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Multiscale assessment of drinking water treatment residuals as a phosphorus sorbing amendment in stormwater bioretention systems

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MULTISCALE ASSESSMENT OF DRINKING WATER TREATMENT RESIDUALS AS A PHOSPHORUS SORBING AMENDMENT IN STORMWATER BIORETENTION SYSTEMS.

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ABSTRACT

Bioretention systems can reduce stormwater runoff volumes and filter pollutants. However, bioretention soil media can have limited capacity to retain phosphorus (P), and can even be a P source, necessitating P-sorbing amendments. Drinking water treatment residuals (DWTRs) have promise as a bioretention media amendment due to their high P sorption capacity. This research explores the potential for DWTRs to mitigate urban P loads using a combination of lab experiments, field trials, and an urban watershed model.

In the laboratory portion of this research, I investigated possible tradeoffs between P retention and hydraulic conductivity in DWTRs to inform bioretention media designs. Batch isotherm and flow-through column studies demonstrated that DWTRs have high but variable P sorption capacities, which correlated inversely with hydraulic conductivity. Large column studies showed that when applied as a solid layer within bioretention media, DWTRs can restrict water flow and exhibit only partial P removal. However, mixed layers of sand and DWTRs were shown to alleviate flow restrictions and exhibit complete P removal. These results suggest that mixing DWTRs with sand is an effective strategy for achieving stormwater drainage and P removal goals.

In the field portion of this research, I assessed the capacity of a DWTR-amended media to remove different chemical species of P from stormwater in roadside bioretention systems. I also explored whether DWTRs affect system hydraulics or leach heavy metals in the field. Significant reductions in dissolved P and total P concentrations and loads were observed in both the Control and DWTR media. However, the removal efficiency percentages (RE) of the DWTR cells were greater than those of the Control cells for all P species, and this difference increased substantially from the first to the second monitoring season. Furthermore, the DWTR used in this study was not shown to affect bioretention system hydraulics or to significantly leach heavy metals. These results indicate that DWTRs have potential to improve P retention without causing unintended consequences.

In the third phase of this research, I used the EPA - Storm Water Management Model (SWMM) to assess the impacts of different bioretention P removal performances and infiltration capacities on catchment-scale P loads, runoff volumes, and peak flow rates. Model outputs, which measured the cumulative effects of widespread bioretention use, showed that both P removal performance and infiltration capacity (i.e., presence or absence of an impermeable liner) have major impacts on watershed P loads. Infiltrating bioretention systems showed the capacity to reduce urban P loads and stormwater volumes, even with media that exhibited low P removal. Notably, P-sorbing amendments can be a limited resource and infiltration is not feasible in all locations. These results therefore suggest that water quantity and quality goals can be effectively achieved through a mixture of infiltrating bioretention and strategic use of P-sorbing amendments.

Together, this research shows that DWTRs have significant potential to improve P removal within bioretention systems, but that fine-scale processes (e.g., P sorption capacity, hydraulic conductivity) must inform media designs if bioretention systems are to effectively reduce catchment-scale P loads and eutrophication risks.

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CHAPTER 1: INTRODUCTION

1.1 Background

The rapid rate of urbanization experienced in recent decades has increased the spatial footprint of developed landscapes around the world [1,2]. These landscapes often contain large impervious surface areas, which increase stormwater runoff volumes by preventing rainfall from infiltrating into the soil[3]. In addition to causing hydrologic problems[4] (e.g. surface flooding and streambank erosion), stormwater runoff can degrade water quality by transporting pollutants from urban surfaces to receiving waters bodies [5,6]. Consequently, stormwater runoff is considered a leading cause of surface water impairment within the United States [7].

Bioretention systems are a popular form of green stormwater infrastructure (GSI) used for hydrologic control and water quality improvements in urban environments [8]. Bioretention designs vary, but generally contain vegetation and a soil media composed of mixtures of sand and organic amendments (e.g., compost, topsoil, woodchips) positioned above one or more layers of gravel or stone that facilitates drainage [9,10]. From a hydrologic perspective, bioretention systems can promote runoff reduction, peak flow reduction, and groundwater recharge by capturing stormwater, temporarily storing it, and slowly releasing it into the soil or storm sewer network[11]. From a water quality perspective, bioretention systems can filter sediments and particulate matter and can treat a variety of dissolved pollutants through chemical and biological removal processes [12,13]. As urban areas continue to invest in GSI to manage increased surface runoff volumes associated with urbanization and climate change, the prevalence of bioretention systems in developed landscapes will likely increase.

Despite their ability to provide hydrologic control and water quality improvement, bioretention systems have demonstrated variable capacity to remove phosphorus (P) from stormwater, and some systems can function as net sources of P [14–19]. Poor P retention performances in field bioretention studies have been attributed to P leaching from organic soil amendments and the limited P sorption capacity of sand [10,14,17,18]. P control is a primary water quality objective for many municipalities because excessive P loading contributes to eutrophication and harmful algal blooms in freshwater ecosystems [20,21]. Cities are often located on major freshwater bodies and rely on those water bodies as sources of drinking water and recreation. Widespread implementation of bioretention systems that leach P could exacerbate urban P loading and further degrade surface water quality and aquatic health. Innovative design solutions that improve P retention within bioretention media are therefore needed [22].

Drinking water treatment residuals (DWTRs) have potential to significantly improve P removal within bioretention systems and thus urban water quality. These materials are a widely generated byproduct of the drinking water treatment process and contain high concentrations of metal hydroxides, which have a strong affinity for dissolved P [23]. Benchtop experiments have shown that DWTRs can remove large amounts of P from solution via chemical adsorption and precipitation processes [24–26]. Incorporating DWTRs into bioretention media could significantly enhance media abilities to retain the dissolved P that enters via runoff as well as the P that is internally released from compost, plant tissues, and accumulated sediment. DWTRs may be particularly important for P removal in cold climates that lack biological uptake mechanisms during winter months. This practice also represents a beneficial reuse opportunity whereby cities can use a waste product to reduce urban P loads, while avoiding DWTR disposal costs [23,27].

Amending bioretention media with DWTRs has potential to mitigate urban P loading, but is still a relatively unproven technology and significant practical questions remain at multiple scales[22]. Consequently, stormwater professionals and governmental agencies lack the practical knowledge needed to make bioretention media design decisions or to predict the long-term P removal potential of this practice. Broader use of DWTRs within bioretention and other GSI requires an improved understanding of this technology that integrates fine-scale processes into the design of large-scale systems. The following sections highlight the scientific background and critical unknowns associated with applying DWTRs to bioretention systems at different scales.

1.2 Summary of Key Information and Knowledge Gaps

1.2.1 Micro-Scale

1.2.1.1 *Phosphorus Sorption*

The term "sorption" is often used to refer to both the processes of chemical adsorption and precipitation [24,28,29]. Adsorption is the adherence of dissolved ions to a solid surface and precipitation is the creation of a solid from two or more dissolved molecules [30]. Dissolved P ions (e.g. $H_2PO_4^-$, HPO_4^{2-}) have negative charges, which are electrostatically attracted to the positive surface charges of metal hydroxides[31]. Once near the exchange complex, phosphate can replace hydroxyl groups and permanently associate with the central metal ion via strong, largely irreversible, ligand exchange reactions [31]. Dissolved P ions can also interact with certain dissolved metals (e.g. aluminum (Al) and iron (Fe)) to form insoluble precipitates [28]. The presence of dissolved metals, however, is pH dependent, so soil acidity can regulate the potential for precipitation to occur in both natural and engineered systems[30].

1.2.1.2 *Quantifying P Sorption Capacity*

P sorption capacity is a metric used to describe the maximum amount of P a material can bind through adsorption and precipitation reactions [26,28,32]. This metric can be a critical design parameter for bioretention systems because it determines how much of a P-sorbing amendment is needed within bioretention media for long-term P removal [33,34]. The P sorption capacity of a material can be quantified using multiple methods, but these methods can yield very different values [32,35]. No standardized method currently exists for quantifying P sorption capacities within GSI contexts.

Batch isotherms are perhaps the most common method for quantifying the P sorption capacity of a material [24,29,36]. This method involves adding a fixed amount of material to a centrifuge tube along with a fixed volume of P-rich solution and analyzing P concentrations after shaking the tubes for a given length of time [37]. The initial P concentrations and equilibrium P concentrations are used as inputs to the Langmuir adsorption equation to calculate the maximum quantity of P (Q_{max}) that can be retained by the media [38,39]. However, the Q_{max} values generated by batch isotherms have been criticized as being unrealistically high (for what can be expected from bioretention media) because the method uses mechanical shaking, prolonged contact times, and very high P concentrations [29,32,34].

As an alternative, authors have recommended quantifying P sorption capacities using flow-through column experiments, run to the point of P saturation [26,32,34]. These experiments require significantly more time and resources than batch isotherms, but more realistically represent the hydraulic dynamics that occur in bioretention systems. However, the P sorption capacity values yielded by these experiments can vary dramatically depending on the experimental design parameters. For example, experiments that use low flow rates and high influent P concentrations will produce P sorption capacity values much higher than those that use high flow rates and low influent P concentrations [26,35]. Additional research is needed to determine the extent to which experimental methodologies influence P sorption capacity values and to establish a standardized procedure for quantifying this parameter in the context of GSI performance.

1.2.1.3 *Physicochemical Drivers of P Sorption Capacity in DWTRs*

DWTRs are heterogenous materials that exhibit a wide range of P sorption capacity values [23,24,40]. However, few screening metrics exist to aid in the process of DWTR source selection [22]. The total abundance of Al, Fe, and calcium (Ca) in DWTRs sets the upper limit on their P sorption capacity because these are the major elements involved in sorption reactions [40–42]. These elements can only sorb P if exposed to solution, so a given DWTR's sorption potential may be further influenced by surface area [43,44]. The physical structure of these metallic elements, whether they are in crystalline or amorphous forms, can also influence P sorption capacities [40,42]. Fine-grained DWTRs with high concentrations of amorphous metal hydroxides and high surface areas likely have the greatest P sorption capacity. The establishment of physically- and chemically-based selection criteria could help stormwater practitioners determine whether a particular DWTR source is appropriate for GSI applications. It could also incentivize water treatment plants to adopt management practices that improve the P sorption capacity of their residual products.

1.2.1.4 *Potential Hydraulic Tradeoffs with P Sorption*

P-sorbing materials with fine grains and high surface areas may have very high P sorption capacities, but they may also exhibit low hydraulic conductivities [22,33,45]. If the hydraulic conductivity of DWTRs is significantly less than that of the other media constituents, then incorporating DWTRs within bioretention media could restrict water flow. Flow restrictions could cause bioretention systems to backup and flood during storm events, undermining their primary hydrologic functions. Flow restrictions could also create preferential flow paths that prevent P sorption by allowing stormwater to bypass the DWTRs. Conversely, DWTRs with high hydraulic conductivity may have very low P sorption capacity and greater quantities of these materials may be needed for long-term P removal. Yan *et al*. (2017) demonstrated that DWTRs can decrease hydraulic conductivity in column experiments but did not investigate possible tradeoffs with P removal. Improved mechanistic knowledge of the potential tradeoff between P sorption capacity and hydraulic conductivity in DWTRs is needed to determine whether DWTRs are appropriate for bioretention applications and to inform material selection criteria.

1.2.1.5 *Potential Leaching of Heavy Metals*

In addition to containing Al and Fe, DWTRs can contain high concentrations of other metals such as manganese (Mn) and zinc (Zn) [23]. These metals can be toxic to plant and animal life and have been shown to leach from DWTRs in some column studies [46,47]. The concentration of heavy metals leaching from DWTRs in previous studies have not been high enough to pose toxicity risks[22,48,49], but heavy metal leaching is a common concern that could limit broader use of DWTRs in field applications [23]. Additional laboratory and field research is needed to determine the mobility of heavy metals under varying conditions, and thus the toxicity risk DWTRs may pose in different environments.

1.2.2 Meso-Scale

Although DWTRs have shown effective dissolved P removal in many column experiments, it is unclear how they should be added to bioretention media for optimal performance [22]. Some studies have added DWTRs as a solid layer within the media profile [49], while others have mixed them with various media constituents to form a homogenous blend [42,48,50]. Theoretically, a solid layer design would ensure that any phosphate ions passing through the media would encounter DWTRs, thereby facilitating P sorption. However, a solid layer design could cause hydraulic restrictions and promote preferential flow if the DWTRs exhibit finer textures than the other media constituents. A mixed layer design could alleviate potential hydraulic restrictions imposed by DWTRs but may also be less effective for P removal. The impact that DWTR incorporation strategies have on P removal and hydraulic performance, however, have not been systematically evaluated or linked to specific physicochemical properties of DWTRs [22].

Another design factor that may influence media performance is the amount of DWTR that is incorporated into bioretention media [22]. Not adding enough DWTRs to media could prevent effective long-term P removal by limiting the number of binding sites available for P sorption to occur. Conversely, adding too much DWTR could cause hydraulic issues and increase risks of heavy metal leaching. Overuse of DWTRs in bioretention media could also decrease the overall availability of DWTRs from a supply and demand perspective, and therefore their potential to mitigate P loading at broader scales. Previous studies have added DWTRs to bioretention media at 3%-10% of the total media volume [42,48–50], but have not based these application rates on any quantitative assessments (e.g. P sorption capacities or P loading rates). Accordingly, it is difficult to attribute the observed P removal performances to a particular mechanism. It is also unclear whether these application rates would be effective for other DWTR sources that exhibit physicochemical properties different from those used in a particular study. Clear and generalizable guidance is therefore needed on how to use DWTRs from varying sources within bioretention media to simultaneously achieve hydraulic control and P removal.

1.2.3 Field-Scale

A number of environmental factors can influence the hydraulic and P removal performance of bioretention systems in field contexts [10,13,17,51]. These factors could produce large performance discrepancies between bioretention experiments conducted in the laboratory and the field [52]. However, few studies have assessed DWTRs in field bioretention experiments, so it is uncertain whether their P removal performance is affected by environmental variability.

1.2.3.1 *Stormwater Chemistry and Competitive Adsorption*

The chemical composition of stormwater runoff can affect P sorption dynamics by creating competition for adsorption sites [31,53]. While metal hydroxides have a strong affinity for phosphate anions, other anions can compete with P for binding sites and reduce the overall capacity of DWTRs to sorb P [28,54,55]. In particular, ligand exchange reactions between metal hydroxides and dissolved organic carbon (DOC) can substantially reduce the availability of anion binding sites [53]. For example, Wang *et al.* (2012) reported a greater than 50% reduction in P sorption as DOC concentrations increased from 0.5 to 50 mg/L[54]. Competition for binding sites between P and other chemical species may be particularly pronounced in bioretention systems that receive large inputs of organic matter and dissolved nutrients.

1.2.3.2 *pH*

Stormwater pH can also influence sorption dynamics because it affects both the surface charge of metal hydroxides as well as the speciation and charge of phosphate ions [56]. Under acidic conditions, hydroxyl groups on the surface of Al and Fe-hydroxides can become protonated and assume a positive charge, which attracts $H_2PO_4^-$ ions via ion and ligand exchange reactions [31]. Under basic conditions, however, surface hydroxyl groups become deprotonated and assume a negative charge, which can repel PO_4^{3-} ions and prevent sorption reactions [31]. The rate and magnitude of P adsorption onto Al- and Fe-hydroxides are thus highest in acidic environments[29,36]. Acidic environments can also increase the solubility of Al and Fe, which can form solid precipitates with P ions when dissolved [30]. However, soil pH values tend to range between 6 and 8 in bioretention systems[13], so precipitation between P ions and dissolved Al and Fe likely plays a smaller role than adsorption for P removal in these systems. Differences in bedrock minerology, acid deposition, and stormwater organic content could affect the pH of runoff and thus the efficacy of P adsorption by DWTRs in field contexts.

