp_long)
summary(fit_biochar)
par(mfrow=c(2,2), mex=0.6)
plot(fit_biochar)
par(mfrow=c(1,1), mex=1)
TukeyHSD(fit_biochar)
plot(TukeyHSD(fit_biochar))

# anova with control removed
fit_biochar <- aov(lnbsorbedadd15 ~ biochar, data=sorp_longnocontrol)
summary(fit_biochar)
par(mfrow=c(2,2), mex=0.6)
plot(fit_biochar)
par(mfrow=c(1,1), mex=1)
TukeyHSD(fit_biochar)
plot(TukeyHSD(fit_biochar))
```

```
################### PLOTS #####################################


### plotting sorption
# manipulating data for plot
# dropping unneeded variables (http://stackoverflow.com/questions/4605206/drop-data-frame-
columns-by-name)
drops <-
c("Control_mgL","Control_mgkg","CS600_mgkg","MH_mgkg","RH_mgkg","Control_mgLnor
m","CS600_mgLnorm","MH_mgLnorm","RH_mgLnorm","X","X.1")
sorpraw_mgL <- sorp_raw[,!(names(sorp_raw) %in% drops)]
# converting wide dataframe to long dataframe (http://seananderson.ca/2013/10/19/reshape.html)
sorpdatalong <- melt(sorpraw_mgL, id.vars="Solution_mgL")
sorpdatalong_clean <- subset(sorpdatalong, sorpdatalong$value!="NA")
# ggplot of sorption
ggplot(data = sorpdatalong_clean, aes(x = Solution_mgL, y=value)) +
  geom_line(aes(linetype=variable)) +
  xlab("Solution Concentration of DP (mg/L)") +
  ylab("DP Concentration (mg/L)") +
  theme_bw(base_size=10) +
  theme(axis.text=element_text(size=14), axis.title=element_text(size=14,face="bold")) +
  theme(plot.margin= unit(c(0.1,0.1,0.1,0.1), units="cm")) +
  theme(legend.key = element_rect(colour=NA), legend.text=element_text(size=14)) + #
http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-
entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-
r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title
```

Laboratory Filter Experiment

Linear Interpolation for Calculation of Removal Rates and Totals

```
# Stephanie Houston 4/14/2018
#
# Code for conducting piecewise linear regression
# And calculating amount removed

setwd("C:/Users/Stephanie/Documents/VT/Research/Data/Kinetics")

rm(list=ls())

library("ggplot2", lib.loc="~/R/win-library/3.2")

# assigning specific nutrient variables to piecewise universal variables
analysis<-'SEAL'  # 'Metals' or 'SEAL'
scenario<-'DL3'   # 'L3' for Pb because no D/T
nutrient<-'PO4'   # 'PO4', 'NO3', or 'Pb'

#####################################################################
#           READING IN DATA
####################################################################

# read in CSV data
Metals <-read.csv("finaldata_Metalsdiff.csv")
SEALdiffcor <-read.csv("finaldata_SEALdiffcor.csv")
#attach(x)


################################################################
#   DEFINE VARIABLES
################################################################

##### General
TimePoint<-c(0,2,4,8,12,24,48,72,96,120,144)
TimeTreatment <- aggregate(PO4diff_mgpL ~ TimePoint+Treatment, data=SEALdiffcor,
FUN="mean")
TimeTreatment$PO4diff_mgpL<-NULL
# average flow rates for boxes; first value is low concentration, second is high
flowrateL<-data.frame(In=numeric(1), BF=numeric(1), NF=numeric(1), NS=numeric(1),
WS=numeric(1))
flowrateL$In<-24.6
flowrateL$BF<-24.1
flowrateL$NF<-24.3
flowrateL$NS<-24.9
```

```
flowrateL$WS<-25.1
flowrateH<-data.frame(In=numeric(1), BF=numeric(1), NF=numeric(1), NS=numeric(1),
WS=numeric(1))
flowrateH$In<-24.8
flowrateH$BF<-24.8
flowrateH$NF<-24.7
flowrateH$NS<-25.4
flowrateH$WS<-24.3

##### Metals
Metals$TreatLoc <- paste(Metals$Treatment, Metals$Location, sep="_")
Metals$TreatLoc <- as.factor(Metals$TreatLoc)
Metals$dummyBF <- as.numeric(Metals$Treatment=="BF")
Metals$dummyNF <- as.numeric(Metals$Treatment=="NF")
Metals$dummyNS <- as.numeric(Metals$Treatment=="NS")
Metals$dummyWS <- as.numeric(Metals$Treatment=="WS")
Metals$dummyIn <- as.numeric(Metals$Treatment=="In")
Metals$dummyLoc1 <- as.numeric(Metals$Location=="1")
Metals$dummyLoc2 <- as.numeric(Metals$Location=="2")
Metals$dummyLoc3 <- as.numeric(Metals$Location=="3")

Metals_L<- subset(Metals, Storm=="L") #filter to low concentration storm
Metals_H<- subset(Metals, Storm=="H") #filter to high concentration storm


# subsetting "Metals" to sampling locations
Metals_LIn <- subset(Metals_L, Location=="In")
Metals_L1 <- subset(Metals_L, Location=="1")
Metals_L2 <- subset(Metals_L, Location=="2")
Metals_L3 <- subset(Metals_L, Location=="3")
Metals_HIn <- subset(Metals_H, Location=="In")
Metals_H1 <- subset(Metals_H, Location=="1")
Metals_H2 <- subset(Metals_H, Location=="2")
Metals_H3 <- subset(Metals_H, Location=="3")


##### SEAL

# copying original "SEALdiffcor" variable to another variable name
# all code below uses "SEALdiffcor", don't want to change so many variable names, so making
copy of original just in case
SEALdiffcor_original<-SEALdiffcor

# adding variables to "SEALdiffcor"
SEALdiffcor$expTimePoint <- exp(SEALdiffcor$TimePoint)
SEALdiffcor$sqTimePoint <- SEALdiffcor$TimePoint^2
```

```
SEALdiffcor$TreatLoc <- paste(SEALdiffcor$Treatment, SEALdiffcor$Location, sep="_")
SEALdiffcor$TreatLoc <- as.factor(SEALdiffcor$TreatLoc)
SEALdiffcor$dummyBF <- as.numeric(SEALdiffcor$Treatment=="BF")
SEALdiffcor$dummyNF <- as.numeric(SEALdiffcor$Treatment=="NF")
SEALdiffcor$dummyNS <- as.numeric(SEALdiffcor$Treatment=="NS")
SEALdiffcor$dummyWS <- as.numeric(SEALdiffcor$Treatment=="WS")
SEALdiffcor$dummyIn <- as.numeric(SEALdiffcor$Treatment=="In")
SEALdiffcor$dummyLoc1 <- as.numeric(SEALdiffcor$Location=="1")
SEALdiffcor$dummyLoc2 <- as.numeric(SEALdiffcor$Location=="2")
SEALdiffcor$dummyLoc3 <- as.numeric(SEALdiffcor$Location=="3")

# subsetting "SEALdiffcor" to dissolved/total and high/low
SEALdiffcor_DL <- subset(SEALdiffcor, Dissolved_Total=="D" & Storm=="L")
SEALdiffcor_DH <- subset(SEALdiffcor, Dissolved_Total=="D" & Storm=="H")
SEALdiffcor_TL <- subset(SEALdiffcor, Dissolved_Total=="T" & Storm=="L")
SEALdiffcor_TH <- subset(SEALdiffcor, Dissolved_Total=="T" & Storm=="H")


# subsetting "SEALdiffcor" to sampling locations
SEALdiffcor_DLIn <- subset(SEALdiffcor_DL, Location=="In")
SEALdiffcor_DL2 <- subset(SEALdiffcor_DL, Location=="2")
SEALdiffcor_DL3 <- subset(SEALdiffcor_DL, Location=="3")
SEALdiffcor_DHIn <- subset(SEALdiffcor_DH, Location=="In")
SEALdiffcor_DH2 <- subset(SEALdiffcor_DH, Location=="2")
SEALdiffcor_DH3 <- subset(SEALdiffcor_DH, Location=="3")
SEALdiffcor_DH3noT120 <- subset(SEALdiffcor_DH, Location=="3" & TimePoint!=120)
SEALdiffcor_TLIn <- subset(SEALdiffcor_TL, Location=="In")
SEALdiffcor_TL2 <- subset(SEALdiffcor_TL, Location=="2")
SEALdiffcor_TL3 <- subset(SEALdiffcor_TL, Location=="3")
SEALdiffcor_THIn <- subset(SEALdiffcor_TH, Location=="In")
SEALdiffcor_TH2 <- subset(SEALdiffcor_TH, Location=="2")
SEALdiffcor_TH3 <- subset(SEALdiffcor_TH, Location=="3")


##############################################################################

# assigning specific nutrient variables to piecewise universal variables
#scenario<-'DL3'
#nutrient<-'PO4'
combo_nutrientscenario<-paste(nutrient,scenario,sep="")

if (analysis=="Metals") {
  # assigning nutrient scenario dataframe to universal dataframe
  scenariodf_cmdstr<-paste('nutrient_originaldf<-Metals',scenario, sep='_')
  eval(parse(text=scenariodf_cmdstr))
  # assigning nutrient scenario pollutant values to universal vector
```

```
  nutrientdiffvector_cmdstr<-paste('nutrient_diff<--
1*nutrient_originaldf$',nutrient,'diffnull_mgpL',sep=")
  eval(parse(text=nutrientdiffvector_cmdstr))
  nutrientvalvector_cmdstr<-paste('nutrient_val<--
1*nutrient_originaldf$',nutrient,'rev_mgpL',sep=")
  eval(parse(text=nutrientvalvector_cmdstr))
  if (scenario=="L2" | scenario=="L3") {
    nutrientIn_df<-Metals_LIn
  } else if (scenario=="H2" | scenario=="H3") {
    nutrientIn_df<-Metals_HIn
  } else {
    print("error in SEAL, In universal variable assignment")
  }
  if (nutrient=="Pb") {
    nutrientInvector_cmdstr<-paste('nutrientIn_vector<-nutrientIn_df$',nutrient,'rev_mgpL',sep=")
    eval(parse(text=nutrientInvector_cmdstr))
  } else if (nutrient=="Fe") {
    nutrientInvector_cmdstr<-paste('nutrientIn_vector<-
nutrientIn_df$',nutrient,'rev_mgFEpL',sep=")
    eval(parse(text=nutrientInvector_cmdstr))
  } else {
    print("error in assigning Inlet values to vector")
  }
} else if (analysis=="SEAL") {
  # assigning nutrient scenario dataframe to universal dataframe
  scenariodf_cmdstr<-paste('nutrient_originaldf<-SEALdiffcor',scenario, sep='_')
  eval(parse(text=scenariodf_cmdstr))
  # assigning nutrient scenario pollutant values to universal vector
  nutrientdiffvector_cmdstr<-paste('nutrient_diff<-
nutrient_originaldf$',nutrient,'diff_i.f_mgpL',sep=")
  eval(parse(text=nutrientdiffvector_cmdstr))
  if (scenario=="DL2" | scenario=="DL3") {
    nutrientIn_df<-SEALdiffcor_DLIn
  } else if (scenario=="DH2" | scenario=="DH3") {
    nutrientIn_df<-SEALdiffcor_DHIn
  } else if (scenario=="TL2" | scenario=="TL3") {
    nutrientIn_df<-SEALdiffcor_TLIn
  } else if (scenario=="TH2" | scenario=="TH3") {
    nutrientIn_df<-SEALdiffcor_THIn
  } else {
    print("error in SEAL, In universal variable assignment")
  }
  if (nutrient=="NO3") {
    nutrientInvector_cmdstr<-paste('nutrientIn_vector<-nutrientIn_df$',nutrient,'_mgNpL',sep=")
    eval(parse(text=nutrientInvector_cmdstr))
  } else if (nutrient=="PO4") {
```