1.2.3.3 *Stormwater P Concentrations and Speciation*

P sorption is governed by equilibrium dynamics and is therefore favored at high P concentrations [24,28,29]. Many of the experiments used to quantify the P sorption capacity of DWTRs and other materials use relatively high P concentrations in the influent water to saturate the sorption complex in a reasonable period of time [34,57,58]. However, dissolved P concentrations in stormwater runoff can sometimes be very low (e.g < 0.05 mg P/L) [17,59]. Using stormwater with comparatively low P concentrations could reduce the overall efficacy of P removal, or even favor desorption, depending on the degree of P saturation of the adsorbent [60]. Furthermore, dissolved organic P (DOP) can be a major constituent in stormwater runoff, but DOP removal by bioretention media and DWTRs has rarely been investigated [59,61]. Low P concentrations in stormwater influent and P speciation dynamics within field bioretention systems may therefore lead field experiments to differ from laboratory studies, creating discrepancies between what is observed in the laboratory and actual bioretention performance in the field.

1.2.3.4 *Bioretention System Hydraulics*

Hydraulic performances observed in laboratory environments may also differ substantially from those observed in the field. First, plants can create preferential flow paths through bioretention media along their root networks [62–64]; yet plants are often not included in lab column studies [42,48,65,66]. Second, prolonged antecedent dry periods have been shown to increase the hydraulic conductivity of soil media [16,67]; yet it’s difficult to mimic wetting and drying cycles in lab environments. The interactive effects of plant roots and rainfall variability could increase pore sizes and connectivity within soil media, thereby increasing flow rates and allowing stormwater to hydraulically bypass portions of the media. Finally, lab column experiments often simulate storms under saturated hydraulic conditions [45,48,49,68], but saturated flow may only be experienced in the field during large rainfall events. Unsaturated flow may promote preferential flow paths and only partial media contact. These hydraulic variables could reduce the P removal performance of DWTRs in the field by limiting contact times and enabling P ions to avoid large fractions of the media and thus DWTR amendments.

1.2.3.5 *P Removal by DWTRs in Field Experiments*

The ability of DWTRs to enhance P removal in bioretention systems have only been investigated in two field experiments to date [52,59]. Significant reductions in dissolved P concentrations by DWTR-amended media were not observed in either of these experiments, despite effective dissolved P removal in corresponding column experiments [52,69]. Failures to reduce dissolved P concentrations in these studies were attributed to media bypass, equilibrium dynamics, and non-uniform distributions of

DWTRs within the media[59]. Poor P removal performances in these studies casts doubt on the ability of DWTRs to remove P in highly variable field environments. Additional research is needed to determine whether DWTRs have the capacity to reduce P concentrations in their intended applications, in real-life settings, and if so, which environmental factors most influence their P removal performance.

1.2.4 Catchment-Scale

DWTR-amended bioretention systems would need to be implemented broadly within a watershed to have measurable impacts on urban P loading and eutrophication risks to receiving waters. However, few studies have assessed the effect of bioretention P removal performances on catchment-scale P loads. It is therefore unclear how widespread implementation of DWTR-amended bioretention systems would impact downstream water quality and what scale of implementation would be needed to achieve P load reductions associated with water management goals such as Total Maximum Daily Loads (TMDLs) for P.

Infiltration, whether a bioretention system is lined or unlined, can also affect the hydrologic and water quality performance of bioretention systems. For example, unlined bioretention systems constructed on permeable soils can dramatically decrease stormwater volumes and peak flow rates by infiltrating stormwater [62]. Infiltrated stormwater can carry dissolved P into the subsoil, thereby reducing the mass of P that is released as bioretention effluent [70]. However, opportunities for infiltration can be limited in highly developed areas or areas that contain low permeability clay soils [71,72]. Understanding how the infiltration capacity of bioretention systems interacts with their soil-media-based P removal performances to influence catchment-scale P loading has important watershed management implications.

1.3 Dissertation Structure

The goal of this research is to investigate the potential for DWTRs to reduce urban stormwater P loads by improving P retention within bioretention media. A systematic approach to this goal requires research that integrates basic and applied knowledge across multiple scales to inform bioretention media designs and watershed management strategies. Chapter 1 has explained the broader context of this research and summarized the important scientific background pertaining to this technology at different scales of implementation. Chapter 2 was previously published as Ament *et al*. (2021), and explores the physicochemical properties that govern P sorption and hydraulic conductivity in DWTRs and uses this information to inform bioretention media designs. It then tests the P removal and hydraulic impacts of different DWTR layering strategies to provide practical media design recommendations. Chapter 3 evaluates the P removal performance of a recommended bioretention media design in a two-year field experiment. It also explores the potential for DWTRs to impact system hydraulics and leach heavy metals in field contexts. Chapter 4 uses the EPA - Storm Water Management Model (SWMM) to construct an urban watershed model that investigates the impact of different bioretention P removal performances (low removal and high removal media) and infiltration capacities (lined and unlined systems) on catchment-scale P loads, stormwater volumes, and peak flow rates. Finally, Chapter 5 summarizes the key findings of this research and highlights the topic areas where future research is needed. A cumulative bibliography is provided after Chapter 5.

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CHAPTER 2: BALANCING HYDRAULIC CONTROL AND PHOSPHORUS REMOVAL IN BIORETENTION MEDIA AMENDED WITH DRINKING WATER TEATMENT RESIDUALS

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Keywords: green stormwater infrastructure, phosphorus, bioretention, sorption, hydraulic conductivity, drinking water treatment residuals, column study

Abstract

Green stormwater infrastructure like bioretention can reduce stormwater runoff volumes and trap sediments and pollutants. However, bioretention soil media can have limited capacity to retain phosphorus (P) or even be a P source, necessitating addition of P-sorbing materials. We investigated the potential tradeoff between P removal by drinking water treatment residuals (DWTRs) and hydraulic conductivity to inform bioretention media design. Batch isotherm and flow-through column experiments showed that P removal varied greatly among three DWTRs and across methodologies, which has implications for design requirements. We also conducted a large column experiment to determine the hydraulic and P removal effects of amending bioretention media with solid and mixed layers of DWTRs. When applied to bioretention media, the impact of DWTRs on hydraulic conductivity and P removal depended on layering strategy. Although DWTR addition in solid and mixed layer designs improved P removal, the solid layer restricted water flow and exhibited incomplete P removal, while the mixed layer had no effect on flow and removed nearly 100% of P inputs. We recommend that DWTRs be mixed with sand in bioretention media to simultaneously achieve stormwater drainage and P reduction goals, while also representing beneficial reuse of a waste product.

2.1. Introduction

Stormwater volumes and pollutant loads are detrimental to the health of surface water bodies[1] and are expected to increase due to the interactive effects of urbanization and climate change [2,3]. As an alternative to conventional “gray” infrastructure, some cities are implementing green stormwater infrastructure (GSI) to provide both hydrologic control and water quality improvement. Mitigating phosphorus (P) in runoff is of particular importance in many regions because excessive P loading causes eutrophication and harmful algal blooms in freshwater ecosystems, degrading water quality [4]. However, while GSI performs well for mitigating runoff volumes and sediments, P removal has been highly variable in field studies, with some systems functioning as net sources of P [5–10].

One way to enhance P retention within GSI systems is through addition of materials with high P sorption capacity [11–13]. Industrial byproducts, such as steel slag, fly ash and drinking water treatment residuals, are promising amendments for GSI due to their availability, low-cost, and high concentration of metal-oxides [14,15]. Incorporating these otherwise waste products into GSI for eutrophication control represents a potential win-win opportunity for many municipalities. However, P-sorbing materials tend to have very fine grains, large surface areas, and low hydraulic conductivity [16–19]. This tradeoff between hydraulic conductivity and P sorption capacity poses a significant challenge for simultaneously achieving stormwater drainage goals and P load reductions with GSI.

The tradeoff between hydraulic conductivity and P sorption is particularly relevant for bioretention systems. These GSI systems are designed to reduce peak flow rates and pollutant loads by infiltrating stormwater through a porous media, which typically consists of mixtures of sand and compost [20]. Despite their well-documented ability to remove particulate P, bioretention systems have exhibited inconsistent ability to retain dissolved P [21,22]. Authors attribute this inconsistency to the low P sorption capacity of sand[16,23], the short contact time of P with media surfaces [24], as well as leaching of P from compost, organic sediments, and plant residues [5,7,12,13]. Amending bioretention media with P-sorbing materials could enhance dissolved P removal, but it could also restrict infiltration rates and cause preferential flow, excessive ponding or localized flooding during storm events. Clear guidance on how to use these materials in bioretention media to achieve long-term P removal, without adversely affecting hydraulic conductivity, is therefore needed [15].

The manner in which P-sorbing materials are incorporated into bioretention media may significantly impact both system hydraulics and P removal. Studies investigating P-sorbing materials in bioretention have applied them as solid layers within the media profile [5,25] and mixed them with the other media constituents [11,25–27]. Solid layers of P-sorbing materials may restrict water flow because their hydraulic conductivity tends to be lower than that of sand [16,28]. Mixed layers of P-sorbing materials may mitigate their hydraulic impacts, but reduce their P removal efficiency [25]. Mechanistic knowledge of how amendment layering strategies influence tradeoffs between hydraulic conductivity and P removal is essential for bioretention media design. While a few studies have evaluated the hydraulic effects of P-sorbing amendments[16,25,29], no study has determined how these effects impact P removal dynamics or offered solutions for mitigating potential tradeoffs between hydraulic conductivity and P removal.

The amount of P-sorbing material added to bioretention media may also affect system hydraulics and P removal. For example, adding too much P-sorbing material may have undesirable hydraulic impacts that lead to media bypass and flooding. Conversely, adding too little may prevent long-term P removal by limiting the number of P sorption sites and their contact time with phosphate ions. The recommended amount of P-sorbing material to add to bioretention media varies widely across studies and media amendments [11,26,30]. Ultimately, the amount to include depends on the amount of P a material can retain in field conditions and the total dissolved P load a system will receive over its operational lifetime [28]. However, different methods for quantifying P removal capacity can yield very different results [31–34], and a standardized method for estimating this metric in GSI contexts has not yet been established.

In this study, we conducted several laboratory-scale experiments to investigate the application of drinking water treatment residuals (DWTRs) to bioretention media for enhanced P removal from stormwater, with emphasis on providing novel insights into balancing hydraulic conductivity and P sorption. DWTRs were selected for analysis due to their near-universal availability and high P sorption capacity in laboratory studies [35–39]. Our specific study objectives were to:

a) Quantify the P removal capacity that DWTRs exhibit across a range of P concentrations, contact times, and experimental methodologies.

b) Determine the physicochemical properties of DWTRs that govern hydraulic conductivity and P removal.

c) Determine the hydraulic and P removal impacts of two different DWTR layering strategies in bioretention media.

d) Offer practical media design recommendations for simultaneously achieving hydrologic control and long-term P removal in bioretention systems.

2.2 Materials and Methods

2.2.1 DWTR Sources

Three different DWTRs were obtained from the Champlain Water District (Burlington, VT, USA), the Portsmouth Regional Water System (Portsmouth, NH, USA), and the University of New Hampshire Water Treatment Plant (Durham, NH, USA). These DWTR sources will henceforth be referred to as CWD, PORT, and UNH, respectively. The CWD plant uses aluminum sulfate (“alum”) along with cationic polymer as a coagulant, while the PORT and UNH plants use polyaluminum chloride. Alum and polyaluminum chloride are the two most commonly used coagulants for drinking water treatment in the Northeast United States and other regions of the world[39]. All materials were dewatered via freeze-thaw cycling, air-dried, and passed through a 2-mm sieve before testing.

2.2.2 Material Characterization

2.2.2.1 *Physical Properties*

The particle size distributions of the DWTRs were determined with the conventional dry-sieving technique [40]. Grain-size distribution plots were used to estimate effective grain sizes (d_{10}) and uniformity coefficients (d_{60}/d_{10}). Specific surface areas (m^2

g^{-1}) were obtained using the 3-point BET N_2 gas adsorption method (Particle Lab Technologies, Downers Grove, IL). Bulk densities (g cm^{-3}) were determined by calculating the dry weight to bulk volume ratio of the media [41]. Porosities (%) were measured as the amount of water needed to saturate a known volume of media [42]. Saturated hydraulic conductivities (K_{sat}; cm h^{-1}) were obtained using a constant head permeameter. Collected water volumes were converted to saturated hydraulic conductivity using Darcy's law[16].

2.2.2.2 *Chemical Properties*

DWTR chemical compositions were obtained using acid digestion, lithium borate fusion and ICP-MS analysis (ALS Geochemistry, Reno, NV). Amorphous aluminum (Al) and iron (Fe) oxide contents were determined using a 1:100 material to solution extraction ratio in 0.2 *M* acid ammonium oxalate [43]. Samples were analyzed for oxalate-extractable Al, Fe, and P using ICP-AES analysis. The P saturation ratio was calculated as $[(P_{ox}) / 0.5\times(Al_{ox} + Fe_{ox})]$ [44], with P_{ox}, Al_{ox}, and Fe_{ox} expressed as mmol kg^{-1}.

2.2.3 Phosphorus Retention

Batch isotherm and flow-through column experiments were performed in triplicate to quantify the capacity of DWTRs to remove P from solution under different experimental conditions. All water samples in this study were filtered through a 0.45 micron filter before being analyzed for soluble reactive P (SRP) using the Murphy-Riley molybdate blue method[45] on a Lachat colorimetric flow injection system (Lachat Instruments QuickChem8000 AE, Hach Inc., Loveland, CO). The analytical detection limit for PO_4-P was 0.01 mg P L^{-1} and samples that measured below that value were set to 0.005 mg P L^{-1} for statistical purposes[8,11,26]. All P removal values are expressed on an oven-dry mass basis.

2.2.3.1 *Batch Isotherm Experiment*

A multipoint batch isotherm technique [46] was used to estimate the maximum P sorption capacity of the DWTRs. 20 mL of eight P concentrations (0, 1, 10, 25, 50, 75, 150 and 300 mg P L^{-1} in 0.01 *M* KCl) added as KH_2PO_4 were continuously shaken (~175 RPM) with 1g of DWTR in centrifuge tubes for 24 h. Water samples were then centrifuged and analyzed for SRP. Three additional P concentrations of 600, 900 and 1200 mg P L^{-1} were used for the CWD DWTR to ensure saturation of its sorption complex. Maximum P sorption capacity (Q_{max}) was estimated using an optimization program[47] to fit the non-linear Langmuir adsorption equation:

$$Q_e = \frac{Q_{max} K C_e}{1 + K C_e}$$

where Q_e is the quantity of P bound to the adsorbent at equilibrium (mg P kg^{-1}), Q_{max} is the maximum P sorption capacity of the adsorbent (mg P kg^{-1}), K is the Langmuir binding strength constant, and C_e is the equilibrium P concentration (mg P L^{-1}).

2.2.3.2 *Flow-Through Column Experiments*

Two continuous vertical upflow column experiments were conducted to determine P retention for each DWTR in flow-through conditions under opposing environmental extremes. The first experiment assessed the P retention of DWTRs under conditions ideal for sorption (i.e., high P concentration, low pH, prolonged media contact time), while the second assessed P retention under field-like conditions (i.e., low P concentration, neutral pH, short media contact time). These experiments will henceforth be referred to as the “High P/ Low Flow” experiment and the “Low P/High Flow” experiment, respectively.