```
    nutrientInvector_cmdstr<-paste('nutrientIn_vector<-
nutrientIn_df$',nutrient,'rev_mgPpL',sep='')
    eval(parse(text=nutrientInvector_cmdstr))
  } else {
    print("error in assigning Inlet values to vector")
  }

} else {
  print("error in Metal/SEAL universal variable assignment")
}

nutrient_originaldf$nutrient_diff<-nutrient_diff
nutrientIn_df$nutrientIn_val<-nutrientIn_vector
filename_cmdstr<-paste("filename<-'R_", combo_nutrientscenario, "_LI.csv'",sep='')
eval(parse(text=filename_cmdstr))

# calculating difference in concentration between time points and treatments
timestep<-1:144 # time steps to use for interpolation
nutrient_df<-data.frame(TimePoint=integer(132), In=numeric(132), BF=numeric(132),
NF=numeric(132), NS=numeric(132), WS=numeric(132)) # creating dataframe to compile
original data
nutrient_df$TimePoint<-nutrient_originaldf$TimePoint[nutrient_originaldf$Treatment=="BF"]
nutrient_df$BF<-nutrient_originaldf$nutrient_diff[nutrient_originaldf$Treatment=="BF"]
nutrient_df$NF<-nutrient_originaldf$nutrient_diff[nutrient_originaldf$Treatment=="NF"]
nutrient_df$NS<-nutrient_originaldf$nutrient_diff[nutrient_originaldf$Treatment=="NS"]
nutrient_df$WS<-nutrient_originaldf$nutrient_diff[nutrient_originaldf$Treatment=="WS"]

# assigning variables in dataframe to vectors
nutrient_TimePoint<-nutrient_originaldf$TimePoint[nutrient_originaldf$Treatment=="BF"]
nutrientval_BF<-nutrient_originaldf$nutrient_diff[nutrient_originaldf$Treatment=="BF"]
nutrientval_NF<-nutrient_originaldf$nutrient_diff[nutrient_originaldf$Treatment=="NF"]
nutrientval_NS<-nutrient_originaldf$nutrient_diff[nutrient_originaldf$Treatment=="NS"]
nutrientval_WS<-nutrient_originaldf$nutrient_diff[nutrient_originaldf$Treatment=="WS"]

#LP_BF<-approx(nutrient_TimePoint, nutrientval_BF, timestep) #doesn't work - doesn't output
interpolated numbers

# code interpolation and get points
LP_In <- data.frame(with(nutrientIn_df, approx(TimePoint, nutrientIn_val, xout = seq(1, 144, by
= 1),
                                        method = "linear")),method = "approx()")
LP_BF <- data.frame(with(nutrient_df, approx(TimePoint, BF, xout = seq(1, 144, by = 1),
                                      method = "linear")),method = "approx()")
LP_NF <- data.frame(with(nutrient_df, approx(TimePoint, NF, xout = seq(1, 144, by = 1),
                                      method = "linear")),method = "approx()")
LP_NS <- data.frame(with(nutrient_df, approx(TimePoint, NS, xout = seq(1, 144, by = 1),
```

```
                              method = "linear")),method = "approx()")
LP_WS <- data.frame(with(nutrient_df, approx(TimePoint, WS, xout = seq(1, 144, by = 1),
                              method = "linear")),method = "approx()")

# applying flow rates to get mass removal/hour by treatment
removal<-data.frame(TimePoint=numeric(144))
removal$TimePoint<-timestep
removal$pred_concIn<-LP_In$y
removal$pred_concdiffBF<-LP_BF$y
removal$pred_concdiffNF<-LP_NF$y
removal$pred_concdiffNS<-LP_NS$y
removal$pred_concdiffWS<-LP_WS$y
removal$massperhr_In<-LP_In$y*flowrateL$In*60/1000
removal$massdiffperhr_BF<-LP_BF$y*flowrateL$BF*60/1000
removal$massdiffperhr_NF<-LP_NF$y*flowrateL$NF*60/1000
removal$massdiffperhr_NS<-LP_NS$y*flowrateL$NS*60/1000
removal$massdiffperhr_WS<-LP_WS$y*flowrateL$WS*60/1000
# getting total
removal_totals<-colSums(removal, na.rm=TRUE)

# write results into file, including removal_totals
write.csv(removal,filename)

# displaying removal_totals as check
removal_totals

# plotting raw PO4diff by treatment vs. predicted values
ggplot(data=nutrient_originaldf,aes(x=TimePoint, y=nutrient_diff, colour=Treatment)) +
  xlab('Time (h)') + ylab('Nutrient (mg/L)') + geom_point() +
  scale_colour_manual(values = c("Red", "Green", "Blue", "Purple")) +
  geom_line(data = removal, aes(x = TimePoint, y = pred_concdiffBF), color = "red") +
  geom_line(data = removal, aes(x = TimePoint, y = pred_concdiffNF), color = "green") +
  geom_line(data = removal, aes(x = TimePoint, y = pred_concdiffNS), color = "blue") +
  geom_line(data = removal, aes(x = TimePoint, y = pred_concdiffWS), color = "purple")
```

Piecewise Linear Regression for Trend Analysis and Saturation Points

```
# Stephanie Houston 4/14/2018
#
# Code for conducting piecewise linear regression
# And calculating amount removed
# code works for nutrients, not for metals because not needed anymore (5/31/2018)


setwd("C:/Users/Stephanie/Documents/VT/Research/Data/Kinetics")


# opening packages
library(NADA)
library(plyr) # need this package to do rename factors
library("lme4", lib.loc="~/R/win-library/3.2") # linear mixed model
library("lmerTest", lib.loc="~/R/win-library/3.2") # tests for linear mixed models?
library("piecewiseSEM", lib.loc="~/R/win-library/3.2")
library("ggplot2", lib.loc="~/R/win-library/3.2")
library(grid)
library(gtable)
library(minpack.lm)
library(segmented)
library(car)



rm(list=ls())

# assigning specific nutrient variables to piecewise universal variables
scenario<-'DH2'
nutrient<-'NO3'

############################################################
#		READING IN DATA
###########################################################

# read in CSV data
SEALdiffcor <-read.csv("finaldata_SEALdiffcor.csv")
Metals <-read.csv("finaldata_Metals.csv")


########################################################
#	DEFINE VARIABLES
########################################################
```

```
##### General
TimePoint<-c(0,2,4,8,12,24,48,72,96,120,144)
TimeTreatment <- aggregate(PO4diff_mgpL ~ TimePoint+Treatment, data=SEALdiffcor, FUN="mean")
TimeTreatment$PO4diff_mgpL<-NULL
# average flow rates for boxes; first value is low concentration, second is high
flowrateL<-data.frame(BF=numeric(1), NF=numeric(1), NS=numeric(1), WS=numeric(1))
flowrateL$BF<-24.1
flowrateL$NF<-24.3
flowrateL$NS<-24.9
flowrateL$WS<-25.1
flowrateH<-data.frame(BF=numeric(1), NF=numeric(1), NS=numeric(1), WS=numeric(1))
flowrateH$BF<-24.8
flowrateH$NF<-24.7
flowrateH$NS<-25.4
flowrateH$WS<-24.3

##### Metals
Metals$TreatLoc <- paste(Metals$Treatment, Metals$Location, sep="_")
Metals$TreatLoc <- as.factor(Metals$TreatLoc)
Metals$dummyBF <- as.numeric(Metals$Treatment=="BF")
Metals$dummyNF <- as.numeric(Metals$Treatment=="NF")
Metals$dummyNS <- as.numeric(Metals$Treatment=="NS")
Metals$dummyWS <- as.numeric(Metals$Treatment=="WS")
Metals$dummyIn <- as.numeric(Metals$Treatment=="In")
Metals$dummyLoc1 <- as.numeric(Metals$Location=="1")
Metals$dummyLoc2 <- as.numeric(Metals$Location=="2")
Metals$dummyLoc3 <- as.numeric(Metals$Location=="3")

Metals_L<- subset(Metals, Storm=="L") #filter to low concentration storm
Metals_H<- subset(Metals, Storm=="H") #filter to high concentration storm

##### SEAL

# copying original "SEALdiffcor" variable to another variable name
# all code below uses "SEALdiffcor", don't want to change so many variable names, so making copy of original just in case
SEALdiffcor_original<-SEALdiffcor

# adding variables to "SEALdiffcor"
SEALdiffcor$expTimePoint <- exp(SEALdiffcor$TimePoint)
SEALdiffcor$sqTimePoint <- SEALdiffcor$TimePoint^2
SEALdiffcor$TreatLoc <- paste(SEALdiffcor$Treatment, SEALdiffcor$Location, sep="_")
SEALdiffcor$TreatLoc <- as.factor(SEALdiffcor$TreatLoc)
SEALdiffcor$dummyBF <- as.numeric(SEALdiffcor$Treatment=="BF")
SEALdiffcor$dummyNF <- as.numeric(SEALdiffcor$Treatment=="NF")
```

```
SEALdiffcor$dummyNS <- as.numeric(SEALdiffcor$Treatment=="NS")
SEALdiffcor$dummyWS <- as.numeric(SEALdiffcor$Treatment=="WS")
SEALdiffcor$dummyIn <- as.numeric(SEALdiffcor$Treatment=="In")
SEALdiffcor$dummyLoc1 <- as.numeric(SEALdiffcor$Location=="1")
SEALdiffcor$dummyLoc2 <- as.numeric(SEALdiffcor$Location=="2")
SEALdiffcor$dummyLoc3 <- as.numeric(SEALdiffcor$Location=="3")


# subsetting "SEALdiffcor" to dissolved/total and high/low
SEALdiffcor_DL <- subset(SEALdiffcor, Dissolved_Total=="D" & Storm=="L")
SEALdiffcor_DH <- subset(SEALdiffcor, Dissolved_Total=="D" & Storm=="H")
SEALdiffcor_TL <- subset(SEALdiffcor, Dissolved_Total=="T" & Storm=="L")
SEALdiffcor_TH <- subset(SEALdiffcor, Dissolved_Total=="T" & Storm=="H")


# subsetting "SEALdiffcor" to sampling locations
SEALdiffcor_DL2 <- subset(SEALdiffcor_DL, Location=="2")
SEALdiffcor_DL3 <- subset(SEALdiffcor_DL, Location=="3")
SEALdiffcor_DH2 <- subset(SEALdiffcor_DH, Location=="2")
SEALdiffcor_DH3 <- subset(SEALdiffcor_DH, Location=="3")
SEALdiffcor_DH3noT120 <- subset(SEALdiffcor_DH, Location=="3" & TimePoint!=120)
SEALdiffcor_TL2 <- subset(SEALdiffcor_TL, Location=="2")
SEALdiffcor_TL3 <- subset(SEALdiffcor_TL, Location=="3")
SEALdiffcor_TH2 <- subset(SEALdiffcor_TH, Location=="2")
SEALdiffcor_TH3 <- subset(SEALdiffcor_TH, Location=="3")