In the High P/ Low Flow experiment, 500g of each DWTR were added to PVC columns (50-cm length; 5-cm diameter) and a peristaltic pump was used to continuously feed a synthetic P solution (300 mg P L^{-1} in 0.01 *M* KCl; pH 4.6) vertically through the columns at a hydraulic loading rate of 1.5 L d^{-1} (~5-9 h media contact time). In the Low P/High Flow experiment, 5g of each DWTR were mixed with 15g of sand to prevent media bypass and added to miniature columns (10-cm length; 2.5-cm diameter). A peristaltic pump was used to continuously feed a synthetic P solution (1 mg P L^{-1} in 0.01 *M* KCl; pH 7) vertically through the columns at a hydraulic loading rate of 4.5 L d^{-1} (~3 min media contact time). The DWTR masses, P concentrations, and hydraulic loading rates used in these experiments were selected to capture the range of parameter values used in column studies[15,34,38,48,49].

In both experiments, effluent volumes and P concentrations were repeatedly measured until effluent P concentrations equaled influent P concentrations (i.e., P saturation). Overall P retention values were determined by summing the total amount of P retained during each sampling interval [49]. When P saturation was achieved, columns were drained and oven-dried at 40^{o} C for two weeks. To quantify the effects of prolonged dry periods on potential regeneration of P sorption capacity, dried columns were refed P solution until the DWTRs returned to a state of P saturation. Finally, a P-free 0.01 *M*

KCl solution was continuously fed through the columns for 1 week to measure P desorption.

2.2.4 P Removal Kinetics

A batch kinetics experiment was conducted in triplicate to determine the rate of P removal by DWTRs. Rates of P removal were determined by measuring P removal across a range of shake times. 20 mL of P solution (10 mg P L^{-1} in 0.01 *M* KCl) were added to 1g of DWTR in centrifuge tubes and shaken continuously for variable lengths of time (1, 10, 60, 360 min). P removal was calculated by subtracting effluent P concentrations from influent P concentrations. A flow-through kinetics experiment was also performed to determine P removal rates under more realistic conditions (influent P concentration = 0.2 mg P L^{-1}, contact times = 1, 2, 4, 8, and 16 minutes), where P ions have limited contact opportunities with media surfaces (see Appendix A).

2.2.5 Large Column Experiment

A large column experiment was conducted in triplicate to determine how DWTRs affect the hydraulic and P removal performance of bioretention media. Two different DWTR layering strategies (solid versus mixed; Figure 1) were assessed among the three DWTR sources and compared to a non-amended control.

2.2.5.1 *Bioretention Media Constituents and Designs*

The control media tested in this experiment consisted of washed gravel (2.5-cm diameter), washed pea stone (0.5-cm diameter), washed sand (< 2-mm diameter), and a relatively small quantity of “low-P” compost derived from leaf litter (Figure 1). For the solid layer DWTR design, DWTR was placed on top of the pea stone, replacing 10%

(3.05-cm) of the sand layer volume (Figure 1). For the mixed layer DWTR design, DWTR was mixed into the sand layer in 90% sand 10% DWTR proportions (Figure 1). 10% DWTR by volume was added to the sand layer for all DWTR treatments, representing 5% of the total media volume above the pea stone layer (i.e., 5% of the volume in the top 61 cm of each column).

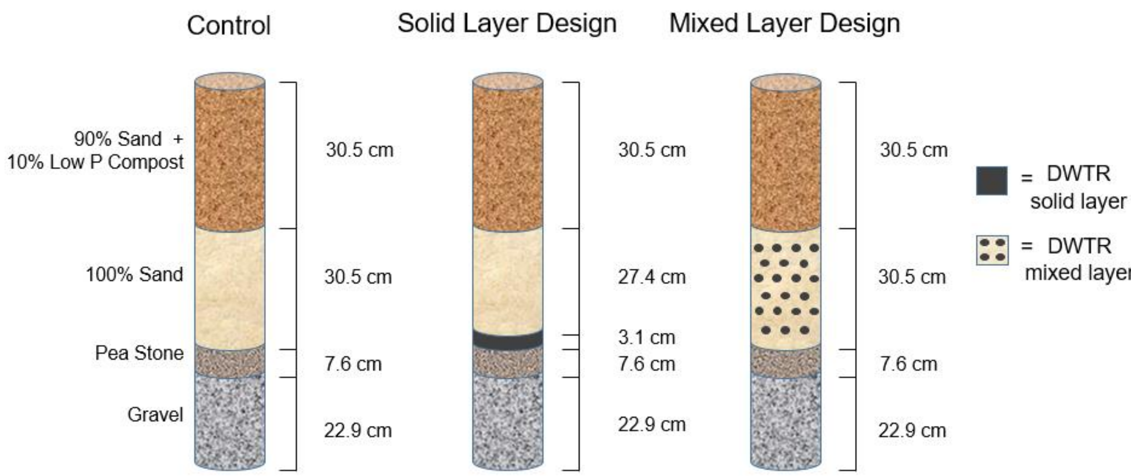

Figure 1. Profile of bioretention media designs used in large column experiment. Columns were 1.3 m in length and 15 cm in diameter. Drinking water treatment residuals (DWTR) were added to offset 10% of the sand layer volume in both the solid and mixed layer designs. This amount of DWTR represents 5% of the total media volume above the pea stone layer (i.e., the top 61 cm).

2.2.5.2 *Experimental Setup and Design*

Test columns were composed of bioretention media in clear polycarbonate tubes (1.3-m length; 15-cm diameter) held in place by PVC end caps (15 cm diameter). For each of 10 days, columns received a 15-L dose of synthetic stormwater (0.5 mg L^{-1} NH_4-N, 0.5 mg L^{-1} NO_3-N, and 0.2 mg L^{-1} PO_4-P in 0.01 *M* KCl; pH 7). Based on design assumptions of a 20:1 catchment to treatment area ratio, 100 cm of annual rainfall, a runoff coefficient of 1.0, and an average dissolved P concentration of 0.1 mg P L^{-1}, each dose of synthetic stormwater was approximately a 2.5-cm storm event and the total P added over the 10-day period was roughly equivalent to a 1-year P load. The parameter values listed above are based on results from bioretention field studies conducted in the eastern USA[5,7,8,13,50,51] and assume a 100% impervious drainage area typical of parking lot and roadside environments. Before the experiment began, 15L of reverse osmosis water was passed through each of the columns to remove potential air pockets within the media and reduce the influence of capillary suction forces.

The daily simulated storms events were administered with constant-head Mariotte bottles, which maintained a 10-cm ponding depth above the media surface and facilitated top-down flow. Effluent volumes were collected for one minute to calculate saturated hydraulic conductivity[16]. These volumes were collected when more than three quarters of the synthetic stormwater had passed through the columns to allow maximum time for a steady state to be achieved. When the entire volume passed through the column and into an effluent container, the effluent was stirred, and one sample was collected from each container and analyzed for P to determine P removal for that event. Four columns could be tested at a time, so six iterations of the experiment were performed over a 12-week period.

2.2.6 Statistical Analyses

Statistical analyses were performed in R[52]. For the P sorption/retention experiments, one-way ANOVAs were used to determine whether the three DWTR sources differed in their P sorption capacity and P retention values. To assess how the DWTR sources differed, the glht function in the multcomp package [53] was used to perform post-hoc pairwise comparisons with the Tukey HSD test. For the large column experiment, two-way ANCOVAs were used to assess the interactive effects of DWTR source and layering strategy on hydraulic conductivity and P removal. Linear models were fit to the data that regarded DWTR source and layering strategy as fixed categorical variables and simulated storm number as a fixed continuous variable. When linear models violated the assumptions of error normality and homogeneity, the gls function in the nlme package [54] was used to generate unique variance structures for each DWTR source by layering strategy combination using varIdent. To assess how the DWTR source and layering strategy affected hydraulic conductivity and P removal, post-hoc pairwise comparisons were performed using the Tukey HSD test.

2.3 Results and Discussion

2.3.1 Material Characterization

DWTRs analyzed in this study differed substantially in their physical and chemical properties. As indicated by the effective grain size and uniformity coefficient values (Table 1), UNH was the coarsest material and CWD was the finest material, though similar to PORT. The coarsest material (UNH) had the highest K_{sat} value, while the finer materials (CWD and PORT) had lower K_{sat} values (Table 1). These results indicate that material texture and particle size exert strong control over hydraulic conductivity. CWD and PORT exhibited K_{sat} values 41% and 34% less than that of washed sand (89.3 ± 7.6 cm h^{-1}), respectively. However, the K_{sat} of UNH was slightly higher than that of washed sand, suggesting that additions of UNH to bioretention media would have little impact on water flow. Despite their similar textures, CWD exhibited more than 7 times the specific surface area of PORT (Table 1). This discrepancy between texture and specific surface area was due in part to the fact that PORT was nearly twice as dense as CWD (Table 1). CWD may also have contained more colloidal particles and micropores, which contribute greatly to a material's surface area.

Table 1. Summary of physical properties for each drinking water treatment residual source

DWTR	Effective grain size (d_{10})	Uniformity coefficient (d_{60} / d_{10})	Specific surface area (m^2 g^{-1})	Bulk density (g cm^{-3})^a	Porosity (%)^b	K_{sat} (cm h^{-1})^c
CWD	75.4	5.76	12.25	0.55 ± 0.01	0.62 ± 0.02	53.1 ± 8.6
PORT	82.7	5.54	1.69	0.93 ± 0.02	0.51 ± 0.02	59.0 ± 10.0
UNH	211.6	3.77	3.21	0.79 ± 0.02	0.46 ± 0.01	98.5 ± 15.1

^{a}Bulk density, ^{b}porosity, and $^c K_{sat}$ values are means ± 1 SD (n = 3).

Al-oxides were the dominant form of metal oxides found in these DWTRs, accounting for 15-28% of their overall mass (Table 2). PORT and UNH contained similar amounts of Al-oxides, which were nearly twice that of CWD (Table 2). PORT and UNH also contained greater amounts of amorphous Al and Fe oxides and lower P saturation ratios, meaning that a smaller percentage of their amorphous metal-oxides were already occupied by P. Amorphous metal-oxide content has been shown to correlate with P sorption capacity [24,43], as it better represents the metal-oxides that exist at mineral surfaces where sorption occurs.

Table 2. Summary of chemical properties for each drinking water treatment residual source.

DWTR	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Oxalate-extractable (mmol kg^{-1})[a] Al_{ox}	Fe_{ox}	P_{ox}	P saturation ratio (%)[b]
CWD	15.05	1.99	0.87	0.51	2417.2 ± 89.2	54.9 ± 3.6	46.0 ± 2.5	3.66
PORT	25.5	2.28	0.31	0.19	2618.1 ± 183.4	129.5 ± 7.2	14.1 ± 1.1	1.04
UNH	28.4	1.78	0.25	0.09	2710.6 ± 257.4	199.7 ± 16.6	17.9 ± 2.6	1.22

[a]Oxalate-extractable Al, Fe and P values are means ± 1 SD (*n*=3). [b]P saturation ratio was calculated as $[(P_{ox}) / 0.5\times(Al_{ox} + Fe_{ox})]$.

Although the DWTRs analyzed in this study exhibited large physicochemical variation, the observed values are comparable to those of DWTRs from other studies. For example, the few studies that have measured the specific surface areas of DWTRs with the BET N_2 gas adsorption method reported values ranging from 3.0 to 36.0 m^2 g^{-1}[46,55]. Total Al-oxide contents range from 2.9 to 16.9 percent and amorphous Al-oxide contents range from 516 to 6,133 mmol kg^{-1} in past studies [16,24,35,38,55]. K_{sat} values of DWTR-amended bioretention media range from 52.2 to 95.7 cm hr^{-1} in the literature [16,25], but the K_{sat} of pure DWTRs has rarely been assessed. The physicochemical differences between DWTRs observed in this and other studies likely arise from differences in the composition of source water, the type and dosage of coagulants used during water treatment, and the DWTR management strategies used [39,56].

2.3.2 Phosphorus Retention

Substantial variation in P retention was observed among the DWTRs and across the three experiments. In all of the experiments, the P sorption capacity (isotherm experiment) or retention values (column experiments) of the DWTR sources showed significant differences ($p < 0.001$), with CWD exhibiting much higher values than both PORT and UNH (Tukey's post hoc contrasts; $p < 0.001$). In the batch isotherm experiment, CWD, PORT, and UNH exhibited P sorption capacity (Q_{max}) values of 11,675 ± 440, 1,347 ± 645, and 1,479 ± 35 mg P kg^{-1}, respectively (Figure 2). These values were similar to the P retention values derived from the Low P/High Flow experiment, where CWD, PORT, and UNH retained 9,576 ± 50, 1,463 ± 13, and 1,284 ± 49 mg P kg^{-1}, respectively (Figure 3a). P retention values derived from the High P/Low Flow experiment, however, were substantially greater, with CWD, PORT, and UNH retaining 40,026 ± 1,069, 10,019 ± 3,702 and 8,668 ± 662 mg P kg^{-1}, respectively (Figure 3b). Additionally, DWTRs in both flow-through column experiments exhibited large, but variable, increases in P retention after columns were dried, regaining 13 to 78 percent of their initial P retention capacities (Appendix B; Appendix C). Furthermore, DWTRs only desorbed 3-8% of the total P they retained in the column experiments, suggesting that the P sorbed by DWTRs is largely stable (Appendix B; Appendix C).

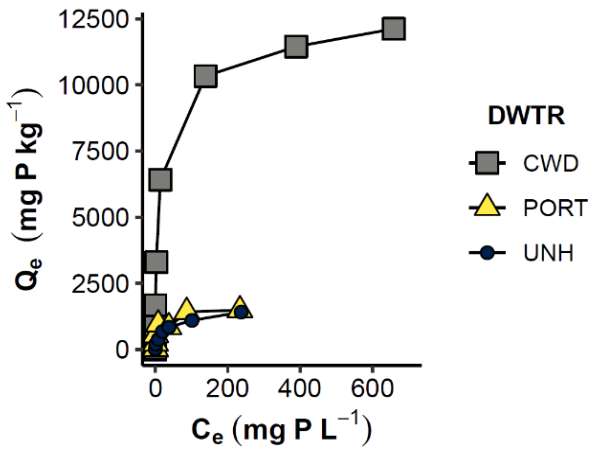

Figure 2. Phosphorus (P) sorption results from batch isotherm experiments. The points on the graph represent the mean (n=3) quantity of P retained at equilibrium (Qe) and the corresponding mean equilibrium concentrations (Ce) across a range of influent concentration (0, 1, 10, 25, 50, 75, 150, and 300 mg P L^{-1}). The values are expressed on an oven-dry mass of drinking water treatment residual (DWTR) basis. DWTRs form Champlain Water District (CWD), Portsmouth Regional Water System (PORT), and the University of New Hampshire Water Treatment Plant (UNH) were analyzed.

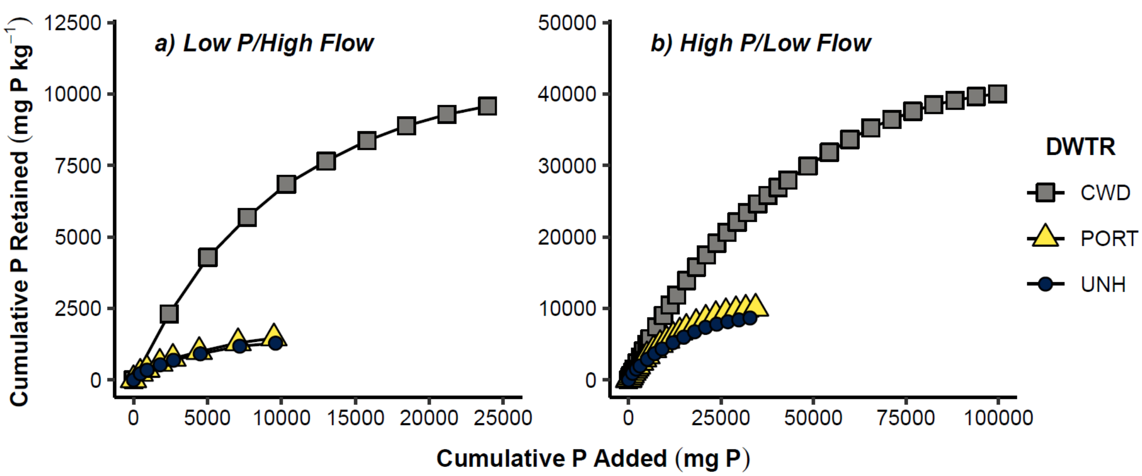

Figure 3. Phosphorus (P) retention results from a) Low P/High Flow column experiment (influent concentration = 1 mg P L-1, contact time = 3 minutes) and b) High P/Low Flow column experiment (influent concentration = 300 mg P L-1, contact time = 5-9 hours). The points on the graph represent the mean cumulative P retained (*n*=3) by drinking water treatment residuals (DWTR) from Champlain Water District, Portsmouth Regional Water System (PORT), and the University of New Hampshire Water Treatment Plant (UNH) were analyzed. Note: the x and y-axes differ between graphs a and b.

Differences in P sorption capacity or retention between the DWTRs were more associated with physical properties than chemical properties. For the three materials tested, the ranking of total and amorphous metal oxide contents did not correspond with the ranking of P sorption capacity or retention values. CWD exhibited more than four times the P removal of PORT and UNH across all experiments, despite its lower Al-oxide content and higher P saturation ratio (Table 2). Of the physical properties measured, specific surface area was the best indicator of P sorption capacity, as CWD exhibited by far the highest surface area and sorption capacity. These results suggest that surface area is the dominant factor governing P sorption in DWTRs when chemical properties (i.e., amorphous metal-oxide content) are similar. This finding has been reported in other studies [55,57] and aligns with the understanding of sorption as a surface process.

Results from this study clearly illustrate a tradeoff between hydraulic conductivity and P removal for DWTRs. CWD was the finest material and it had the lowest K_{sat} and highest P sorption capacity. UNH was the coarsest material and it had the highest K_{sat} and the lowest P sorption capacity. However, hydraulic conductivity was driven mostly by texture and particle size, whereas P sorption was driven mostly by surface area. Consequently, fine materials with low hydraulic conductivity may have lower than expected sorption capacities if their surface area is low (e.g., PORT) and coarse materials with high hydraulic conductivity may have higher than expected sorption capacity (e.g., UNH) if they have a large surface area due to micropores and colloidal particles. The effectiveness of DWTRs as bioretention amendments therefore depends critically upon the physicochemical properties of the DWTR source.

2.3.3 Variation in P sorption capacity among DWTRs and Experimental Methods

The large differences in P removal values observed between the DWTRs in this study have major implications for bioretention media design recommendations. Previous studies have added P-sorbing materials to bioretention media at 3-30% by volume [11,24,25,27,30,58], but have not based those values on a quantitative assessment. A recent review of P-sorbing amendments found that the P retention of Al-DWTRs taken to saturation in column studies ranged from 1,400 to 55,300 mg P kg^{-1} amendment [15]. Similarly, the DWTRs in this study varied more than four-fold in their P sorption capacity or retention values across experimental methods (batch isotherms = 1,347 – 11,675 mg P kg^{-1}, Low P/High Flow = 1,284 – 9,576 mg P kg^{-1}, High P/Low Flow = 8,668 – 40,026 mg P kg^{-1}). In light of this variability, generic recommendations that ignore P removal capacity estimates in their designs risk dramatically underusing, or overusing, P-sorbing amendments.

Inter-methodological differences in P removal values may account for some of the variation described above and have implications for bioretention media design recommendations. While most column studies use synthetic stormwater with P concentrations less than 5 mg P L^{-1} [15], some have used very high P concentrations (5-400 mg P L^{-1}) [36,37,49,59]. The use of unrealistically high P concentrations in column experiments could inflate P retention estimates and lead to media designs that perform poorly in the field. Furthermore, total cumulative P retention in the column studies was greater than the Q_e values predicted by the final Langmuir models with C_e set equal to the column influent concentrations (i.e., 1 or 300 mg P L^{-1}) (Appendix D).

In this study, the High P/Low Flow experiment yielded 4-7 times greater P retention values than the Low P/High Flow experiment. The P retention values from the High P/Low Flow experiment represent the theoretical P retention capacity of the DWTRs under conditions ideal for P removal, where high P concentration with prolonged media contact drives increased adsorption, P diffusion into micropores, and precipitation processes[49,55]. The High P/Low Flow experiment therefore captures P retention mechanisms beyond those that typically occur in bioretention systems and the high P retention values obtained from this experiment are unlikely to be observed in field applications. Conversely, values from the Low P/High Flow experiment represents the P sorption capacity that can realistically be expected in field bioretention contexts, where P concentrations and contact times are relatively low and rapid ligand exchange reactions are likely the dominant mechanisms of P removal[28,58]. The large discrepancy in P removal between these experiments highlights the importance of basing media designs on experiments that accurately reflect field conditions. If P-sorbing amendments like DWTRs are suggested for use in stormwater design manuals or other regulations, media design recommendations should vary by the method used to quantify P removal capacity for a particular amendment.

The batch isotherm experiment yielded P sorption capacity values nearly identical to the cumulative P retention observed in the Low P/High Flow experiment. Batch isotherms have been criticized as unrealistic due to their mechanical shaking, prolonged contact times, and use of very high P concentrations[32,34]. Flow-through column experiments have been recommended as a more realistic alternative to batch isotherms experiments[32,34] but are often avoided due to the high time and resource requirements of achieving P saturation. Given that the Low P/High Flow experiment is most representative of field bioretention conditions, its similarity to batch isotherm P sorption capacity values suggests that isotherms based on the methods used in this study can produce reasonable estimates of DWTR P sorption capacity in GSI contexts. However, estimates of Q_{max} using the Langmuir model can be influenced by batch experiment parameters[49,60], and similar agreement between batch isotherm experiments and column studies may not be observed for other P-sorbing materials[34]. Consequently, we recommend that application rates for DWTRs and other P-sorbing materials in GSI be informed by either Low P/High Flow column experiments that approximate field conditions or predictive models calibrated by field parameters (e.g., P concentration, pH, water residence time). Future research should test these recommendations on additional materials and consider the potential for competing anions and dissolved organic matter to reduce the P sorption capacity of amendments in field settings.

2.3.4 Sorption Kinetics

The rate of P sorption was rapid for all DWTRs in the batch kinetics (Figure 4) and flow-through kinetics (Figure 5) experiments. After 1 minute of shaking in the batch experiment, CWD, PORT, and UNH removed approximately 90, 67, and 62% of added P, respectively (Figure 4). After 360 minutes of shaking, CWD, PORT, and UNH removed approximately 100, 100, and 94% of added P, respectively (Figure 4). In the flow-through experiment, all DWTRs removed a maximum 97.5% of P inputs (due to detection limits) across all contact times (1, 2 4, 8 and 16 minutes), though the influent concentration was 0.2 mg P L^{-1} instead of the 10 mg P L^{-1} used in the batch experiment. These results indicate that P sorption is rapid enough to be effective in relatively high-flow bioretention contexts, but can be improved with extended contact time. They also indicate that sorption processes are highly effective, even at low P concentrations common in stormwater runoff.

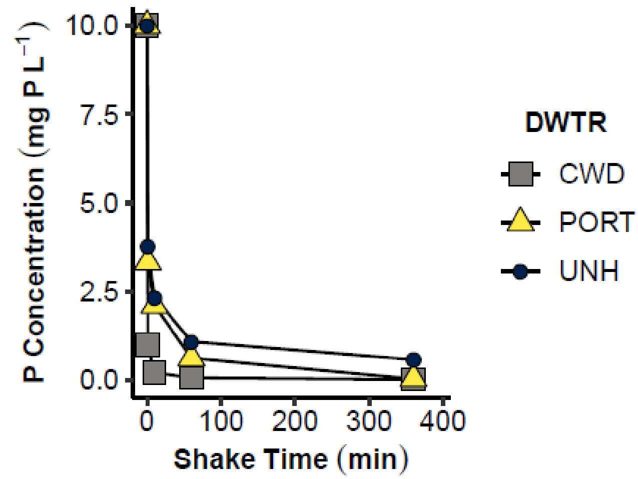

Figure 4. Batch kinetics experiment results. Graph points represent the mean phosphorus (P) concentration (*n*=3) of supernatant across shake times of 1, 10, 60 and 360 minutes. The initial P concentration of the added solution was 10 mg P L-1. Drinking water treatment residuals (DWTR) from Champlain Water District, Portsmouth Regional Water System (PORT), and the University of New Hampshire Water Treatment Plant (UNH) were analyzed.

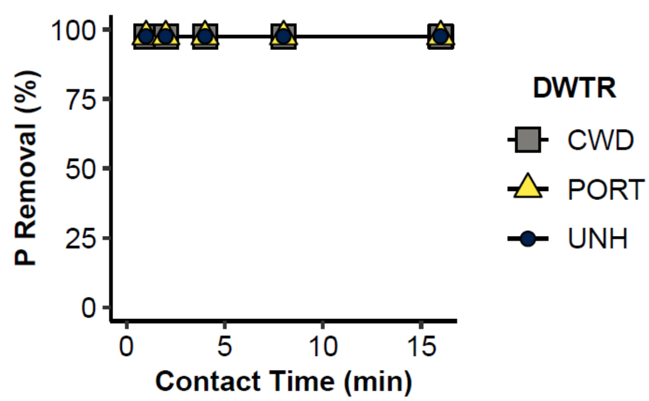

Figure 5. Flow-through kinetics experiment results. Graph points represent the mean phosphorus removal (n=3) after different contact times (1, 2, 4, 8 and 16 minutes). The initial P concentration of the added solution was 0.2 mg P L-1, so a maximum of 97.5% removal was possible due to an analytical detection limit of 0.01 mg P L^{-1}.

2.3.5 Large Column Experiment

The effect that DWTRs had on the hydraulic performance of the media designs depended on both the DWTR source and layering strategy (DWTR source × layering strategy interaction; $p < 0.001$). In the solid layer design, the addition of CWD and PORT significantly reduced hydraulic conductivity relative to the control (Tukey's post hoc contrasts; $p < 0.001$), but the addition of UNH had no relative impact on hydraulic conductivity (Figure 6; Tukey's post hoc contrasts; $p > 0.1$). These results correspond with the K_{sat} values from Table 1, which show that CWD and PORT have lower hydraulic conductivities than sand and UNH has a slightly higher hydraulic conductivity than sand. Solid layers of CWD and PORT would thus restrict flow rates relative to the sand control, but a solid layer UNH would not (Figure 6a and Figure 6b). In the mixed layer design, however, addition of DWTRs had no impact on hydraulic conductivity relative to the control (Tukey's post hoc contrasts; $p > 0.1$), regardless of DWTR source (Figure 6a and Figure 6c). These results demonstrate that fine-textured amendments such as DWTRs can restrict water flow when amendment K_{sat} values are less than that of the surrounding media. However, these hydraulic restrictions can be alleviated by mixing DWTRs with slightly coarser constituents like sand.

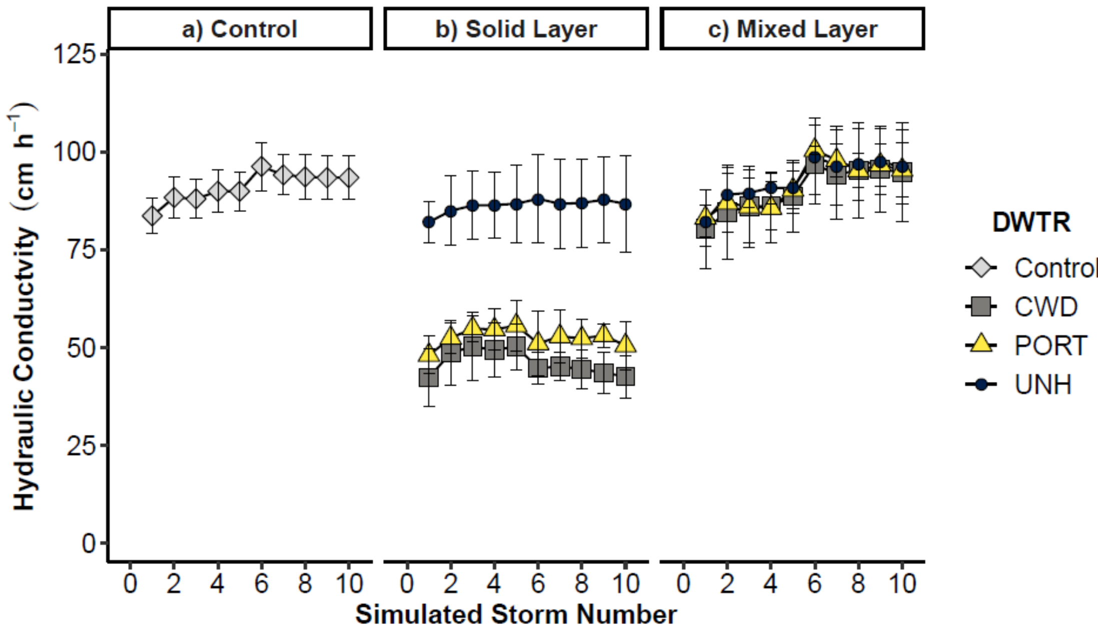

Figure 6. Large column hydraulic conductivity results. The points on the graph represent the mean hydraulic conductivity 1 SD (n=3) for each simulated storm event. Drinking Water treatment residuals (DWTR) from Champlain Water District (CWD), Portsmouth Regional Water System (PORT) and the University of New Hampshire Water Treatment Plant (UNH) were analyzed.

Similar to the hydraulic conductivity results, the effect of DWTRs on P removal performance depended on both the DWTR source and layering strategy (DWTR source × layering strategy interaction; $p < 0.001$). The P removal performance of DWTR-amended media was dramatically better than the control across all DWTR source and layering strategy combinations (Figure 7; Tukey's post hoc contrasts; $p < 0.001$). However, the mixed layer design exhibited better P removal than the solid layer design for UNH and PORT (Figure 7). The P sorption capacity of the added DWTRs (2670, 690, and 535 mg P for CWD, PORT, and UNH, respectively, based on results from the Low P/High Flow experiment) far surpassed that of the experimental P load (30 mg P). Consequently, the failure of UNH, and to a lesser extent PORT, to remove all of the P inputs is likely due to hydraulic bypassing of the DWTRs in the solid layer design. The higher K_{sat} of UNH relative to sand (Table 1) may have produced an unstable wetting front in the DWTR layer, which allowed preferential flow paths to develop through the layer, in a process called "finger flow" [61,62]. Conversely, the lower K_{sat} of PORT relative to sand may have stifled water flow through the media and promoted preferential flow paths around the column edges or through particularly porous flow paths. The decreasing removal efficiency of UNH and PORT shown in Figure 6b supports the notion of preferential flow paths, which may have become saturated with P over the course of the experiment. Evidence of preferential flow was not found, however, in the mixed layer designs. These results suggest that the uniform hydraulic conditions promoted by the mixed layer design allowed water to come into better contact with DWTRs, resulting in near-complete P removal. The mixed layer design therefore achieved better hydraulic and P removal results than the solid layer design.