# cleaning data
SEALdiffcor_DL2$NO3diff_i.f_mgpL[SEALdiffcor_DL2$TimePoint==12 &
SEALdiffcor_DL2$Treatment=="BF" & SEALdiffcor_DL2$Location=="2" &
SEALdiffcor_DL2$Replicate=="B"]<-NA




#####################################################################
#           PIECEWISE
####################################################################
########### Piecewise

# assigning specific nutrient variables to piecewise universal variables
combo_nutrientscenario<-paste(nutrient,scenario,sep=")
scenariodf_cmdstr<-paste('nutrient_originaldf<-SEALdiffcor',scenario, sep='_')
eval(parse(text=scenariodf_cmdstr))

nutrientorigadd_cmdstr<-paste('nutrient_originaldf$nutrientvals<-
nutrient_originaldf$',nutrient,'diff_i.f_mgpL',sep=")
```

```
eval(parse(text=nutrientorigadd_cmdstr))

# assigning nutrient values to a vector
nutrientvector_cmdstr<-paste('nutrient_diff<-nutrient_originaldf$',nutrient,'diff_i.f_mgpL',sep='')
eval(parse(text=nutrientvector_cmdstr))

# setting up file name convention
filename_cmdstr<-paste("filename<-'R_", combo_nutrientscenario, "_rev.csv'",sep='')
eval(parse(text=filename_cmdstr))
filenameregout_cmdstr<-paste("filenameregout<-'R_", combo_nutrientscenario,
"_regout.txt'",sep='')
eval(parse(text=filenameregout_cmdstr))

# aggregating original dataframe
nutrient_aggmean<-aggregate(nutrientvals~TimePoint+Treatment, data=nutrient_originaldf,
FUN="mean")
nutrient_aggmin<-aggregate(nutrientvals~TimePoint+Treatment, data=nutrient_originaldf,
FUN="min")
nutrient_aggmax<-aggregate(nutrientvals~TimePoint+Treatment, data=nutrient_originaldf,
FUN="max")
nutrient_agg<-nutrient_aggmean
nutrient_agg$repmin<-nutrient_aggmin$nutrientvals
nutrient_agg$repmax<-nutrient_aggmax$nutrientvals

###### product of TimePoint and Treatment using dummy variables
# used for piecewise regression

dummyBF<-nutrient_originaldf$dummyBF
dummyNF<-nutrient_originaldf$dummyNF
dummyNS<-nutrient_originaldf$dummyNS
dummyWS<-nutrient_originaldf$dummyWS
TimePointBF<-nutrient_originaldf$TimePoint*nutrient_originaldf$dummyBF
TimePointNF<-nutrient_originaldf$TimePoint*nutrient_originaldf$dummyNF
TimePointNS<-nutrient_originaldf$TimePoint*nutrient_originaldf$dummyNS
TimePointWS<-nutrient_originaldf$TimePoint*nutrient_originaldf$dummyWS


# (4/25/2018) replacing NO3, DH2 and NO3, DL2 with linear regression, looks like better fit -
not much better
# fitting linear regression
fit_lm<-
lm(nutrient_diff~0+dummyBF+dummyNF+dummyNS+dummyWS+TimePointBF+TimePointN
F+TimePointNS+TimePointWS)
summary(fit_lm)
```

```
# piecewise linear regression call
if (scenario=='DL2' & nutrient=='NO3') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=96, TimePointNF=96, TimePointNS=96,
TimePointWS=96)) # was 24, 72 works
} else if (scenario=='DL2' & nutrient=='PO4') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=48, TimePointNF=48, TimePointNS=48,
TimePointWS=48))
} else if (scenario=='DL3' & nutrient=='NO3') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=4, TimePointNF=4, TimePointNS=4, TimePointWS=4))
} else if (scenario=='DL3' & nutrient=='PO4') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=24, TimePointNF=24, TimePointNS=24,
TimePointWS=24))
} else if (scenario=='DH2' & nutrient=='NO3') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=24, TimePointNF=24, TimePointNS=24,
TimePointWS=24))
} else if (scenario=='DH2' & nutrient=='PO4') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=20, TimePointNF=20, TimePointNS=20,
TimePointWS=20))
} else if (scenario=='DH3' & nutrient=='NO3') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=24, TimePointNF=24, TimePointNS=24,
TimePointWS=24))
} else if (scenario=='DH3' & nutrient=='PO4') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=8, TimePointNF=8, TimePointNS=8, TimePointWS=8))
} else if (scenario=='TL2' & nutrient=='NO3') {
  fit_seg<- segmented(fit_lm,
                      seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                      psi=list(TimePointBF=24, TimePointNF=24, TimePointNS=24,
TimePointWS=24))
} else if (scenario=='TL2' & nutrient=='PO4') {
```

```
  fit_seg<- segmented(fit_lm,
                    seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                    psi=list(TimePointBF=24, TimePointNF=24, TimePointNS=24,
TimePointWS=24))
} else if (scenario=='TL3' & nutrient=='NO3') {
  fit_seg<- segmented(fit_lm,
                    seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                    psi=list(TimePointBF=8, TimePointNF=8, TimePointNS=8, TimePointWS=8))
} else if (scenario=='TL3' & nutrient=='PO4') {
  fit_seg<- segmented(fit_lm,
                    seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                    psi=list(TimePointBF=12, TimePointNF=8, TimePointNS=48, TimePointWS=72))
} else if (scenario=='TH2' & nutrient=='NO3') {
  fit_seg<- segmented(fit_lm,
                    seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                    psi=list(TimePointBF=24, TimePointNF=24, TimePointNS=24,
TimePointWS=24))
} else if (scenario=='TH2' & nutrient=='PO4') {
  fit_seg<- segmented(fit_lm,
                    seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                    psi=list(TimePointBF=48, TimePointNF=48, TimePointNS=48,
TimePointWS=48))
} else if (scenario=='TH3' & nutrient=='NO3') {
  print('this is in NO3, TH3')
  fit_seg<- segmented(fit_lm,
                    seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                    psi=list(TimePointBF=96, TimePointNF=96, TimePointNS=96,
TimePointWS=96))
} else if (scenario=='TH3' & nutrient=='PO4') {
  fit_seg<- segmented(fit_lm,
                    seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
                    psi=list(TimePointBF=8, TimePointNF=8, TimePointNS=8, TimePointWS=8))
} else {
  print('something is wrong')
  # fit_seg<- segmented(fit_lm,
  #                   seg.Z = ~TimePointBF+TimePointNF+TimePointNS+TimePointWS,
  #                   psi=list(TimePointBF=8, TimePointNF=8, TimePointNS=8, TimePointWS=8))

}

fitseg_CI<-confint(fit_seg)

# creating data frame of x values for prediction values of piecewise regression results
Treatment<-c("BF","NF","NS","WS")
counter<-0
testzeros<-integer(576)
```

```
pred_BFdummy<-integer(576)
pred_NFdummy<-integer(576)
pred_NSdummy<-integer(576)
pred_WSdummy<-integer(576)
pred_BFtime<-integer(576)
pred_NFtime<-integer(576)
pred_NStime<-integer(576)
pred_WStime<-integer(576)
for (i in 1:144) {
  for (j in 1:4) {
    counter=counter+1
    #predTimePoint[counter]=i
    if (j==1) {
      pred_BFdummy[counter]<-1
      pred_BFtime[counter]<-i
    }  else if (j==2) {
      pred_NFdummy[counter]<-1
      pred_NFtime[counter]<-i
    } else if (j==3) {
      pred_NSdummy[counter]<-1
      pred_NStime[counter]<-i
    } else {
      pred_WSdummy[counter]<-1
      pred_WStime[counter]<-i
    }
  }
}

# creating data frame of independent variables to apply predictions to
# values are based on by hour and by treatment so can calculate % removal/hr
pred_df<-data.frame(dummyBF=integer(576),
                    dummyNF=integer(576),
                    dummyNS=integer(576),
                    dummyWS=integer(576),
                    TimePointBF=integer(576),
                    TimePointNF=integer(576),
                    TimePointNS=integer(576),
                    TimePointWS=integer(576))
pred_df$dummyBF<-pred_BFdummy
pred_df$dummyNF<-pred_NFdummy
pred_df$dummyNS<-pred_NSdummy
pred_df$dummyWS<-pred_WSdummy
pred_df$TimePointBF<-pred_BFtime
pred_df$TimePointNF<-pred_NFtime
pred_df$TimePointNS<-pred_NStime
pred_df$TimePointWS<-pred_WStime
```

```
# predicting values based on hourly independent variables
pred_df$predictedvalue<-predict(fit_seg, pred_df)

if (scenario=='DH2' & nutrient=='PO4') {
  pred_df$predictedvalue<-predict(fit_lm, pred_df)
}

# separating out predicted values by treatment - preserving whole dataframe as a check
pred_concdiffBF<-subset(pred_df, pred_BFdummy==1)
pred_concdiffNF<-subset(pred_df, pred_NFdummy==1)
pred_concdiffNS<-subset(pred_df, pred_NSdummy==1)
pred_concdiffWS<-subset(pred_df, pred_WSdummy==1)
# collecting values into a removal variable
removal<-data.frame(TimePoint=numeric(144), pred_concdiffBF=numeric(144),
pred_concdiffNF=numeric(144),
                    pred_concdiffNS=numeric(144), pred_concdiffWS=numeric(144))
removal$TimePoint<-c(1:144)
removal$pred_concdiffBF<-pred_concdiffBF$predictedvalue
removal$pred_concdiffNF<-pred_concdiffNF$predictedvalue
removal$pred_concdiffNS<-pred_concdiffNS$predictedvalue
removal$pred_concdiffWS<-pred_concdiffWS$predictedvalue
# applying flow rates to get mass removal/hour by treatment
removal$massdiffperhr_BF<-removal$pred_concdiffBF*flowrateL$BF*60/1000
removal$massdiffperhr_NF<-removal$pred_concdiffNF*flowrateL$NF*60/1000
removal$massdiffperhr_NS<-removal$pred_concdiffNS*flowrateL$NS*60/1000
removal$massdiffperhr_WS<-removal$pred_concdiffWS*flowrateL$WS*60/1000
# getting total
removal_totals<-colSums(removal)

write.csv(removal,filename)


#### calculating saturation point
PWslope<-slope(fit_seg)
PWint<-intercept(fit_seg)
PWcoeff<-coef(fit_seg)
satpoints<-data.frame(BF=numeric(1), NF=numeric(1), NS=numeric(1), WS=numeric(1))
satpoints$BF<--1*(PWint$TimePointBF[2]+PWcoeff[1])/PWslope$TimePointBF[2]
satpoints$NF<--1*(PWint$TimePointNF[2]+PWcoeff[2])/PWslope$TimePointNF[2]
satpoints$NS<--1*(PWint$TimePointNS[2]+PWcoeff[3])/PWslope$TimePointNS[2]
satpoints$WS<--1*(PWint$TimePointWS[2]+PWcoeff[4])/PWslope$TimePointWS[2]