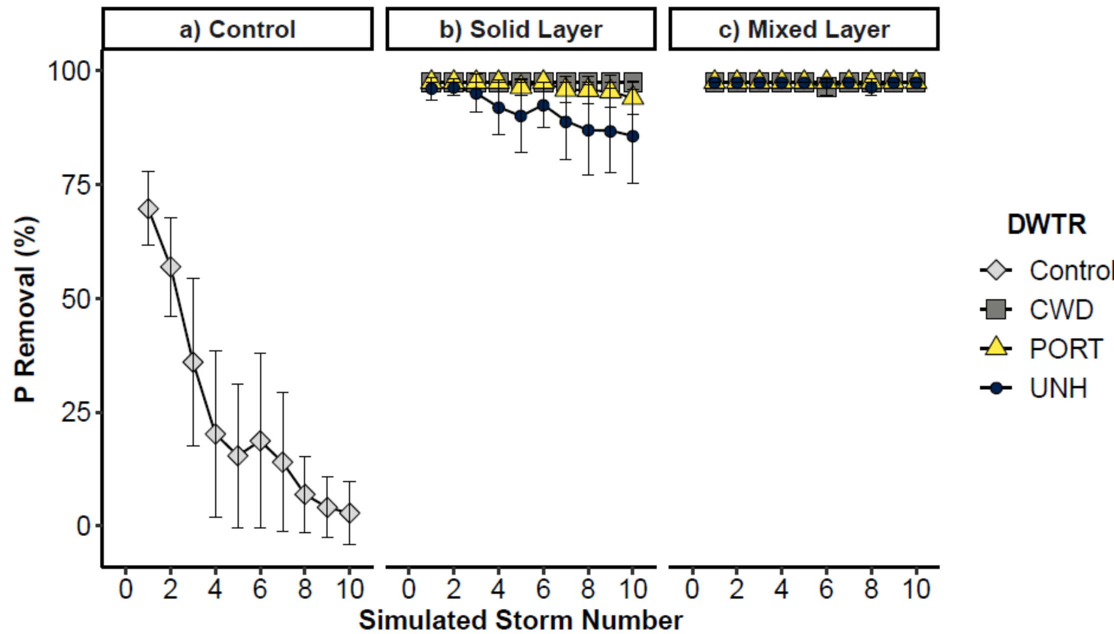

Figure 7. Large column phosphorus (P) removal results. The points on the graph represent the mean P removal (%)   1 SD (n=3) for each simulated storm event. Drinking Water treatment residuals (DWTR) from Champlain Water District (CWD), Portsmouth Regional Water System (PORT) and the University of New Hampshire Water Treatment Plant (UNH) were analyzed.

Despite these promising large column results, various environmental factors could alter how the mixed and solid layer designs perform in the field. For example, prolonged antecedent dry periods can increase the hydraulic conductivity of soils and engineered media[63,64]. Plants may also facilitate preferential flow along root networks, allowing water to bypass portions of the media[65–68]. The hydraulic and P removal impacts of these and other field dynamics should be directly addressed in future research to field-validate our results. However, natural phenomena that increase pore sizes and connectivity would likely produce greater hydraulic bypassing in solid layer designs, where flow through areas adjacent to preferential flow paths is more restricted.

Based on P retention values from the Low P/High Flow experiment and the design assumptions stated above (see *Experimental Setup and Design*), 5% DWTR by total media volume above the pea stone layer would provide approximately 89, 23 and 18 years of P removal for CWD, PORT and UNH, respectively. These longevity estimates should be interpreted with some caution. They do not account for the additional P sorption that can occur following prolonged dry periods in the field (Appendix B; Appendix C). However, P removal efficiencies decrease rapidly as P-sorbing materials saturate (Figure 3), which limits their effectiveness over time, and hydraulic bypassing is possible (especially for solid layer designs). Competing anions in stormwater may further reduce P sorption capacities in the field[69] and some fraction of P-sorbing materials could migrate out of the media during storm events and repeated wetting and drying cycles [24]. While 5% DWTR by total media volume may be a sufficient quantity for high-performing materials like CWD, larger proportions may be required for DWTR amendments with lower P sorption capacities, or in cases where P-rich compost is included in the bioretention media.

2.4 Conclusion

This is the first study to clearly document the possible tradeoff between hydraulic conductivity and P removal that can emerge when using fine-textured P-sorbing materials in stormwater bioretention systems. Our batch isotherm and flow-through column experiments demonstrated that materials with high P removal capacity tend to have relatively fine-grains and low hydraulic conductivity, while those with lower P removal capacity tend to have relatively coarse grains and greater hydraulic conductivity. Results from our large column experiment show that solid layers of DWTRs can decrease hydraulic conductivity and promote preferential flow paths that allow hydraulic bypassing of DWTRs and incomplete P removal. These findings validate the concern that P-sorbing materials can restrict flow and cause clogging when applied to bioretention media[15,16,25,29] and show that P removal performance is linked to hydraulic performance in bioretention systems.

Furthermore, our results have practical implications that can inform media design specifications. Our Low P/High Flow column experiments, which most closely resemble field conditions, indicate that 5% DWTR by total media volume above the pea stone layer is likely a sufficient quantity for long-term (e.g., >10 years) P removal in urban bioretention systems, provided that other DWTR sources have physicochemical properties similar to the DWTRs used in this study. However, field data are required to confirm long-term performance. Finally, the mixed layer design in our large column experiment exhibited better hydraulic and P removal performance than the solid layer design. We therefore suggest mixing fine-textured P-sorbing materials with slightly coarser materials, such as washed sand, to mitigate potential tradeoffs between hydraulic conductivity and P removal in bioretention media designs.

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CHAPTER 3: PHOSPHORUS REMOVAL, METALS LEACHING, AND HYDRAULICS IN STORMWATER BIORETENTION SYSTEMS AMENDED WITH DRINKING WATER TREATMENT RESIDUALS

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Keywords: *bioretention, drinking water treatment residuals, phosphorus removal, green stormwater infrastructure, hydraulic conductivity, heavy metals, field study*

Abstract

Bioretention systems are increasingly used to manage stormwater volumes and pollutant loads, yet they exhibit variable capacity to remove phosphorus (P) from runoff. Drinking water treatment residuals (DWTRs) are a promising media amendment for enhancing P removal in bioretention systems, but substantial removal of dissolved P by DWTRs has not been demonstrated in field experiments. We investigated the capacity of a non-amended control media (Control) and a DWTR-amended treatment media (DWTR) to remove soluble reactive P (SRP), dissolved organic P (DOP), particulate P (PP), and total P (TP) from stormwater in a two-year roadside bioretention experiment. Significant reductions in SRP, PP and TP concentrations and loads were observed in both the Control and DWTR media. However, the removal efficiency (RE) percentages of the DWTR cells were greater than those of the Control cells for all P species. Differences in P RE values between the Control and DWTR cells increased substantially from the first to second monitoring seasons, indicating that DWTRs can effectively increase P sorption capacity of media in the field. Furthermore, P load reductions were driven primarily by reductions in P concentration (versus reductions in stormwater volumes), which played a greater role in P removal for the DWTR cells. Additionally, the DWTR cells exhibited better P

removal than the Control cells during large storm events, which can contribute disproportionately to stormwater P loads in urban environments. We also investigated the potential of the DWTR we used to restrict water flow through bioretention media or leach heavy metals. Neither hydraulic detention times nor peak flow ratios of the bioretention cells were affected by DWTR presence, and there was no evidence of heavy metal leaching from DWTRs. Contrasting these results with past studies highlights the importance of media design in bioretention system performance and suggests DWTRs can effectively capture and retain P if properly incorporated into bioretention media.

3.1. Introduction

Urban landscapes contain substantial amounts of phosphorus (P) originating from lawn fertilizer, pet waste, soil particles, plant litter and atmospheric deposition [1–3]. The transport of urban P sources to surface waterbodies via runoff is a leading cause of eutrophication and harmful algal blooms in freshwater ecosystems [4–6]. Bioretention systems are a form of green stormwater infrastructure increasingly used in developed areas for hydrologic control and water quality improvement [7,8]. While bioretention systems have proven effective for reducing peak flow rates, sediment loads, and concentrations of certain pollutants[9], their capacity to remove P from stormwater is highly variable and some studies have even shown net release of P[10–15].

Because P does not have a gaseous phase relevant in the context of stormwater [16], the long-term P removal performance of bioretention systems depends on their ability to retain the P that passes through them. Bioretention P removal effectiveness varies across the chemical species of P [17]. While conventional bioretention media constituents (e.g.

sand and compost) effectively filter particulate P (PP), they have limited capacity to adsorb dissolved P[17,18]. Consequently, dissolved organic P (DOP) and dissolved inorganic P (measured as soluble reactive P; SRP) can pass through bioretention systems in solution as P sorption complexes saturate [17–19]. Long-term P retention is further complicated by leaching of dissolved P from organic media substrates and mineralization of P from plant litter and trapped organic sediments[20–23]. Novel media designed specifically for P retention is therefore needed for bioretention systems to capture and retain P over decadal timeframes that match anticipated system lifespans.

P retention can be enhanced in bioretention systems by amending the soil media with P-sorbing materials. Many industrial byproducts contain high concentrations of metal (hydr)oxides, which can bind dissolved P through chemical adsorption or precipitation processes[24,25]. Incorporating these materials into bioretention systems may reduce P entering water bodies via stormwater runoff, and subsequently reduce eutrophication, while also representing an opportunity to beneficially reuse waste products that municipalities would otherwise pay to landfill[26]. Drinking water treatment residuals (DWTRs) are a byproduct of the drinking water treatment process and have promise as a bioretention amendment due to their widespread availability, low cost, and high P sorption capacity[27–29]. P sorption by aluminum (Al)-based DWTRs is relatively insensitive to soil redox conditions[30,31], which allows them to retain P despite any fluctuations in oxygen availability. Furthermore, incorporating Al-DWTRs into bioretention media has potential to reduce urban P loads in cold climates where biological P uptake mechanisms are dormant during late fall to early spring months.

Many studies have demonstrated enhanced removal of dissolved P by DWTR-amended bioretention media in laboratory column experiments[19,32–36], but these results have not been adequately validated in the field. In fact, a recent review of P-sorbing amendments in bioretention media by Marvin *et al*.[37] identified only two unique field installations (results presented in Liu and Davis[17], Roseen and Stone[38], and Houle[39]) that have evaluated the P removal performance of DWTRs in urban bioretention. In both of these installations, the DWTR-amended media failed to significantly reduce stormwater SRP concentrations, despite effective SRP removal in corresponding column experiments[32,38]. Liu and Davis[17] also investigated the potential for DWTRs to retain DOP, but found no evidence of DOP removal. Authors speculated that poor dissolved P removal performances were due to equilibrium adsorption dynamics [17], short-circuiting of the media volume [38], and non-uniform distributions of DWTRs in the filter media[38]. Further research is needed to establish whether DWTRs can, in fact, enhance dissolved P removal in field contexts and to determine the factors that regulate P removal by DWTRs in urban bioretention systems.

Another dimension of adding DWTRs to bioretention media is whether this practice produces unintended consequences. The high P sorption capacity of DWTRs has been linked to their large surface areas and fine-grained texture[40,41], which could cause flow restrictions in DWTR-amended media. Ament *et al*.[40] and Yan *et al.*[42] demonstrated that additions of DWTRs to bioretention media can reduce hydraulic conductivity in column experiments. Such hydraulic restrictions in field contexts could produce preferential flow paths that facilitate media short-circuiting or clogging of outlets that lead to excessive ponding or backflow.

Additionally, DWTRs can contain high concentrations of heavy metals[27,43], which could potentially leach from bioretention systems amended with these materials and pose risks to surface and ground water resources. Metals, such as Al, manganese (Mn), and zinc (Zn), can be toxic to humans and aquatic life and have been shown to leach from DWTRs in column studies[36,44,45]. However, urban runoff can contain heavy metals such as arsenic (As) and cadmium (Cd)[46], which some P-sorbing materials can adsorb[47–49]. The potential leaching of heavy metals from industrial byproducts is a common concern that limits broader use of DWTRs in field applications[43], yet few studies have investigated heavy metal dynamics in field bioretention systems amended with DWTRs[38].

Here, we conducted a two-year experiment to investigate the potential for Al-DWTRs to enhance the P removal performance of bioretention systems under field conditions. This study builds upon a previous laboratory study by Ament *et al.*[40], which developed design recommendations for balancing hydraulic control and P removal in DWTR-amended bioretention media. Results from that study indicated that mixing DWTRs with sand and placing them beneath a surface layer of mixed sand and “low-P” compost can provide long-term (> 10 years) P retention, while alleviating hydraulic restrictions imposed by fine-grained DWTRs. However, laboratory studies cannot account for natural variations in temperature, hydraulic loading, stormwater chemistry and other environmental factors, so field experiments are needed to validate laboratory results. The objectives of this study were therefore to:

a) Investigate the capacity of a bioretention media amended with DWTRs to retain SRP, DOP and PP in field contexts

b) Explore the drivers of P removal in bioretention systems with and without DWTRs

c) Determine whether a mixed layer of sand and DWTRs affects bioretention system hydraulics under variable field conditions

d) Assess the potential for DWTRs to leach or adsorb heavy metals (Al, As, Cd, Mn, Zn)

3.2. Materials and Methods

3.2.1 Site Description

This study was conducted at the University of Vermont (UVM) Bioretention Laboratory, which is situated along a road that services a major parking lot on the UVM campus in Burlington, VT. The site contains eight equally sized bioretention cells (3.7 m^2 area, 1 m depth) that receive stormwater inputs from drainage areas of varying sizes[12]. Lined swales covered in gravel (3-5 cm diameter) convey runoff from the asphalt through a curb cut into the bioretention cells. Each bioretention cell is fitted with an impermeable rubber liner, which prevents water exchange with the surrounding soil and allows for mass balance calculations. Each bioretention cell also contains a perforated underdrain raised approximately 12 cm above the bottom of the cell, which creates a small internal water storage zone.

3.2.2 Experimental Design

A field bioretention experiment was conducted to compare differences in water quality improvement between a DWTR-amended treatment medium and a non-amended control medium (henceforth referred to as “DWTR” and “Control”, respectively). In May

2019, four existing bioretention cells were excavated. Two of these cells were retrofitted with the Control medium, while the remaining two cells were retrofitted with the DWTR medium. To account for potential hydrologic variability, the bioretention cells were grouped by the relative size of their drainage areas and randomly assigned the Control or DWTR medium. One group of cells consisted of $43m^2$ and 32 m^2 drainage areas (henceforth referred to as the “Small Drainage Area Control” cell and the “Small Drainage Area DWTR” cell, respectively), while the other group consisted of $59m^2$ and 54 m^2 drainage areas (henceforth referred to as the “Large Drainage Area Control” cell and the “Large Drainage Area DWTR” cell, respectively).

The Control medium contained washed gravel (3-5 cm diameter), washed pea stone (1-2 cm diameter), washed sand (< 2 mm diameter) and compost (Figure 8a). Previous research has shown that conventional bioretention media (e.g., 60% sand, 40% compost) and composts derived from manure feedstocks leach nutrients into bioretention effluent[12,13,22,50,51]. Accordingly, the Control medium in this study contained reduced quantities (10% compost by volume in the top 30.5cm of medium) of a low-P compost (derived from leaf litter feedstocks; 0.19% P by dry mass)[22,52] to limit the internal P content of the medium. The DWTR medium was identical to the Control, except that 10% of the sand layer (located 30.5cm - 71cm below the media surface) volume was replaced with DWTRs (Figure 8b), which Ament *et al*.[40] determined to be enough for long-term (> 10 years) P removal. The DWTRs were passed through a 5mm sieve to remove coarse debris and mixed into the sand with cement mixers. The DWTRs used in this study were obtained from the University of New Hampshire Water Treatment Plant (Durham, NH), which uses polyaluminum chloride as a treatment coagulant and processes its DWTRs via freeze-dry cycling. This material exhibited the lowest P retention capacity of the three DWTR sources evaluated in Ament *et al.*[40] and was selected for this study to provide a conservative estimate of the P removal performance of DWTRs in field bioretention systems. A summary of the physical and chemical properties of this DWTR material is provided in Appendix E.

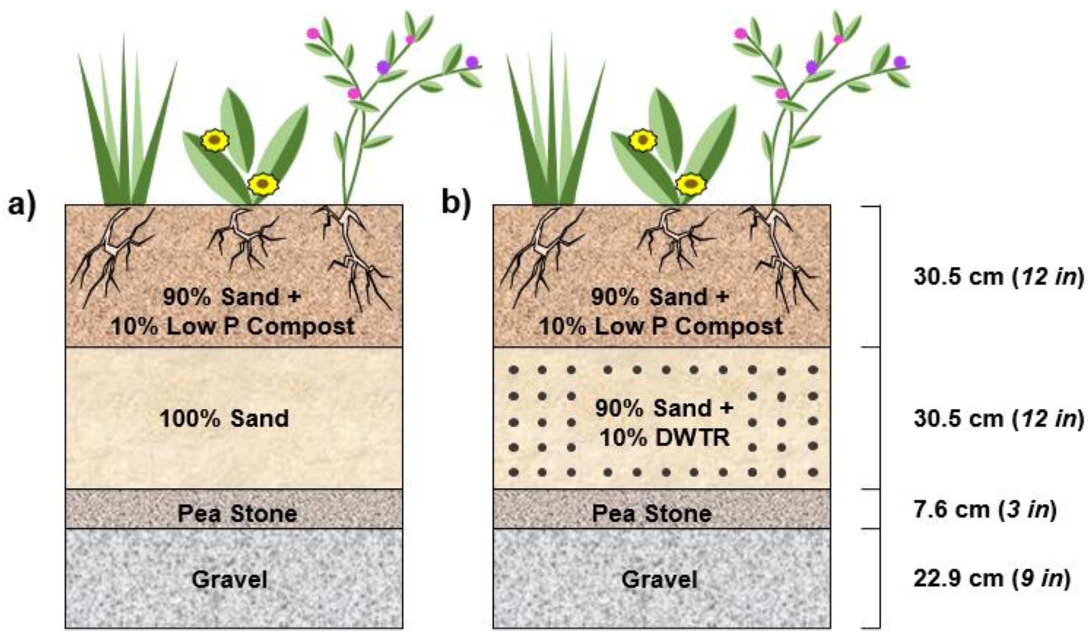

Figure 8. Bioretention media profiles: a) Control medium b) DWTR medium

After retrofit, all four cells were planted with an identical assemblage of species, which consisted of *Asclepias tuberosa* (Butterfly Milkweed, *n*=1 plant per bioretention cell), *Echinacea purpurea* (Echinacea Sp., *n*=2), *Helenium autumnale* (Sneezeweed 'Sombrero', *n*=1), *Iris versicolor* (Harlequin Blueflag, *n*=3), and *Symphyotrichum nova-angliae* (New England Aster, *n*=2). Vegetation was watered every other day for three weeks to ensure plant establishment. The *Helenium autumnale* cultivar did not survive the first season of study and was replaced with *Zizia aurea* (Golden Alexander) in May of 2020.

3.2.3 Stormwater Sampling

Stormwater inflows and outflows from the four bioretention cells were simultaneously monitored with eight autosamplers (Teledyne ISCO 6712, Lincoln, NE). A cedar box equipped with a 90^o v-notch weir was placed at the inlet of each bioretention cell to capture runoff being conveyed from the road (Figure 9, left). Inflow volumes were determined using submerged probe flow modules (ISCO 720) to measure the stage height of water within the weir boxes[53] every minute. Stage height measurements were converted to flow rates using the equation[54]:

$$L/s = 1380\ (\text{stage height m})^{2.5}$$

Outflow volumes were determined similarly. However, instead of using a weir box to measure flow, a sealed sump was used, which drained into a 15 cm diameter PVC pipe equipped with a Thel-Mar weir (Thel-Mar, LLC, Brevard, NC) (Figure 9, right). Submerged probes secured to the bottom of the sumps were used to measure stage heights, which were converted to flow rates using conversion charts provided by Thel-Mar, LLC.

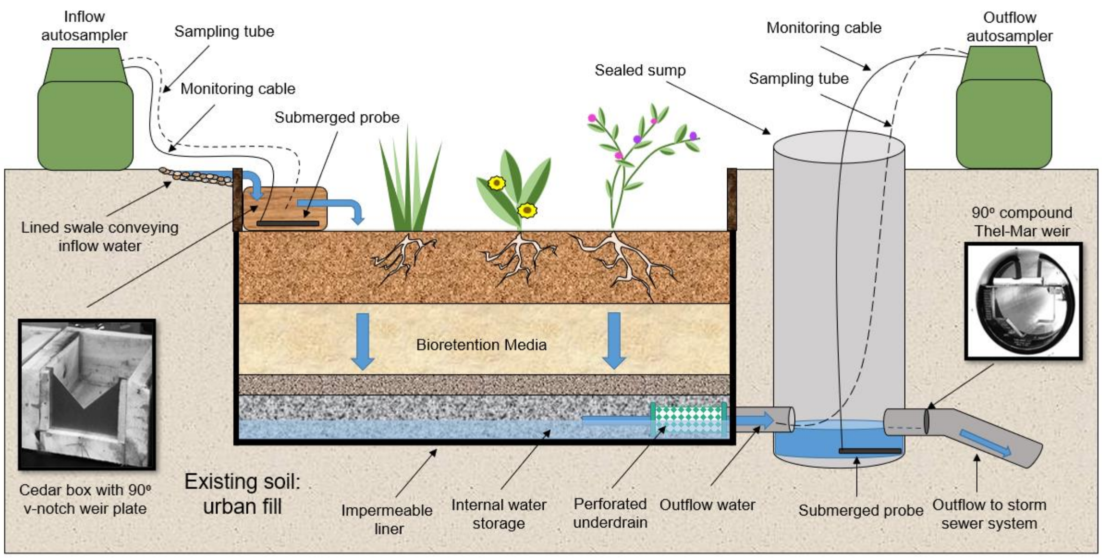

Figure 9. Stormwater inflow and outflow monitoring systems. Weir photos are from Cording *et al*.[53].

Flow-based composite sampling (fifteen 200 ml water samples per bottle) was used to monitor inflow and outflow stormwater quality for the bioretention cells. For a given rainfall event, a maximum of four composited water sampling bottles were obtained from each of the inflow and outflow autosamplers, roughly targeting the rising, peak, and falling limbs of the storm hydrograph. The volumetric sampling intervals (L) needed to capture the entire storm event were calculated from rain forecasts before every storm using unique linear relationships between precipitation depth and runoff volume established for each bioretention cell. The weir boxes were cleaned and the autosamplers were zeroed before every storm. Storms were sampled from September to November in 2019, post-plant establishment, and June to November in 2020. Runoff produced from snowmelt or winter rainfall events was not monitored in this study, thus water quality data only reflects warm weather performances. Every storm forecasted to produce > 5 mm of rainfall was monitored with the autosamplers. However, this research focused on the twenty-one captured storm events that generated accurate inflow and outflow data in all four bioretention cells (Appendix F), which represent the majority of storm events and flow volumes that occurred during the 2019 and 2020 field monitoring periods.

3.2.4 Water Quality Analysis

All water samples were retrieved from the field within 24 hours of the start of each storm event and processed at UVM's Agriculture and Environmental Testing Laboratory. Total P samples were refrigerated for < 1 week before persulfate digestion and dissolved P samples were filtered through a 0.45 μm mesh filter and frozen for holding. Samples were analyzed for total P (TP), total dissolved P (TDP) and SRP following standard methods procedures 4500-PE and 4500-PJ (Appendix G) [55]. PP and DOP were calculated as TP minus TDP and TDP minus SRP, respectively (Appendix G). Method blank corrections were applied to the TP and TDP data to account for potential error introduced by persulfate digestion. A value of half the detection limit was used for any measurements that registered below the detection limits[17,56] (Appendix G). Additionally, small measurement errors can produce negative PP and DOP values when water samples are dominated by SRP (e.g., outflow samples). To eliminate negative concentrations in the data set, we replaced TDP values with SRP values for cases when TDP < SRP. Similarly, we replaced TP values with TDP values for cases when TP < TDP.

Inflow and outflow concentrations of dissolved aluminum (Al), arsenic (As), cadmium (Cd), manganese (Mn) and zinc (Zn) were also analyzed for four storms during the 2019 monitoring season and six storms during the 2020 monitoring season. Specific rainfall events were selected for heavy metal analysis in order to capture a range of storm sizes. The metals analyzed were selected due to their potential prevalence in DWTRs and urban stormwater[43,57–59], as well as their threat to human and aquatic life. After P samples were collected from the sampling bottles of each autosampler, a heavy metal sample was obtained by pouring the remaining water contents of the sampling bottles into a churn splitter and mixing the water to generate one flow-weighted composite sample. These heavy metal samples were filtered through a .45 μm filter, preserved with nitric acid (HNO_3), and analyzed using inductively coupled plasma mass spectrometry (for As) and optimal emission spectrometry (for Al, Cd, Mn and Zn) methods at an external chemistry lab (Endyne, Inc., Williston, VT).

3.2.5 Hydrologic and Water Quality Calculations

Total flow volumes (V) were calculated for each storm by summing the product of the instantaneous flow rate (Q(t)) and the flow measurement time interval (Δt) for the entire runoff period:

$$V = \sum Q(t)\,\Delta t$$

P load masses (M) were calculated for each storm by summing the product of the autosampler bottle P concentrations (C_i) and their corresponding runoff volumes (V_i):

$$M = \sum C_i\,V_i$$

Heavy metal loads were determined by multiplying the concentration of the single flow-weighted composite sample by the total flow volume (V).

When precipitation depths far-exceeded forecasted depths, the programmed volumetric sampling intervals were not broad enough to capture the entire storm event. In the four instances where this occurred, we applied P concentrations from the last sampling bottle to the unsampled portion of the flow volume, which ranged from 1% to 44% of the total runoff volume.

Event mean concentrations (EMC) were calculated for each storm by dividing the total load masses (M) by the total flow volumes (V):

$$EMC = M / V$$

P mass removal efficiency (RE) expressed in percentage were calculated as:

$$RE = ((M_{in} - M_{out})/M_{in}) \times 100$$

Positive values indicate a net retention of P, while negative values indicate a net export of P.

The percentage of P mass load reductions attributable to volume reductions (LR_{vol}) was calculated as:

$$LR_{vol} = [((V_{in} - V_{out}) \times EMC_{out}) / M_{in}] \times 100$$

The percentage of P mass load reductions attributable to concentration reductions (LR_{conc}) was calculated as 100-LR_{vol} .

Hydraulic detention times were calculated for each storm event by the time difference between the center of mass of the inflow and outflow hydrographs[60]. Hydrograph centers of mass were defined as the point at which half of the total stormwater volume had flowed into or out of the bioretention cell. Peak flow ratios (R_{peak}) were also determined for each bioretention cell and storm event and were calculated as the maximum outflow rate divided by the maximum inflow rate[61].

Hydraulic detention time and R_{peak} values were used to assess bioretention system hydraulics.

3.2.6 Statistical Methods

Statistical analyses were performed to assess water quality differences between paired inflow and outflow data for each bioretention cell. Separate storm events were considered replicates for statistical purposes[11,62] and were identified by inter-storm dry periods of at least 12 hours. The paired difference data failed multiple goodness-of-fit tests for normality (i.e. Shapiro-Wilk, Kolmorogov-Smirnov), so a non-parametric Wilcoxon Signed Rank test was used to evaluate differences between inflow and outflow volumes, nutrient loads, and concentrations[11]. A non-parametric Kruskal-Wallis test was used to assess differences in hydraulic detention time and R_{peak} values between the bioretention cells. All statistical analyses were performed in R[63].

3.3 Results

3.3.1 Captured Storms and Flow Volumes

Eight and thirteen distinct storm events were captured in the 2019 and 2020 field monitoring seasons, respectively (Appendix F). During these events, the two Control and two DWTR bioretention cells received combined totals of 99,500 L and 90,500 L of stormwater, respectively (Table 3). Although the experimental groups (Control and DWTR) received similar aggregate inflow volumes, the hydrologic groups (Small Drainage Areas and Large Drainage Areas) did not. Over the course of the experiment, the Small Drainage Area DWTR cell received 20% more inflow than the Small Drainage

Area Control cell and the Large Drainage Area DWTR cell received 35% less inflow than the Large Drainage Area Control cell (Table 3).

Stormwater outflow volumes were significantly less than inflow volumes for all cells monitored in this study ($p < 0.01$). Overall, the Small Drainage Area Control and DWTR cells reduced stormwater flow volumes by 46% and 45%, while the Large Drainage Area Control and DWTR cells reduced volumes by 26% and 52%, respectively.

Table 3. Summary of stormwater inflows and outflows for each bioretention cell. Phosphorus (P) load values represent the cumulative mass (mg) of each P species contained within the bioretention influent and effluent. Event mean concentration (EMC) value represent the average EMC value for all monitored storm events. Stormwater volumes represent the cumulative volume (L) of stormwater that entered and exited each bioretention cell. Removal efficiency values (RE) indicate the percentage of each constituent removed by the bioretention cell.