##########################################################################
```

```
#               DISPLAYING AND SAVING RESULTS
#############################################################################

# display results of linear and piecewise regressions

print("Linear regression results:")
summary(fit_lm)
print("Piecewise regression results:")
summary(fit_seg)
print("Mass removal totals:")
removal_totals

# printing linear and segmented regression summary output into file
fileregout_cmdstr<-paste("sink('", filenameregout, "')",sep='')
eval(parse(text=fileregout_cmdstr))
#sink("test.txt")
print("summary of linear regression:")
print(summary(fit_lm))
print("summary of piecewise regression:")
print(summary(fit_seg))
print("significance of slopes:")
print(davies.test(fit_lm, seg.Z=~TimePointBF))
print(davies.test(fit_lm, seg.Z=~TimePointNF))
print(davies.test(fit_lm, seg.Z=~TimePointNS))
print(davies.test(fit_lm, seg.Z=~TimePointWS))
print("slopes of piecewise regression:")
print(slope(fit_seg))
print("intercepts of piecewise regression:")
print(intercept(fit_seg))
print("coefficients of piecewise regression:")
print(coef(fit_seg))
print("removal totals based from piecewise regression:")
print(removal_totals)
print("saturation points based from piecewise regression:")
print(satpoints)
sink()

dev.off()

########################################################################
#                       PLOTS
#########################################################################


# set y min/max for plots based on scenario and nutrient set at very top of code
# helpful website: https://stackoverflow.com/questions/10128617/test-if-characters-in-string-in-r
```

```
if (grepl("L",scenario) & grepl("P",nutrient)) {
  ymin <- -0.01
  ymax <- 0.5
} else if (grepl("H",scenario) & grepl("P",nutrient)) {
  ymin <- -0.5
  ymax <- 3.5
} else if (grepl("L",scenario) & grepl("N",nutrient)) {
  ymin <- -0.5
  ymax <- 1
} else if (grepl("H",scenario) & grepl("N",nutrient)) {
  ymin <- -0.01
  ymax <- 4
}


# plot raw data with piecewise regression lines, no color
ggplot(data=nutrient_originaldf,aes(x=TimePoint, y=nutrient_diff)) +
  geom_point(aes(shape=Treatment)) +
  scale_shape_manual(values=c(1,2,3,4)) +
  #scale_colour_manual(values = c("Red", "Green", "Blue", "Purple")) +
  geom_line(data=removal, aes(x=TimePoint, y = pred_concdiffBF,
linetype="pred_concdiffBF"), color = "black") +
  geom_line(data=removal, aes(x=TimePoint, y = pred_concdiffNF,
linetype="pred_concdiffNF"), color = "black") +
  geom_line(data=removal, aes(x=TimePoint, y = pred_concdiffNS,
linetype="pred_concdiffNS"), color = "black") +
  geom_line(data=removal, aes(x=TimePoint, y = pred_concdiffWS,
linetype="pred_concdiffWS"), color = "black") +
  scale_linetype_manual("", labels=c("BF","NF","NS","WS"),
                        breaks=c("pred_concdiffBF","pred_concdiffNF", "pred_concdiffNS",
                                 "pred_concdiffWS"), values=c(1,2,3,4)) +
  xlab("Time (h)") + ylab("Mass Removal Rate (mg/h)") + theme_bw(base_size=10) +
  scale_y_continuous(limits = c(ymin, ymax)) +
  #scale_y_continuous(limits = c(-0.01, 0.5)) +
  theme(axis.text.x = element_text(size=10), axis.text.y = element_text(size=10)) +
  theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + #
http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-
entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-
r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

# saving above ggplot that's configured for publication purposes
plotremoval_cmdstr<-paste("ggsave('R_", combo_nutrientscenario, "_ggplot.png', width=84,
height=60, units='mm')",sep='')
eval(parse(text=plotremoval_cmdstr))
```

Code for Graphing Total Mass Removed by Sampling Location and Treatment

```
# Stephanie Houston          5/25/2018
#
# Bar graph for total pollutants removed


# setting directory
setwd("C:/Users/Stephanie/Documents/VT/Research/Data/Kinetics")

# reading in data
data_removal <-read.csv("R_RemovalResults20180525rev.csv")
data_removal$SampleLocationStr <- as.character(data_removal$SampleLocation)
data_removal$Treatment <- factor(data_removal$Treatment, levels=c("Inlet", "BF", "NF", "NS", "WS"))
data_removal$SampleLocation <- factor(data_removal$SampleLocationStr, levels=c("Inlet", "2", "3"))


# data manipulation
removal_DPL<-subset(data_removal, Concentration=="Low" & Nutrient=="PO4")
removal_DPH<-subset(data_removal, Concentration=="High" & Nutrient=="PO4")
removal_NO3L<-subset(data_removal, Concentration=="Low" & Nutrient=="NO3")
removal_NO3H<-subset(data_removal, Concentration=="High" & Nutrient=="NO3")
removal_TPL<-subset(data_removal, Concentration=="Low" & Nutrient=="TP")
removal_TPH<-subset(data_removal, Concentration=="High" & Nutrient=="TP")
removal_TNL<-subset(data_removal, Concentration=="Low" & Nutrient=="TN")
removal_TNH<-subset(data_removal, Concentration=="High" & Nutrient=="TN")


# nested bar graph, works!!
# used 427 x 366 when saving graphs manually


# DPL
ggplot(data = removal_DPL, aes(x = SampleLocationStr, y = RemainingTotal)) +
  labs(x ="Treatment and Sampling Location", y = "Remaining Total Mass (mg)") +
  geom_bar(stat="identity") +
  facet_wrap(~Treatment, nrow=1, switch = "x", scales = "free_x") +
  theme(panel.margin = unit(0, "lines"), strip.background = element_blank()) +
  scale_x_discrete(limits=c("Inlet","2", "3")) +
  scale_y_continuous(limits = c(0, 80)) +
  theme(axis.text.x = element_text(size=9), axis.text.y = element_text(size=9)) +
  theme(panel.border = element_blank(),
        #panel.border = element_rect(linetype="solid", fill=NA),   # element_blank() = not there
        panel.background = element_rect(fill=NA, linetype=NULL),
```

```
        panel.grid.major = element_line(color="grey85"),
        axis.line = element_line(color="black"),
        strip.text.x = element_text(size = 9),
        axis.title=element_text(size=9))
theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + # http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

ggsave("removal_DPL.png", width=80, height=60, units='mm')

# TPL
ggplot(data = removal_TPL, aes(x = SampleLocationStr, y = RemainingTotal)) +
  labs(x ="Treatment and Sampling Location", y = "Remaining Total Mass (mg)") +
  geom_bar(stat="identity") +
  facet_wrap(~Treatment, nrow=1, switch = "x", scales = "free_x") +
  theme(panel.margin = unit(0, "lines"), strip.background = element_blank()) +
  scale_x_discrete(limits=c("Inlet","2", "3")) +
  scale_y_continuous(limits = c(0, 80)) +
  theme(axis.text.x = element_text(size=9), axis.text.y = element_text(size=9)) +
  theme(panel.border = element_blank(),
        #panel.border = element_rect(linetype="solid", fill=NA),   # element_blank() = not there
        panel.background = element_rect(fill=NA, linetype=NULL),
        panel.grid.major = element_line(color="grey85"),
        axis.line = element_line(color="black"),
        strip.text.x = element_text(size = 9),
        axis.title=element_text(size=9))
theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + # http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

ggsave("removal_TPL.png", width=80, height=60, units='mm')

# NO3L
ggplot(data = removal_NO3L, aes(x = SampleLocationStr, y = RemainingTotal)) +
  labs(x ="Treatment and Sampling Location", y = "Remaining Total Mass (mg)") +
  geom_bar(stat="identity") +
  facet_wrap(~Treatment, nrow=1, switch = "x", scales = "free_x") +
  theme(panel.margin = unit(0, "lines"), strip.background = element_blank()) +
  scale_x_discrete(limits=c("Inlet","2", "3")) +
  scale_y_continuous(limits = c(0, 220)) +
```

```
  theme(axis.text.x = element_text(size=9), axis.text.y = element_text(size=9)) +
  theme(panel.border = element_blank(),
        #panel.border = element_rect(linetype="solid", fill=NA),   # element_blank() = not there
        panel.background = element_rect(fill=NA, linetype=NULL),
        panel.grid.major = element_line(color="grey85"),
        axis.line = element_line(color="black"),
        strip.text.x = element_text(size = 9),
        axis.title=element_text(size=9))
theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + #
http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-
entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-
r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

ggsave("removal_NO3L.png", width=80, height=60, units='mm')

# TNL
ggplot(data = removal_TNL, aes(x = SampleLocationStr, y = RemainingTotal)) +
  labs(x ="Treatment and Sampling Location", y = "Remaining Total Mass (mg)") +
  geom_bar(stat="identity") +
  facet_wrap(~Treatment, nrow=1, switch = "x", scales = "free_x") +
  theme(panel.margin = unit(0, "lines"), strip.background = element_blank()) +
  scale_x_discrete(limits=c("Inlet","2", "3")) +
  scale_y_continuous(limits = c(0, 220)) +
  theme(axis.text.x = element_text(size=9), axis.text.y = element_text(size=9)) +
  theme(panel.border = element_blank(),
        #panel.border = element_rect(linetype="solid", fill=NA),   # element_blank() = not there
        panel.background = element_rect(fill=NA, linetype=NULL),
        panel.grid.major = element_line(color="grey85"),
        axis.line = element_line(color="black"),
        strip.text.x = element_text(size = 9),
        axis.title=element_text(size=9))
theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + #
http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-
entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-
r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

ggsave("removal_TNL.png", width=80, height=60, units='mm')


# DPH
ggplot(data = removal_DPH, aes(x = SampleLocationStr, y = RemainingTotal)) +
  labs(x ="Treatment and Sampling Location", y = "Remaining Total Mass (mg)") +
```

```
  geom_bar(stat="identity") +
  facet_wrap(~Treatment, nrow=1, switch = "x", scales = "free_x") +
  theme(panel.margin = unit(0, "lines"), strip.background = element_blank()) +
  scale_x_discrete(limits=c("Inlet","2", "3")) +
  scale_y_continuous(limits = c(0, 800)) +
  theme(axis.text.x = element_text(size=9), axis.text.y = element_text(size=9)) +
  theme(panel.border = element_blank(),
        #panel.border = element_rect(linetype="solid", fill=NA),   # element_blank() = not there
        panel.background = element_rect(fill=NA, linetype=NULL),
        panel.grid.major = element_line(color="grey85"),
        axis.line = element_line(color="black"),
        strip.text.x = element_text(size = 9),
        axis.title=element_text(size=9))
theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + #
http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-
entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-
r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

ggsave("removal_DPH.png", width=80, height=60, units='mm')

# TPH
ggplot(data = removal_TPH, aes(x = SampleLocationStr, y = RemainingTotal)) +
  labs(x ="Treatment and Sampling Location", y = "Remaining Total Mass (mg)") +
  geom_bar(stat="identity") +
  facet_wrap(~Treatment, nrow=1, switch = "x", scales = "free_x") +
  theme(panel.margin = unit(0, "lines"), strip.background = element_blank()) +
  scale_x_discrete(limits=c("Inlet","2", "3")) +
  scale_y_continuous(limits = c(0, 800)) +
  theme(axis.text.x = element_text(size=9), axis.text.y = element_text(size=9)) +
  theme(panel.border = element_blank(),
        #panel.border = element_rect(linetype="solid", fill=NA),   # element_blank() = not there
        panel.background = element_rect(fill=NA, linetype=NULL),
        panel.grid.major = element_line(color="grey85"),
        axis.line = element_line(color="black"),
        strip.text.x = element_text(size = 9),
        axis.title=element_text(size=9))
theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + #
http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-
entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-
r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

ggsave("removal_TPH.png", width=80, height=60, units='mm')
```

```
# NO3H
ggplot(data = removal_NO3H, aes(x = SampleLocationStr, y = RemainingTotal)) +
  labs(x ="Treatment and Sampling Location", y = "Remaining Total Mass (mg)") +
  geom_bar(stat="identity") +
  facet_wrap(~Treatment, nrow=1, switch = "x", scales = "free_x") +
  theme(panel.margin = unit(0, "lines"), strip.background = element_blank()) +
  scale_x_discrete(limits=c("Inlet","2", "3")) +
  scale_y_continuous(limits = c(0, 1000)) +
  theme(axis.text.x = element_text(size=9), axis.text.y = element_text(size=9)) +
  theme(panel.border = element_blank(),
        #panel.border = element_rect(linetype="solid", fill=NA),   # element_blank() = not there
        panel.background = element_rect(fill=NA, linetype=NULL),
        panel.grid.major = element_line(color="grey85"),
        axis.line = element_line(color="black"),
        strip.text.x = element_text(size = 9),
        axis.title=element_text(size=9))
theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + #
http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-
entries-in-ggplot2-legend-when-usin
  theme(legend.title=element_blank()) # http://www.cookbook-
r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

ggsave("removal_NO3H.png", width=80, height=60, units='mm')

# TNH
ggplot(data = removal_TNH, aes(x = SampleLocationStr, y = RemainingTotal)) +
  labs(x ="Treatment and Sampling Location", y = "Remaining Total Mass (mg)") +
  geom_bar(stat="identity") +
  facet_wrap(~Treatment, nrow=1, switch = "x", scales = "free_x") +
  theme(panel.margin = unit(0, "lines"), strip.background = element_blank()) +
  scale_x_discrete(limits=c("Inlet","2", "3")) +
  scale_y_continuous(limits = c(0, 1000)) +
  theme(axis.text.x = element_text(size=9), axis.text.y = element_text(size=9)) +
  theme(panel.border = element_blank(),
        #panel.border = element_rect(linetype="solid", fill=NA),   # element_blank() = not there
        panel.background = element_rect(fill=NA, linetype=NULL),
        panel.grid.major = element_line(color="grey85"),
        axis.line = element_line(color="black"),
        strip.text.x = element_text(size = 9),
        axis.title=element_text(size=9))
theme(plot.margin= unit(c(0,0,0,0), units="cm")) +
  theme(legend.key = element_rect(colour=NA)) + #
http://stackoverflow.com/questions/26972905/how-to-remove-grey-borders-around-individual-
entries-in-ggplot2-legend-when-usin
```

```
  theme(legend.title=element_blank()) # http://www.cookbook-r.com/Graphs/Legends_(ggplot2)/#hiding-the-legend-title