Bioretention Cell	Constituent		2019			2020			2-Year Totals		
			Inflow	Outflow	RE	Inflow	Outflow	RE	Inflow	Outflow	RE
Small Drainage Area Control (43 m^2 drainage area)	Stormwater	Volume (L)	13152	4310	67	23340	15422	34	36492	19733	46
	SRP	Load (mg)	232.3	8.6	96	130.8	25.8	80	363.2	34.4	91
		EMC (mg/L)	0.050	0.008	85	0.020	0.008	61	0.032	0.008	75
	DOP	Load (mg)	32.7	2.2	93	6.6	8.9	-36	39.3	11.1	72
		EMC (mg/L)	0.007	0.004	36	0.002	0.004	-93	0.004	0.004	-9
	PP	Load (mg)	191.5	0.0	100	134.1	20.5	85	325.5	20.5	94
		EMC (mg/L)	0.054	0.0	100	0.027	0.008	70	0.037	0.005	87
	TP	Load (mg)	456.5	10.8	98	271.5	55.3	80	728.0	66.1	91
		EMC (mg/L)	0.110	0.012	89	0.050	0.020	59	0.073	0.017	77
Small Drainage Area DWTR (32 m^2 drainage area)	Stormwater	Volume (L)	14957	6400	57	28841	17581	39	43798	23981	45
	SRP	Load (mg)	576.8	10.1	98	274.2	19.7	93	851.0	29.7	97
		EMC (mg/L)	0.105	0.006	95	0.030	0.006	80	0.059	0.006	90
	DOP	Load (mg)	111.8	3.1	97	24.6	6.4	74	136.5	9.5	93
		EMC (mg/L)	0.015	0.002	86	0.003	0.002	53	0.008	0.002	77
	PP	Load (mg)	421.2	0.0	100	355.0	12.3	97	776.2	12.3	98
		EMC (mg/L)	0.106	0.0	100	0.056	0.006	90	0.075	0.004	95
	TP	Load (mg)	1109.8	13.2	99	653.7	38.3	94	1763.6	51.5	97
		EMC (mg/L)	0.226	0.008	97	0.089	0.013	85	0.141	0.011	92
Large Drainage Area Control (59 m^2 drainage area)	Stormwater	Volume (L)	23743	17233	27	39340	29193	26	63083	46426	26
	SRP	Load (mg)	444.3	48.2	89	110.7	77.3	30	555.1	125.5	77
		EMC (mg/L)	0.068	0.010	86	0.012	0.010	18	0.034	0.010	71
	DOP	Load (mg)	29.9	5.6	81	31.6	19.2	39	61.4	24.8	60
		EMC (mg/L)	0.002	0.001	40	0.002	0.004	-59	0.002	0.003	-20
	PP	Load (mg)	298.6	38.1	87	357.8	77.1	78	656.4	115.3	82
		EMC (mg/L)	0.055	0.008	86	0.047	0.010	78	0.050	0.009	82
	TP	Load (mg)	772.8	92.0	88	500.1	173.6	65	1272.8	265.5	79
		EMC (mg/L)	0.126	0.019	85	0.062	0.024	61	0.086	0.022	75
Large Drainage Area DWTR (54 m^2 drainage area)	Stormwater	Volume (L)	15267	7410	51	31313	15116	52	46580	22526	52
	SRP	Load (mg)	264.9	14.6	94	153.7	13.9	91	418.5	28.6	93
		EMC (mg/L)	0.080	0.006	92	0.021	0.005	75	0.044	0.006	87
	DOP	Load (mg)	36.7	2.8	92	9.7	7.6	21	46.4	10.4	77
		EMC (mg/L)	0.009	0.002	77	0.002	0.002	-18	0.005	0.002	53
	PP	Load (mg)	222.7	0.0	100	214.1	7.1	97	436.8	7.1	98
		EMC (mg/L)	0.054	0.0	100	0.033	0.004	88	0.041	0.002	94
	TP	Load (mg)	524.3	17.5	97	377.4	28.7	92	901.7	46.1	95
		EMC (mg/L)	0.143	0.008	94	0.056	0.012	79	0.089	0.010	88

3.3.2 Stormwater P Species Composition and Removal

The concentration of TP in inflow samples ranged from 0.012 mg P L^{-1} to 0.52 mg P L^{-1}, with a median value of 0.072 mg P L^{-1} (Figure 10). Influent TP was composed of 43% SRP, 5% DOP, and 52% PP on average. Median concentrations of SRP, DOP and PP were 0.022 mg P L^{-1}, 0.002 mg P L^{-1}, and 0.036 mg P L^{-1}, respectively. These values came from a university campus roadway and are much lower than the SRP, PP and TP values reported in other urban bioretention studies[11,13,53]. Additionally, average influent SRP concentrations in 2020 were 76% lower than those of 2019, which could be due to having sampled more summer storms (which are less influenced by leaf litter P loads than fall storms) in 2020 than 2019, or decreased road traffic due to COVID-19 restrictions. Stormwater DOP concentrations are rarely analyzed, but the influent DOP concentrations measured in this study were roughly an order of magnitude lower than those reported by Liu and Davis[17] and Song *et al.*[64].

All of the bioretention cells in this study functioned to significantly decrease both P concentrations and loads for SRP, PP and TP ($p < 0.01$; Figures 3 and 4). Significant reductions in DOP concentrations and loads were not observed in any cell ($p > 0.1$), but DOP concentrations were very low in both inflows and outflows (91% of samples registered below 0.01 mg P L^{-1}).

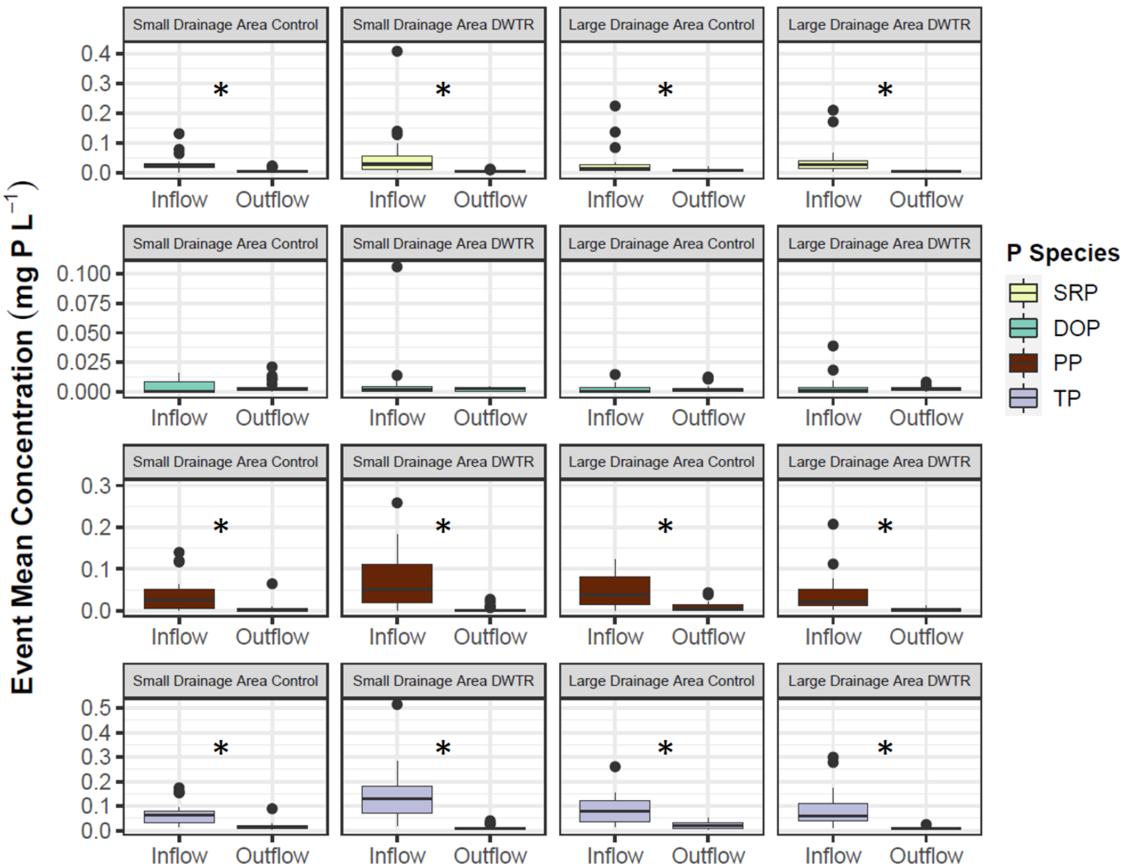

Figure 10. Phosphorus (P) inflow and outflow event mean concentrations (EMC) for each bioretention cell and P species. Box and whisker plots represent the distribution of EMC inflow and outflow data for soluble reactive P (SRP), dissolve organic P (DOP), particulate P (PP), and total P (TP) during all storm events captured during the 2019 and 2020 monitoring seasons (n = 21). Asterisks (*) between bars denote significant differences between inflow and outflow EMCs ($\alpha = 0.05$). Note that the y-axes differ between P species.

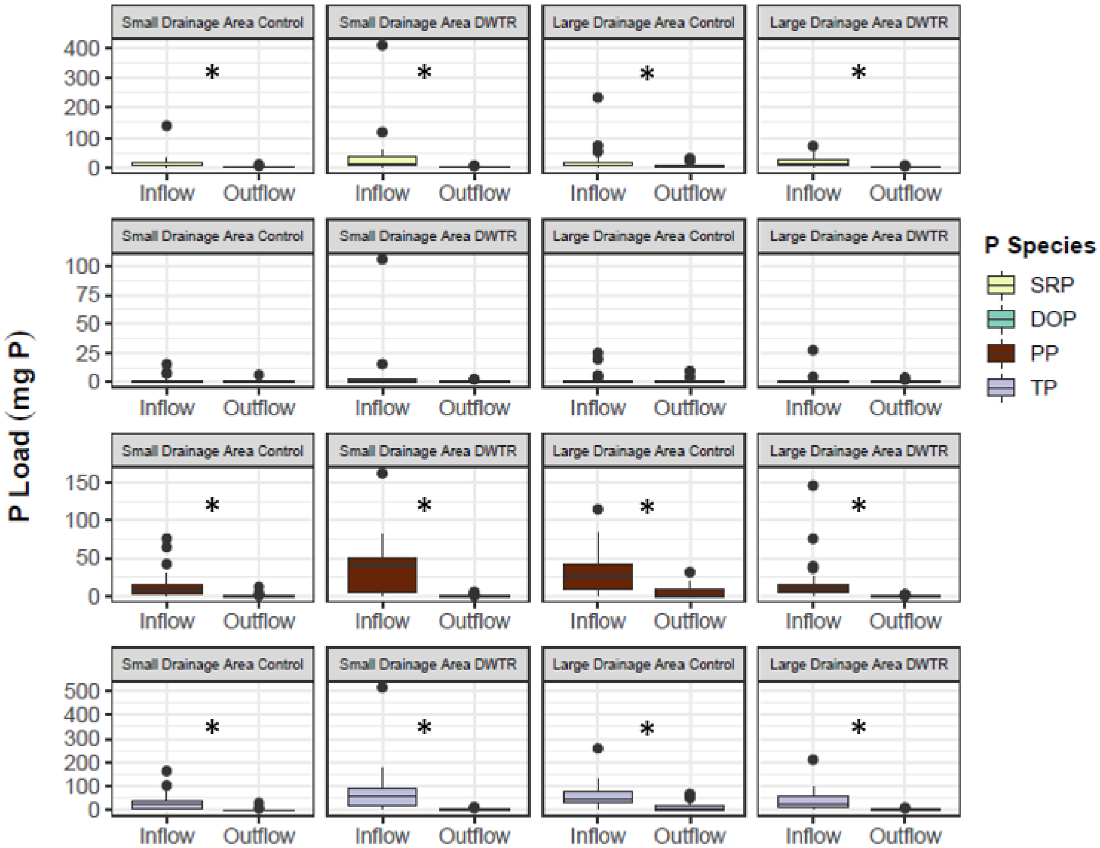

Figure 11. Phosphorus (P) inflow and outflow mass loads for each bioretention cell and P species. Box and whisker plots represent the distribution of inflow and outflow P load data for soluble reactive P (SRP), dissolved organic P (DOP), particulate P (PP), and total P (TP) for all storm events captured during the 2019 and 2020 monitoring seasons (n = 21). Asterisks (*) between bars denote significant differences between inflow and outflow P loads (α = 0.05). Note that the y-axes differ between P species.

While all bioretention cells demonstrated significant capacity to remove P, the DWTR cells exhibited better P removal performance than the Control Cells for all P species (Figure 12;). The 2-year total mass RE values for TP were 91% and 79% for the Small and Large Drainage Area Control cells, but 97% and 95% for the Small and Large Drainage Area DWTR cells, respectively (Table 3). This difference in TP removal between the Control and DWTR cells was driven primarily by a major drop in SRP mass RE for the Control cells relative to the DWTR cells in the second (2020) monitoring season (Figure 12). During this period, the Control cells retained 30%-80% of SRP loads, while the DWTR cells retained 91%-93% of SRP loads (Table 3). Differences in P removal performance between the Control and DWTR cells also grew for PP during the 2020 monitoring season, with the DWTR cells exhibiting higher PP removal (Table 3). Furthermore, analytical assumptions regarding P detection limits accounted for 12% of outflow SRP loads for the Control cells, but 43% of outflow SRP loads for the DWTR cells, indicating that reported SRP removal performance by DWTRs is inherently conservative in this study. P removal performances are also inherently conservative in this study for both the Control and DWTR treatments because storm events that did not generate outflow (i.e., exhibited complete retention of stormwater volumes and P loads) were not analyzed.

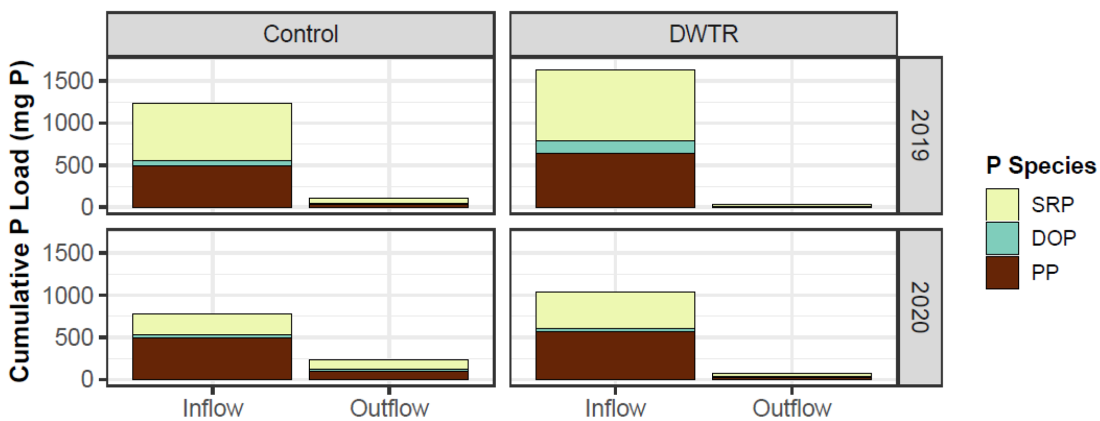

Figure 12. Phosphorus (P) inflow and outflow loads for the Control media (2 bioretention cells) and drinking water treatment residual (DWTR) media (2 bioretention cells) cells. Bars represent the cumulative sum of loads captured in each of the media treatments during the 2019 (September-November; n=8 storms) and 2020 (June-November; n=13 storms) monitoring seasons for soluble reactive P (SRP), dissolved organic P (DOP), and particulate P (PP). The summed height of the stacked bars represents the total P (TP) load for each media treatment and monitoring season.

3.3.3 Role of Volume Reductions, Concentration Reductions, and Storm Size in P Removal

The observed P load reductions were due to both stormwater volume reductions (LR_{vol}) and P concentration reductions (LR_{conc}). However, LR_{conc} values far surpassed LR_{vol} values for all bioretention cells and P species (Appendix H), indicating that P concentration reductions were the primary driver of P load reductions. Although the proportion of total load reductions attributable to concentration reductions were high for both media treatments (63% - 99%), the DWTR cells exhibited higher LR_{conc} values than the Control cells for all P species (Appendix H).

Storm size also influenced P removal dynamics in this study. Both the Control and DWTR cells exhibited uniformly high RE values for all P species during small storm events (rainfall < 25 mm; n=17) (Appendix I). However, RE values dropped substantially for the Control cells during the few large storms (rainfall > 2.5 mm; n=4) but remained relatively consistent across storm sizes for the DWTR cells (Appendix I).

3.3.4 Hydraulic Detention Times and Peak Flow Ratios

The addition of DWTRs to bioretention media did not affect system hydraulics in this study. Hydraulic detention times for the bioretention cells were not statistically different from one another ($p > 0.1$), exhibiting median values of 60-65 minutes for the Control cells and 49-67 minutes for the DWTR cells. Peak flow ratios (R_{peak}) for the bioretention cells were also not statistically different from one another ($p > 0.1$), exhibiting median values of 0.15-0.19 for the Control cells and 0.17-0.19 for the DWTR cells. These results indicate that DWTRs did not have a significant impact on hydraulic detention time and peak flow ratios (Figure 13 and Figure 14, respectively).