ggsave("removal_TNH.png", width=80, height=60, units='mm')
```

APPENDIX B: RAW DATA

Pond Analysis

Pond Features for Water Analysis (Part 1)

BottleID	SiteID	Pond Type	Blank	Date	Date_Built	Date_Dredged	Date_LastRainfall	Time	Pond Location	depth_m	depth_ratio
O1	DP	urb	0	6/30/2014	1937	1986	6/29/2014	9:52	O	0.25	0.153374
O2	DP	urb	0	6/30/2014	1937	1986	6/29/2014	9:57	O	0.5	0.306748
O3	DP	urb	0	6/30/2014	1937	1986	6/29/2014	10:03	O	0.75	0.460123
O4	DP	urb	0	6/30/2014	1937	1986	6/29/2014	10:07	O	1	0.613497
O5	DP	urb	0	6/30/2014	1937	1986	6/29/2014	10:11	O	1.25	0.766871
O6	DP	urb	0	6/30/2014	1937	1986	6/29/2014	10:20	O	1.5	0.920245
O7	DP	urb	0	6/30/2014	1937	1986	6/29/2014	10:29	O	1.63	1
M1	DP	urb	0	6/30/2014	1937	1986	6/29/2014	12:00	M	0.5	0.666667
M2	DP	urb	0	6/30/2014	1937	1986	6/29/2014	12:09	M	0.75	1
I1	DP	urb	0	6/30/2014	1937	1986	6/29/2014	15:05	I	0.1	1
TB	DP	urb	1	6/30/2014	1937	1986	6/29/2014	9:30			
EB	DP	urb	1	6/30/2014	1937	1986	6/29/2014	15:15			
FB	DP	urb	1	6/30/2014	1937	1986	6/29/2014	9:50			
O1	JW	ag	0	7/1/2014	1965	1996	6/30/2014	9:26	O	0.25	0.238095
O2	JW	ag	0	7/1/2014	1965	1996	6/30/2014	9:32	O	0.5	0.47619
O3	JW	ag	0	7/1/2014	1965	1996	6/30/2014	9:38	O	0.75	0.714286
O4	JW	ag	0	7/1/2014	1965	1996	6/30/2014	9:43	O	1	0.952381
O5	JW	ag	0	7/1/2014	1965	1996	6/30/2014	9:50	O	1.05	1
M1	JW	ag	0	7/1/2014	1965	1996	6/30/2014	10:08	M	0.25	0.2
M2	JW	ag	0	7/1/2014	1965	1996	6/30/2014	10:15	M	0.5	0.4
M3	JW	ag	0	7/1/2014	1965	1996	6/30/2014	10:22	M	0.75	0.6
M4	JW	ag	0	7/1/2014	1965	1996	6/30/2014	10:28	M	1	0.8
M5	JW	ag	0	7/1/2014	1965	1996	6/30/2014	10:31	M	1.25	1

I1	JW	ag	0	7/1/2014	1965	1996	6/30/2014	10:55	I	0.45	1
TB	JW	ag	1	7/1/2014	1965	1996	6/30/2014	8:20			
EB	JW	ag	1	7/1/2014	1965	1996	6/30/2014	9:30			
FB	JW	ag	1	7/1/2014	1965	1996	6/30/2014	11:00			
O1	ID	urb	0	7/3/2014	2011	2011	6/30/2014	9:00	O	0.25	
O2	ID	urb	0	7/3/2014	2011	2011	6/30/2014	9:07	O	0.5	
O3	ID	urb	0	7/3/2014	2011	2011	6/30/2014	9:14	O	0.75	
O4	ID	urb	0	7/3/2014	2011	2011	6/30/2014	9:20	O	1	
M1	ID	urb	0	7/3/2014	2011	2011	6/30/2014	10:06	M	0.25	
I1	ID	urb	0	7/3/2014	2011	2011	6/30/2014	10:43	I	0.25	
I2	ID	urb	0	7/3/2014	2011	2011	6/30/2014	10:47	I	0.5	
I3	ID	urb	0	7/3/2014	2011	2011	6/30/2014	10:52	I	0.75	
I4	ID	urb	0	7/3/2014	2011	2011	6/30/2014	10:57	I	1	
TB	ID	urb	1	7/3/2014	2011	2011	6/30/2014	8:10			
EB	ID	urb	1	7/3/2014	2011	2011	6/30/2014	11:00			
FB	ID	urb	1	7/3/2014	2011	2011	6/30/2014	8:47			
O1	LP	ag	0	7/10/2014	1965	2011	7/9/2014	9:15	O	0.25	
M1	LP	ag	0	7/10/2014	1965	2011	7/9/2014	9:40	M	0.25	
M2	LP	ag	0	7/10/2014	1965	2011	7/9/2014	9:46	M	0.5	
M3	LP	ag	0	7/10/2014	1965	2011	7/9/2014	9:50	M	0.75	
M4	LP	ag	0	7/10/2014	1965	2011	7/9/2014	9:55	M	1	
I1	LP	ag	0	7/10/2014	1965	2011	7/9/2014	10:27	I	0.1	
TB	LP	ag	1	7/10/2014	1965	2011	7/9/2014	7:55			
EB	LP	ag	1	7/10/2014	1965	2011	7/9/2014	9:10			
FB	LP	ag	1	7/10/2014	1965	2011	7/9/2014	10:40			
O1	GP	golf	0	7/14/2014	1965		7/13/2014	8:36	O	0.25	
O2	GP	golf	0	7/14/2014	1965		7/13/2014	8:41	O	0.5	
M1	GP	golf	0	7/14/2014	1965		7/13/2014	9:05	M	0.25	
M2	GP	golf	0	7/14/2014	1965		7/13/2014	9:10	M	0.5	
M3	GP	golf	0	7/14/2014	1965		7/13/2014	9:15	M	0.75	
M4	GP	golf	0	7/14/2014	1965		7/13/2014	9:21	M	1	

M5	GP	golf	0	7/14/2014	1965	7/13/2014	9:37	M	1.25
I1	GP	golf	0	7/14/2014	1965	7/13/2014	9:53	I	0.25
I2	GP	golf	0	7/14/2014	1965	7/13/2014	9:58	I	0.5
TB	GP	golf	1	7/14/2014	1965	7/13/2014			
FB	GP	golf	1	7/14/2014	1965	7/13/2014			

Pond Features for Water Analysis (Part 2)

BottleID	SiteID	PondLength	PondMidWidth	PondWidth	LWratio	Pond SurfaceArea	WatershedArea	AvePondDepth_m	Volume_m3
O1	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
O2	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
O3	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
O4	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
O5	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
O6	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
O7	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
M1	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
M2	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
I1	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
TB	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
EB	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
FB	DP	268	88.59	83.01333	3.228397	23327	7149824	0.826667	14304.79
O1	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
O2	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
O3	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
O4	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
O5	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
M1	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
M2	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562

M3	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
M4	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
M5	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
I1	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
TB	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
EB	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
FB	JW	60.72	38.94	36.15333	1.679513	2153	27402	0.916667	1598.562
O1	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
O2	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
O3	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
O4	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
M1	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
I1	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
I2	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
I3	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
I4	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
TB	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
EB	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
FB	ID	68.48	14.68	23.04	2.972222	1408	88584	0.75	1227.39
O1	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
M1	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
M2	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
M3	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
M4	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
I1	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
TB	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
EB	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
FB	LP	86.41	25.2	23.56	3.667657	1962	195197	0.45	630.2141
O1	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
O2	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
M1	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84

M2	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
M3	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
M4	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
M5	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
I1	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
I2	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
TB	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84
FB	GP	47.45	27.9	20.53333	2.310877	1166	210854	0.75	1003.84

Pond Water Quality Parameters for Water Analysis

BottleID	SiteID	temp_C	cond_mSpercm	pH	DO_perc	turbidity_NTU	ORP_mVbase199
O1	DP	23.94	0.735	6.97	63	26.4	424.7
O2	DP	23.85	0.734	7.17	62.4	34.8	435.1
O3	DP	23.63	0.727	7.24	62.4	36.9	425.5
O4	DP	23.47	0.723	7.33	6	39	437.4
O5	DP	23.43	0.724	7.37	0.7	42.6	415.4
O6	DP	23.33	0.722	7.42	63.2	46.6	419.8
O7	DP	23.34	0.721	7.46	68.6	48	450.5
M1	DP	24.01	0.722	7.58	73.8	37.2	447.1
M2	DP	23.83	0.723	7.6	185.8	44.2	427.8
I1	DP	27.12	0.753	8.08	100.2	29.1	430.2
TB	DP						391.8
EB	DP						401.8
FB	DP						414.6
O1	JW	26.62	0.397	8.2	144.7	38.5	371.6
O2	JW	26.61	0.397	8.43	146	13.2	362.6
O3	JW	26.58	0.397	8.48	146.7	13.8	379.2
O4	JW	26.51	0.398	8.5	141.4	15.6	355.1
O5	JW	26.45	0.397	8.64	146.6	18.7	366.2
M1	JW	26.8	0.398	8.55	90.2	10.7	351.1

M2	JW	26.8	0.397	8.57	141.7	10.1	347.9
M3	JW	26.81	0.396	8.51	145.2	10.6	267
M4	JW	26.29	0.402	8.47	126.3	18.1	370.7
M5	JW	26.28	0.397	8.47	122.9	21.2	350
I1	JW	27.27	0.399	8.55	150.1	10.6	356.2
TB	JW						379.2
EB	JW						392.1
FB	JW						375.7
O1	ID	25.9	0.339	7.11	48.3	2.6	378.7
O2	ID	25.82	0.338	7.2	48.7	2.8	381.8
O3	ID	25.7	0.338	7.23	42.5	4.8	374
O4	ID	25.5	0.341	7.15	29	33.2	269.3
M1	ID	26.44	0.328	7.69	52.9	13	366.3
I1	ID	25.87	0.342	7.53	109.5	1.1	360
I2	ID	25.79	0.341	7.51	96.5	2	361.5
I3	ID	25.49	0.36	7.34	71.7	4.2	362.5
I4	ID	25.64	0.36	7.39	71.6	4.2	362.1
TB	ID						387.6
EB	ID						320.3
FB	ID						320
O1	LP	23.24	0.263	8.56	52.6	4.1	338.7
M1	LP	23.12	0.267	9.16	68.4	15.5	334.9
M2	LP	23.13	0.267	9.36	78	13.3	329.5
M3	LP	23.12	0.268	9.37	73.1	100.28	329.3
M4	LP	23.11	0.269	9.31	57.9	17.1	325.2
I1	LP	22.75	0.265	9.64	71.2	33.4	289
TB	LP						414.7
EB	LP						408.3
FB	LP						411.9
O1	GP	27.64	0.379	7.84	92.7	6.7	349.1
O2	GP	27.63	0.379	8.02	93	13.5	348

M1	GP	27.83	0.379	8.17	97.1	5.4	355.5
M2	GP	27.81	0.379	8.23	96.2	5.2	353.6
M3	GP	27.77	0.379	8.27	96.9	5	353.1
M4	GP	27.79	0.379	8.36	96.8	6.5	353.7
M5	GP	27.58	0.382	8.32	92.6	22.4	353.9
I1	GP	28.11	0.379	8.32	95.6	4.7	363.5
I2	GP	28	0.379	8.33	96	6.1	357.6
TB	GP						431.5
FB	GP						407.6

Pond Sampling Data for Water Analysis

Bottle ID	Site ID	TN_mgL	TP_mgL	DP_ mgL	DPv2_ mgL	NO3_ mgL	NO3v2_ mgL	SO4_mgL	Fe_ mgL	Zn_ mgL	DOC_ mgL	ratio_CN
O1	DP	1.757412	0.114477	0.014096	0.012351	0.525756	0.5927	13.74888	0.0133	0.0151	6.841	1939.073
O2	DP	1.608399	0.106408	0.01389	0.011734	0.529342	0.592727	13.92229	0.0293	0.0144	6.591	1868.124
O3	DP	1.547139	0.123636	0.01384	0.011631	0.536857	0.580149	14.18361	0.0101	0.0231	6.817	1974.072
O4	DP	1.770485	0.16606	0.016538	0.011403	0.520462	0.575538	13.61805	0.0079	0.0181	6.798	1984.342
O5	DP	1.784183	0.160549	0.01332	0.012827	0.538735	0.566507	14.37987	0.009	0.0155	7.028	2084.184
O6	DP	1.677169	0.141026	0.013353	0.021824	0.542663	0.588634	14.75645	0.016	0.0155	7.248	2068.625
O7	DP	1.744201	0.163257	0.013032	0.013297	0.545225	0.59933	14.02405	0.0127	0.013	6.885	1929.955
M1	DP	1.849616	0.164814	0.015664	0.012399	0.559571	0.618456	14.03824	0.0171	0.0134	7.228	1963.443
M2	DP	1.930346	0.207387	0.013469	0.012271	0.567427	0.606506	15.01466	0.017	0.0166	7.085	1962.52
I1	DP	2.045287	0.142937	0.014203	0.013719	0.924704	0.94388	15.38986	0.0227	0.0139	6.563	1168.14
TB	DP	1.814083		0.004137	0.005596	0.270777	0.227987	0.313692	0.0013	0.0103	0.395	291.0695
EB	DP	1.948494		0.005251	0.006903	0.233034	0.249296	0.334806	0.0031	0.0127	0.574	386.8172
FB	DP	2.034648		0.015193	0.013742	0.282903	0.227769	0.500946	0.0037	0.0116	0.545	401.987
O1	JW	1.808381	0.066442	0.004269	0.005722	0.761094	0.697227	7.688578	0.0137	0.0144	11.87	2860.13
O2	JW	2.010311	0.084792	0.006126	0.006586	0.753409	0.72151	8.070354	0.0158	0.0115	9.776	2276.292
O3	JW		0.090398	0.004492	0.013928	0.76451	0.713313	8.012897	0.0217	0.013	9.419	2218.371
O4	JW		0.07913	0.00403	0.007297	0.780564	0.656177	7.684078	0.023	0.012	10.05	2573.085

O5	JW		0.094713	0.009096	0.00478	0.752214	0.649404	7.951287	0.0199	0.0152	9.833	2543.785
M1	JW		0.050193	0.004731	0.004457	0.765364	0.664422	8.164154	0.0216	0.0127	9.94	2513.343
M2	JW		0.046804	0.007272	0.007404	0.767584	0.620129	7.785839	0.0138	0.0123	9.678	2621.882
M3	JW		0.04858	0.003386	0.005984	0.822918	0.618605	7.807299	0.0148	0.0099	9.492	2577.824
M4	JW		0.058689	0.003238	0.004455	0.766389	0.60843	7.73219	0.0055	0.0117	8.93	2465.755
M5	JW		0.066057	0.00389	0.004407	0.760411	0.599479	7.865102	0.0041	0.0096	8.527	2389.637
I1	JW		0.04672	0.00464	0.01332	0.898233	0.719053	7.92152	0.0214	0.0167	9.851	2301.595
TB	JW		0.014851	0.001893	0.0031	0.2496	0.146321	0.271811	0.0016	0.011	0.819	940.3435
EB	JW		0.028945	-0.00098	0.003664	0.308862	0.203319	0.276657	0.0046	0.0145	1.198	989.8918
FB	JW		0.00801	0.005284	0.001377	0.289222	0.139546	0.317846	0.0029	0.0132	0.587	706.6897
O1	ID		1.41478	0.02875	0.025265	0.093505	0.126052	4.529495	0.1173	0.0184	16.78	22364.14
O2	ID		0.274513	0.028849	0.026121	0.090089	0.137533	4.419427	0.113	0.0139	16.88	20619.31
O3	ID		0.719932	0.032001	0.026165	0.083258	0.132745	4.310398	0.1051	0.0133	16.74	21185.85
O4	ID		0.448608	0.032289	0.027631	0.081038	0.168141	4.452655	0.1272	0.0133	16.01	15996.54
M1	ID		0.293025	0.024583	0.021673	0.063618	0.132091	4.186831	0.1213	0.0136	19.75	25118.97
I1	ID		0.05624	0.004302	0.004333	0.060885	0.163352	10.6926	0.0614	0.0398	13.47	13853.27
I2	ID		0.050488	0.008881	0.004748	0.061568	0.161067	10.9778	0.058	0.0149	13.5	14081.08
I3	ID		0.041498	0.010754	0.00749	0.0684	0.161503	11.10033	0.0498	0.0177	13.33	13866.28
I4	ID		0.051947	0.008997	0.004818	0.098628	0.175433	11.56102	0.0318	0.0157	12.89	12343.89
TB	ID		0.015098	0.002974	0.004425	0.189655	0.261542	0.315077	0.0017	0.0118	0.865	555.6269
EB	ID		0.019784	0.002454	0.005311	0.180092	0.258223	0.258659	0.1406	0.0164	1.45	943.3707
FB	ID		0.01117	0.004137	0.006341	0.195804	0.254414	0.34519	0.0018	0.0112	0.704	464.8808
O1	LP	3.505047	0.282611		0.02516		0.162102	0.197067	0.0729	0.0238	22.15	22955.94
M1	LP	1.452865	0.129626		0.04253		0.100288	0.240665	0.0634	0.016	21.09	35329.59
M2	LP	2.216714	0.242058		0.080873		0.100668	0.234253	0.0604	0.0176	24.39	40703.14
M3	LP	2.333649	0.257028		0.092675		0.105102	0.20476	0.0657	0.0175	25.04	40025.04
M4	LP	2.145605	0.244253		0.130727		0.115411	0.226987	0.0914	0.0148	24.04	34994.35
I1	LP	3.042119	0.387869		0.048905		0.103706	0.258617	0.0502	0.0146	23.21	37599.54
TB	LP	0.271411	0.03918		0.104494		0.263402		0.0019	0.0239	1.074	685.0057
EB	LP	0.343777	0.079377		0.03383		0.205422		0.0046	0.0282	1.526	1248.004
FB	LP	1.012131	0.203961		0.09501		0.24594		0.0052	0.0154	4.442	3034.3

O1	GP	0.785911	0.067514		0.007299		0.11964	6.278148	0.0305	0.0182	11.36	15951.89
O2	GP	0.674435	0.063468		0.007264		0.107225	6.374748	0.0181	0.0126	11.34	17767.46
M1	GP	0.624874	0.04883		0.003607		0.107062	6.372183	0.0121	0.0122	10.73	16837.42
M2	GP	0.620744	0.050676		0.002936		0.104306	6.349102	0.0064	0.0134	10.78	17362.79
M3	GP	0.638377	0.048086		0.002877		0.111727	6.284132	0.0419	0.0123	11.3	16991.39
M4	GP	0.649511	0.051579		0.00989		0.119722	6.470065	0.0701	0.0106	11.5	16137.44
M5	GP	0.674111	0.055639		0.005636		0.121304	6.611545	0.0497	0.0119	10.86	15040.55
I1	GP	0.717962	0.049222		0.003956		0.130035	6.223864	0.0562	0.0193	11.33	14637.89
I2	GP	0.686681	0.05374		0.005531		0.112409	6.202493	0.0552	0.0102	11.15	16664.1
TB	GP	0.222999	0.004969		0.009974		0.235545		0.002	0.0119	1.457	1039.192
FB	GP	0.518713	0.054727		0.011105		0.247768		0.003	0.0111	1.082	733.6537

Pond Features for Sediment Analysis (Part 1)

Analyte	Pond ID	Location	Pond Type	Date Taken	Depth (cm)	Depth Dummy	Date_ Built	Date_ Dredged	Water Depth	MaxWaterDepth
S. Houston 1	DP	I	urb	6/30/2014	0-2	1	1937	1986	0.1	1.63
S. Houston 2	DP	I	urb	6/30/2014	2-6	2	1937	1986	0.1	1.63
S. Houston 3	DP	M	urb	6/30/2014	0-2	1	1937	1986	0.75	1.63
S. Houston 4	DP	M	urb	6/30/2014	2-10	2	1937	1986	0.75	1.63
S. Houston 5	DP	O	urb	6/30/2014	0-2	1	1937	1986	1.63	1.63
S. Houston 6	DP	O	urb	6/30/2014	2-10	2	1937	1986	1.63	1.63
S. Houston 7	GP	I	golf	7/14/2014	0-2	1	1965		0.5	1.25
S. Houston 8	GP	I	golf	7/14/2014	2-10	2	1965		0.5	1.25
S. Houston 9	GP	M	golf	7/14/2014	0-2	1	1965		1.25	1.25
S. Houston 10	GP	M	golf	7/14/2014	2-10	2	1965		1.25	1.25
S. Houston 11	GP	O	golf	7/14/2014	0-2	1	1965		0.5	1.25
S. Houston 12	GP	O	golf	7/14/2014	2-10	2	1965		0.5	1.25
S. Houston 13	ID	I	urb	7/3/2014	0-2	1	2011	2012	1	1
S. Houston 14	ID	I	urb	7/3/2014	2-10	2	2011	2012	1	1
S. Houston 15	ID	M	urb	7/3/2014	0-2	1	2011	2012	0.25	1
S. Houston 16	ID	M	urb	7/3/2014	2-10	2	2011	2012	0.25	1
S. Houston 17	ID	O	urb	7/3/2014	0-2?*	1	2011	2012	1	1
S. Houston 18	ID	O	urb	7/3/2014	2-?*	2	2011	2012	1	1
S. Houston 19	NM	I	ag	7/2/2014	0-4 (~1cm water?)	1	1965	2011	0.05	
S. Houston 20	NM	I	ag	7/2/2014	4-	2	1965	2011	0.05	
S. Houston 21	JW	M	ag	7/1/2014	top?**	1	1965	1996	1.25	1.25
S. Houston 22	JW	M	ag	7/1/2014	bottom?**	2	1965	1996	1.25	1.25
S. Houston 23	JW	O	ag	7/1/2014	0-2	1	1965	1996	1.05	1.25
S. Houston 24	JW	O	ag	7/1/2014	2-10	2	1965	1996	1.05	1.25
S. Houston 25	LP	I	ag	7/10/2014	0-2	1	1965	2011	0.1	1
S. Houston 26	LP	I	ag	7/10/2014	2-10	2	1965	2011	0.1	1
S. Houston 27	LP	M	ag	7/10/2014	0-2	1	1965	2011	1	1

S. Houston	28	LP	M	ag	7/10/2014	2-10	2	1965	2011	1	1
S. Houston	29	LP	O	ag	7/10/2014	0-2	1	1965	2011	0.25	1
S. Houston	30	LP	O	ag	7/10/2014	2-	2	1965	2011	0.25	1

Pond Features for Sediment Analysis (Part 2)

Pond ID	Location	Depth Dummy	PondLength	PondMidWidth	PondWidth	LWratio	PondSurfaceArea	WatershedArea
DP	I	1	268	88.59	83.01333	3.228397	23327	7149824
DP	I	2	268	88.59	83.01333	3.228397	23327	7149824
DP	M	1	268	88.59	83.01333	3.228397	23327	7149824
DP	M	2	268	88.59	83.01333	3.228397	23327	7149824
DP	O	1	268	88.59	83.01333	3.228397	23327	7149824
DP	O	2	268	88.59	83.01333	3.228397	23327	7149824
GP	I	1	47.45	27.9	20.53333	2.310877	1166	210854
GP	I	2	47.45	27.9	20.53333	2.310877	1166	210854
GP	M	1	47.45	27.9	20.53333	2.310877	1166	210854
GP	M	2	47.45	27.9	20.53333	2.310877	1166	210854
GP	O	1	47.45	27.9	20.53333	2.310877	1166	210854
GP	O	2	47.45	27.9	20.53333	2.310877	1166	210854
ID	I	1	68.48	14.68	23.04	2.972222	1408	88584
ID	I	2	68.48	14.68	23.04	2.972222	1408	88584
ID	M	1	68.48	14.68	23.04	2.972222	1408	88584
ID	M	2	68.48	14.68	23.04	2.972222	1408	88584
ID	O	1	68.48	14.68	23.04	2.972222	1408	88584
ID	O	2	68.48	14.68	23.04	2.972222	1408	88584
NM	I	1						
NM	I	2						
JW	M	1	60.72	38.94	36.15333	1.679513	2153	27402
JW	M	2	60.72	38.94	36.15333	1.679513	2153	27402
JW	O	1	60.72	38.94	36.15333	1.679513	2153	27402

JW	O	2	60.72	38.94	36.15333	1.679513	2153	27402
LP	I	1	86.41	25.2	23.56	3.667657	1962	195197
LP	I	2	86.41	25.2	23.56	3.667657	1962	195197
LP	M	1	86.41	25.2	23.56	3.667657	1962	195197
LP	M	2	86.41	25.2	23.56	3.667657	1962	195197
LP	O	1	86.41	25.2	23.56	3.667657	1962	195197
LP	O	2	86.41	25.2	23.56	3.667657	1962	195197

Pond Features for Sediment Analysis (Part 3)

Pond ID	Location	Depth Dummy	PondSideLengths_m	AvePondDepth_m	Volume_m3	Water_pH
DP	I	1	134.52 (TR), 262.81 (BR), 269.68 (TL)	0.826667	14304.79	8.08
DP	I	2	134.52 (TR), 262.81 (BR), 269.68 (TL)	0.826667	14304.79	8.08
DP	M	1	134.52 (TR), 262.81 (BR), 269.68 (TL)	0.826667	14304.79	7.6
DP	M	2	134.52 (TR), 262.81 (BR), 269.68 (TL)	0.826667	14304.79	7.6
DP	O	1	134.52 (TR), 262.81 (BR), 269.68 (TL)	0.826667	14304.79	7.46
DP	O	2	134.52 (TR), 262.81 (BR), 269.68 (TL)	0.826667	14304.79	7.46
GP	I	1	radius = 17.88	0.75	1003.84	8.33
GP	I	2	radius = 17.89	0.75	1003.84	8.33
GP	M	1	radius = 17.90	0.75	1003.84	8.32
GP	M	2	radius = 17.91	0.75	1003.84	8.32
GP	O	1	radius = 17.92	0.75	1003.84	8.02
GP	O	2	radius = 17.93	0.75	1003.84	8.02
ID	I	1	31.43 (L), 59.92 (T), 20.73 (R), 65.58 (B)	0.75	1227.39	7.39
ID	I	2	31.43 (L), 59.92 (T), 20.73 (R),	0.75	1227.39	7.39

			65.58 (B)			
ID	M	1	31.43 (L), 59.92 (T), 20.73 (R), 65.58 (B)	0.75	1227.39	7.69
ID	M	2	31.43 (L), 59.92 (T), 20.73 (R), 65.58 (B)	0.75	1227.39	7.69
ID	O	1	31.43 (L), 59.92 (T), 20.73 (R), 65.58 (B)	0.75	1227.39	7.15
ID	O	2	31.43 (L), 59.92 (T), 20.73 (R), 65.58 (B)	0.75	1227.39	7.15
NM	I	1				
NM	I	2				
JW	M	1	54.89(L), 22.73(T), 42.93(R), 48.58 (B)	0.916667	1598.562	8.47
JW	M	2	54.89(L), 22.73(T), 42.93(R), 48.58 (B)	0.916667	1598.562	8.47
JW	O	1	54.89(L), 22.73(T), 42.93(R), 48.58 (B)	0.916667	1598.562	8.64
JW	O	2	54.89(L), 22.73(T), 42.93(R), 48.58 (B)	0.916667	1598.562	8.64
LP	I	1	37.12 (L), 87.35 (B), 75.77 (T)	0.45	630.2141	9.64
LP	I	2	37.12 (L), 87.35 (B), 75.77 (T)	0.45	630.2141	9.64
LP	M	1	37.12 (L), 87.35 (B), 75.77 (T)	0.45	630.2141	9.31
LP	M	2	37.12 (L), 87.35 (B), 75.77 (T)	0.45	630.2141	9.31
LP	O	1	37.12 (L), 87.35 (B), 75.77 (T)	0.45	630.2141	8.56
LP	O	2	37.12 (L), 87.35 (B), 75.77 (T)	0.45	630.2141	8.56

Pond Sampling Data for Sediment Analysis (Part 1)

Pond ID	Location	Depth Dummy	Al	Cd_raw	Cd	Cr	Cu	Fe	Hg_raw	Hg	Ni	P	Pb	Zn
DP	I	1	48.349	<0.001	0	0.431	0.254	159.27	<0.005	0	0.181	3.719	1.377	1.473
DP	I	2	35.103	<0.001	0	0.286	0.236	146.09	<0.005	0	0.082	3.908	0.508	1.535
DP	M	1	107.46	<0.001	0	0.317	0.867	165.39	<0.005	0	0.155	7.803	0.514	4.027

DP	M	2	115.29	0.002	0.002	0.337	0.889	172.25	<0.005	0	0.164	7.617	0.537	4.052
DP	O	1	138.52	0.002	0.002	0.357	0.971	241.82	0.009	0.009	0.187	9.829	0.537	3.776
DP	O	2	192.51	0.004	0.004	0.422	1.087	271.92	<0.005	0	0.224	10.603	0.601	4.209
GP	I	1	109.55	<0.001	0	0.153	0.248	202.74	<0.005	0	0.162	6.192	0.153	1.111
GP	I	2	116.06	<0.001	0	0.153	0.396	176.42	<0.005	0	0.158	5.898	0.139	1.054
GP	M	1	147.85	<0.001	0	0.189	0.223	225.44	0.006	0.006	0.183	7.302	0.169	0.888
GP	M	2	133.08	<0.001	0	0.174	0.212	198.54	<0.005	0	0.303	5.571	0.151	0.923
GP	O	1	138.63	<0.001	0	0.178	0.189	192.39	0.009	0.009	0.204	6.183	0.158	0.832
GP	O	2	134.32	<0.001	0	0.176	0.185	205.38	<0.005	0	0.181	6.372	0.162	0.848
ID	I	1	207.76	<0.001	0	0.272	0.208	273.14	<0.005	0	0.178	6.619	0.188	1.073
ID	I	2	199.87	<0.001	0	0.245	0.208	258.94	<0.005	0	0.165	6.27	0.241	0.729
ID	M	1	241.66	<0.001	0	0.267	0.179	260.78	<0.005	0	0.155	6.987	0.289	0.723
ID	M	2	128.24	<0.001	0	0.168	0.096	191.03	<0.005	0	0.076	5.72	0.274	0.411
ID	O	1	139.69	<0.001	0	0.226	0.104	264.36	<0.005	0	0.096	4.678	0.861	0.919
ID	O	2	148.39	<0.001	0	0.202	0.082	243.92	0.009	0.009	0.081	4.736	0.689	0.585
NM	I	1	69.287	<0.001	0	0.341	0.096	239.61	0.011	0.011	0.071	4.562	0.314	0.239
NM	I	2	81.012	<0.001	0	0.522	0.129	416.78	<0.005	0	0.089	5.177	0.541	0.279
JW	M	1	171.62	<0.001	0	0.251	0.202	182.56	<0.005	0	0.151	3.18	0.121	0.335
JW	M	2	143.92	<0.001	0	0.217	0.218	166.28	<0.005	0	0.139	3.063	0.118	0.372
JW	O	1	73.422	<0.001	0	0.163	0.068	143.21	<0.005	0	0.073	1.665	0.092	0.167
JW	O	2	66.107	<0.001	0	0.198	0.063	237.64	0.011	0.011	0.081	1.643	0.142	0.221
LP	I	1	125.57	<0.001	0	0.159	0.141	173.88	<0.005	0	0.133	8.137	0.151	0.383
LP	I	2	111.3	<0.001	0	0.165	0.153	193.66	<0.005	0	0.133	9.004	0.174	0.396
LP	M	1	173.82	<0.001	0	0.217	0.187	240.37	0.011	0.011	0.186	8.535	0.149	0.422
LP	M	2	140.12	<0.001	0	0.178	0.169	219.24	<0.005	0	0.158	8.063	0.133	0.374
LP	O	1	114.89	<0.001	0	0.267	0.175	371.03	<0.005	0	0.162	9.216	0.191	0.359
LP	O	2	113.12	<0.001	0	0.195	0.149	290.46	<0.005	0	0.141	7.807	0.151	0.331

Pond Sampling Data for Sediment Analysis (Part 2)

Pond ID	Location	Depth Dummy	Al_mgkg	Cd_mgkg	Cr_mgkg	Cu_mgkg	Fe_mgkg	Hg_mgkg	Ni_mgkg	P_mgkg	Pb_mgkg	Zn_mgkg
DP	I	1	4834.9	0	43.1	25.4	15927	0	18.1	371.9	137.7	147.3
DP	I	2	3510.3	0	28.6	23.6	14609	0	8.2	390.8	50.8	153.5
DP	M	1	10746	0	31.7	86.7	16539	0	15.5	780.3	51.4	402.7
DP	M	2	11529	0.2	33.7	88.9	17225	0	16.4	761.7	53.7	405.2
DP	O	1	13852	0.2	35.7	97.1	24182	0.9	18.7	982.9	53.7	377.6
DP	O	2	19251	0.4	42.2	108.7	27192	0	22.4	1060.3	60.1	420.9
GP	I	1	10955	0	15.3	24.8	20274	0	16.2	619.2	15.3	111.1
GP	I	2	11606	0	15.3	39.6	17642	0	15.8	589.8	13.9	105.4
GP	M	1	14785	0	18.9	22.3	22544	0.6	18.3	730.2	16.9	88.8
GP	M	2	13308	0	17.4	21.2	19854	0	30.3	557.1	15.1	92.3
GP	O	1	13863	0	17.8	18.9	19239	0.9	20.4	618.3	15.8	83.2
GP	O	2	13432	0	17.6	18.5	20538	0	18.1	637.2	16.2	84.8
ID	I	1	20776	0	27.2	20.8	27314	0	17.8	661.9	18.8	107.3
ID	I	2	19987	0	24.5	20.8	25894	0	16.5	627	24.1	72.9
ID	M	1	24166	0	26.7	17.9	26078	0	15.5	698.7	28.9	72.3
ID	M	2	12824	0	16.8	9.6	19103	0	7.6	572	27.4	41.1
ID	O	1	13969	0	22.6	10.4	26436	0	9.6	467.8	86.1	91.9
ID	O	2	14839	0	20.2	8.2	24392	0.9	8.1	473.6	68.9	58.5
NM	I	1	6928.7	0	34.1	9.6	23961	1.1	7.1	456.2	31.4	23.9
NM	I	2	8101.2	0	52.2	12.9	41678	0	8.9	517.7	54.1	27.9
JW	M	1	17162	0	25.1	20.2	18256	0	15.1	318	12.1	33.5
JW	M	2	14392	0	21.7	21.8	16628	0	13.9	306.3	11.8	37.2
JW	O	1	7342.2	0	16.3	6.8	14321	0	7.3	166.5	9.2	16.7
JW	O	2	6610.7	0	19.8	6.3	23764	1.1	8.1	164.3	14.2	22.1
LP	I	1	12557	0	15.9	14.1	17388	0	13.3	813.7	15.1	38.3
LP	I	2	11130	0	16.5	15.3	19366	0	13.3	900.4	17.4	39.6
LP	M	1	17382	0	21.7	18.7	24037	1.1	18.6	853.5	14.9	42.2
LP	M	2	14012	0	17.8	16.9	21924	0	15.8	806.3	13.3	37.4

LP	O	1	11489	0	26.7	17.5	37103	0	16.2	921.6	19.1	35.9
LP	O	2	11312	0	19.5	14.9	29046	0	14.1	780.7	15.1	33.1

Biochar Sorption

C/N Analysis, Zeta Potential, Surface Area

Biochar	Cperc	Cstd	Nperc	Nstd	ZP	ZPstd	ZP_pH	SA (m2/g)
CS400	52.93	0.017	0.83	0.001	-28.9	2.5	7.11/7.48	128.476
CS600	62.22	0.027	0.72	0	-32.3	6.2	7.28/7.49	260.287
MH	77.38	0.121	0	0	-26.6	0.9	8.81/8.87	423.768
RH	39.14	0.026	0	0	-45.7	4.9	7.58/7.75	79.777

pH and EC Before/After Water-Extractable Test

	pH_5min	conduS_5min	pH_1hr	conduS_1hr
Control	7.803333	0.723333	7.823333	0.936667
CS400	9.106667	593	8.736667	466.6667
CS600	9.676667	372.6667	9.423333	380.6667
MH	9.66	511.6667	9.663333	770.3333
RH	9.246667	300.3333	9.076667	267.6667
average	9.4225	444.4167	9.225	471.3333
STD	0.289641	132.2972	0.404946	215.3473
			used in paper	

Water-Extractable Results

	Al mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	P mg/L	Zn mg/L	Al mg/kg	Ca mg/kg	Fe mg/kg	K mg/kg	Mg mg/kg	P mg/kg	Zn mg/kg
Control	0.009	0.115					0.024	0.225	2.875	0	0	0	0	0.6
C400	0.118	2.450	0.154	269.714	1.951	10.703	0.091	2.95	61.25	3.85	6742.85	48.775	267.575	2.275
C600	0.110	1.978	0.208	236.142	1.018	8.205	0.065	2.75	49.45	5.2	5903.55	25.45	205.125	1.625
MH	1.127	6.873	0.014	123.332	2.826	1.629	0.034	28.175	171.825	0.35	3083.3	70.65	40.725	0.85
RH	0.021	0.797	0.028	94.482	1.779	9.245	0.040	0.525	19.925	0.7	2362.05	44.475	231.125	1

Water-Extractable P

CS400 mg/L	CS600 mg/L	MH mg/L	RH mg/L	CS400 mg/kg	CS600 mg/kg	MH mg/kg	RH mg/kg	CS400 mg/L	CS600 mg/L	MH mg/L	RH mg/L
10.70	8.21	1.63	9.25	267.58	205.13	40.73	231.13	0.27	0.21	0.04	0.23

Digestion Results

	Al_mgpkg	Ca_mgpkg	Cr_mgpkg	Cu_mgpkg	Fe_mgpkg	K_mgpkg	Mg_mgpkg	Mn_mgpkg	Ni_mgpkg	P_mgpkg	Pb_mgpkg	Zn_mgpkg
C400	1680.7	11439	4.3	16.2	5291.9	17522	5394.7	124.4	3.6	1007.3	3.6	155.9
C600	2319.2	15834	5.2	16.2	7568.8	16015	6353.3	162.3	4.8	1138.1	2.1	132.4
MH	683.4	5621.5	2.6	9.6	937.3	5332	1064.9	214.9	3.4	589.5	1.6	13.6
RH	98.6	1479.1		3.1	180	8713	777.2	372.2		1558.6	1.6	35.8

Digestion: P Concentration

CS400 mg/L	CS600 mg/L	MH mg/L	RH mg/L	CS400 mg/kg	CS600 mg/kg	MH mg/kg	RH mg/kg	CS400 mg/L	CS600 mg/L	MH mg/L	RH mg/L
10.07	11.38	5.90	15.59	1007.30	1138.10	589.50	1558.60	1.01	1.14	0.59	1.56

Sorption Results

mg/L	Control mg/L	CS600 mg/L	MH mg/L	RH mg/L	Control mg/kg	CS600 mg/kg	MH mg/kg	RH mg/kg	Control mg/L	CS600 mg/L	MH mg/L	RH mg/L
0	0.00	-12.03	-2.02	-10.91	0.00	-300.68	-50.43	-272.79	0.00	-0.30	-0.05	-0.27
0.05	-0.09	-11.44	-2.26	-13.74	-2.20	-286.11	-56.54	-343.56	0.00	-0.29	-0.06	-0.34
0.1	-0.13	-12.00	-2.08	-14.86	-3.17	-299.90	-51.92	-371.56	0.00	-0.30	-0.05	-0.37
0.5	-0.53	-11.15	-1.80	-12.74	-13.31	-278.78	-44.97	-318.40	-0.01	-0.28	-0.04	-0.32
1	-1.09	-10.77	-0.81	-13.34	-27.22	-269.17	-20.35	-333.48	-0.03	-0.27	-0.02	-0.33
2	-2.17	-11.84	-0.33	-13.69	-54.30	-296.04	-8.28	-342.15	-0.05	-0.30	-0.01	-0.34
5	-5.29	-12.04	0.83	-12.29	-132.17	-301.07	20.81	-307.18	-0.13	-0.30	0.02	-0.31
10	-10.52	-11.28	4.64	-12.84	-263.02	-281.96	116.07	-321.12	-0.26	-0.28	0.12	-0.32
15	-15.51	-11.46	5.65	-11.27	-387.67	-286.46	141.35	-281.78	-0.39	-0.29	0.14	-0.28

Laboratory Filter Experiment

Data for this experiment are not included due to performance issues with Microsoft Word if the entire dataset is added.