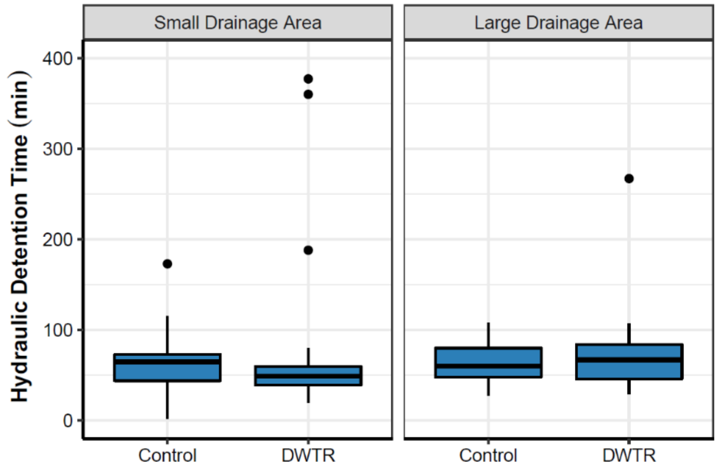

Figure 13. Hydraulic detention times for each bioretention cell. Box and whisker plots represent the distribution of detention times observed during all storms captured in the 2019 and 2020 monitoring seasons (n = 21).

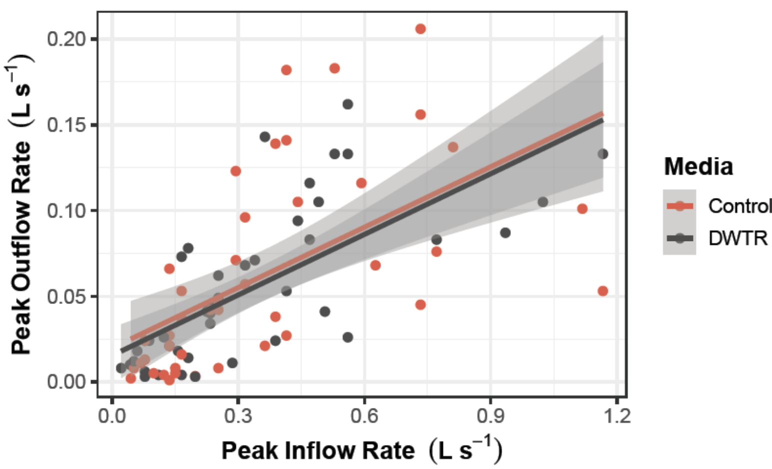

Figure 14. Peak inflow and peak outflow rates from the Control media (2 bioretention cells) and drinking water treatment residual (DWTR) media (2 bioretention cells) for all storm events captured in the 2019 and 2020 monitoring seasons (n = 21). Shaded lines represent the least squares regression line and 95% confidence interval for each media treatment.

3.3.5 Stormwater Heavy Metal Composition and Removal

No evidence of heavy metal leaching from, or adsorption by, DWTRs was found in this study. The concentration of heavy metals in bioretention inflows and outflows were very low for all cells, with nearly all samples registering below the detection limit for As, Cd, and Mn (Figure 15). Outflow concentrations of Al were slightly higher than inflow concentrations for both media treatments, but outflow Al concentrations were not statistically different than inflow concentrations for any bioretention cell (Figure 15a; $p > 0.1$). Inflow concentrations of Zn registered above the detection limit more than other metals, but outflow Zn concentrations were below the detection limit for all bioretention cells, regardless of DWTR presence.

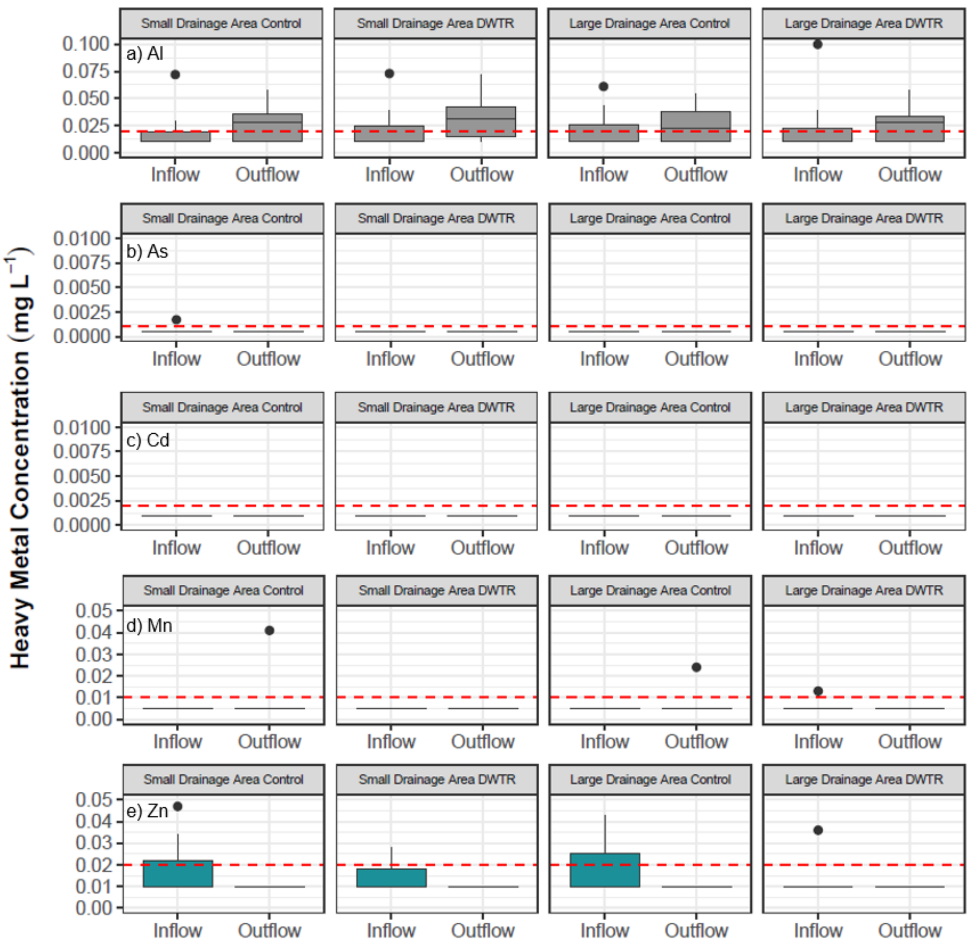

Figure 15. Heavy metal inflow and outflow event mean concentrations (EMC) for each bioretention cell. Box and whisker plots represent the distribution of inflow and outflow EMC data for aluminum (Al), arsenic (As), cadmium (Cd), manganese (Mn), and zinc (Zn) during four storms captured in 2019 and six storms captured in 2020. Red dashed lines indicate the detection limit for each heavy metal specie. Note that the y-axes differ between metal species.

3.4 Discussion

3.4.1 P Removal Performance

Our findings reveal that amending bioretention media with DWTRs can enhance P removal from stormwater in field settings. Overall, the DWTR cells received larger P inputs and released smaller P outputs than the Control cells for all P species (Figure 12, Table 3). The difference in P RE values between the Control and DWTR cells was greater for dissolved P than particulate P (Table 3), which suggests that the enhanced P sorption capacity of the DWTR media was responsible for the improved P removal performance. While SRP RE values dropped by 16% and 59% between the 2019 and 2020 sampling seasons for the Small and Large Drainage Area Control cells, respectively, SRP RE values dropped by only 5% and 3% over the same period for the Small and Large Drainage Area DWTR cells, respectively, despite receiving greater SRP inputs (Table 3). These results suggest that the P sorption complexes of the Control cells become saturated much faster than those of the DWTR cells. Additionally, these results likely underestimate the true P removal potential of DWTRs because they reflect P dynamics in newly retrofitted bioretention systems that experienced relatively small stormwater inflow volumes and low P concentrations. The gap in SRP removal performance between the treatment media will likely expand with time as the Control cells accumulate P and approach P saturation more rapidly than the DWTR cells. The drop in SRP RE observed between 2019 and 2020 for the Large Drainage Area Control cell provides early evidence of this dynamic, as its P sorption complex likely became more saturated than that of the Small Drainage Area Control cell due to greater P inputs (Table 3). Longer-term field studies are needed to clarify the longevity of P removal for both the Control and DWTR media designs.

The DWTR cells also exhibited higher RE values than the Control cells for DOP and PP. Over the course of the study, the Control cells removed 60%-72% of DOP loads while the DWTR cells removed 77%-93% of DOP loads (Table 3). DOP retention by DWTRs has been demonstrated in previous laboratory column studies[65], but not in field bioretention studies[17]. The greater DOP RE values of the DWTR cells compared to the

Control cells is likely due to increased P binding site availability in the DWTR medium. However, inflow and outflow concentrations of DOP were very low in this study and statistically significant DOP removal was not found in any of the bioretention cells (Table 3; Figure 10). Consequently, it is not possible to conclude that DWTRs either increase or decrease field DOP concentrations. DWTRs were not expected to increase PP removal in this study because sand has been shown to effectively filter suspended solids and particulate matter in past studies[11,12,17,38,56]. Nevertheless, the DWTR cells exhibited higher PP RE than the Control cells, particularly in 2020, where PP RE values ranged from 78%-85% for the Control cells but were 97% for the DWTR cells (Table 3). DWTRs may enhance PP retention by improving particulate filtration or by curbing colloidal migration within sand layers. Future research should investigate whether DWTRs affect physical filtration mechanisms or the movement of fine particles within bioretention media.

Although the DWTR cells showed better P retention than the Control cells, P removal by the Control cells was also high compared to other field bioretention studies[10–13]. Over the course of the study, the Control cells exhibited combined RE values of 84% and 82% for TP and SRP (Table 3), respectively, and never released effluent that exceeded 0.025 mg SRP L^{-1} (Figure 10). Effective dissolved P removal performance by the Control cells is noteworthy because many field studies have reported substantial net exports of dissolved P from conventional bioretention media[10,13,66,67], including two studies previously conducted in the exact hydrologic locations of the Control cells[11,12]. Other than slight variation in plant composition, the only difference between the media of previous studies conducted at the UVM Bioretention Laboratory and the Control media in this study was the compost: the Control media in this study used a smaller amount of compost (10% versus 40% compost by volume in the top 30.5cm of media) and used compost derived from low P feedstocks (leaf litter), rather than higher P feedstocks (food and animal waste)[11,12]. The high P retention performance of the Control cells in this study shows that compost selection criteria (quantity and type) for bioretention media designs can have significant impacts on bioretention nutrient removal performance, especially in settings where P-sorbing amendments are not used or available.

3.4.2 Drivers of P Removal

Because P load reductions can be achieved through volume reductions (e.g. infiltration and water absorption by media) and concentration reductions (e.g. chemical adsorption, precipitation, and biological uptake) in bioretention systems[18], both mechanisms must be accounted for to isolate the impact of media designs on system performance[17]. Unlike other bioretention studies that have achieved P load reductions through stormwater volume reductions[17,67], P concentration reductions were the primary driver of P removal for all P species in this study. While both the Control and DWTR cells reduced the concentration of P species in stormwater, effluent P concentrations were lower (Table 3) and LR_{conc} values were higher (Appendix H) in the DWTR cells for all P species. These results indicate that concentration reductions played a larger role in dissolved P removal for the DWTR cells, consistent with results from prior column studies[40].

Because bioretention cells were lined in this study, stormwater volume reductions were only due to absorption by the soil media and evapotranspiration (ET). ET likely had negligible direct effects on stormwater volumes during storm events, but may have indirectly affected outflow volumes by reducing the volumetric water content, and thus increasing the water holding capacity, of the soil media between storms[50,68]. Although total stormwater volume reductions were fairly high in this study (26%-52%) (Table 3), LR_{vol} values were relatively low (1%-37%) (Appendix H). Concentration reductions were the dominant P removal mechanism in this study because effluent P concentrations were much lower than influent P concentrations for all bioretention cells and P species (Table 3).

Storm size also exerted control on the P removal performance of the bioretention cells. While the Control and DWTR cells showed similar P removal performances for small storms, Control cells exhibited lower RE values than DWTR cells during large storms, across all P species (Appendix I). Large storms can contribute disproportionately to annual urban P loads[11], as four large storms (17% of the captured storms) transported 59% of total inflow SRP loads in this study. P removal also tends to be worse during large storms than small storms, with some systems exhibiting substantial dissolved export during large events[11]. The capacity of DWTR-amended media to effectively remove dissolved and particulate P via P concentration reductions during large storm events is particularly relevant for stormwater practitioners seeking to reduce the areal footprint of bioretention systems, while maintaining P removal performance, in urban areas where compacted soils and liners prevent infiltration.

Although DWTR cells showed greater P removal than the Control cells in this field experiment, P retention was not as effective as predicted by prior column studies. In Ament *et al.*[40], the mixed layer UNH medium removed 100% of detectable SRP inputs and was predicted to offer 10+ years of effective P removal based on conservative assumptions of hydraulic loading ratios and SRP concentrations (*see Ament et al.*[40] *Methods and Materials*). While the DWTR cells reduced SRP loads by 93%-97% over the first two years of monitoring, detectable concentrations of SRP were observed in the effluent of DWTR cells during storms in both 2019 and 2020. Various environmental factors could have contributed to this discrepancy between laboratory and field results. First, the lab experiment did not include plants, which can facilitate preferential flow along their root networks[69,70]. These flow paths may allow a portion of the stormwater to bypass the media, preventing P sorption processes. Second, prolonged antecedent dry periods in the field can significantly increase the hydraulic conductivity of bioretention media[71,72] and reduce media contact times. Antecedent dry periods and wetting and drying cycles were not simulated in the Ament *et al.*[40] column study, so it is unclear whether these factors affect P removal by DWTRs. Finally, field SRP inflow concentrations exhibited a median value of 0.022 mg P L^{-1} compared to the 0.2 mg P L^{-1} used in the column study. Because sorption processes are driven by equilibrium dynamics[24,40], very low influent P concentrations could suppress P sorption and even favor P desorption in the field. Any combination of these factors could explain the small discrepancy between field and lab P removal results and should be taken into consideration when designing bioretention systems for water quality improvements.

3.4.3 Hydraulic Effects of DWTRs

Our hydraulic detention time and peak flow ratio results indicate that DWTRs did not affect bioretention system hydraulics in this study (Figures 6 and 7). DWTRs have been shown to reduce the hydraulic conductivity of bioretention media in laboratory column studies[40,42]. However, DWTRs were not expected to impact flow in this study because the mixed DWTR layering strategy implemented here was shown to mitigate potential hydraulic restrictions imposed by DWTRs in Ament *et al.*[40]. Additionally, the UNH DWTRs exhibited higher hydraulic conductivity and coarser texture than sand in Ament *et al*.[40], so incorporating them into a sand-based medium would place minimal restrictions on water flow. Nevertheless, hydraulic concerns can limit the use of P-sorbing amendments in bioretention systems[17,30,35,37,42] and have not been directly evaluated for DWTRs in field studies. These results show that some DWTR sources can be used in bioretention systems to enhance P removal without undermining hydraulic functions. More studies are needed to determine whether mixing DWTRs with sand can alleviate hydraulic constraints imposed by very fine-grained, low hydraulic conductivity DWTRs in the field.

The center of mass method for quantifying hydraulic detention time can produce inaccurate results when applied to irregular, multimodal storm hydrographs[60]. Irregular hydrographs are common in small, flashy watersheds that exhibit short time of concentration values. Consequently, the hydraulic detention time values reported in this study likely do not reflect the true detention time of water in the bioretention systems. However, they do reflect the relative differences in hydraulic detention time between the bioretention cells monitored in this study and demonstrate that the DWTR used did not produce prolonged detention times that can lead to excessive ponding and flooding.

3.4.4 Impact of DWTRs on Heavy Metal Dynamics

The presence of DWTRs did not affect heavy metal adsorption or leaching dynamics in this bioretention study. Influent concentrations of all heavy metals were very low, which prevented assessments of DWTR adsorption for As and Cd. Some evidence of Zn removal was observed in this study, but these results were not unique to the DWTR cells and may be due to Zn adsorption by organic media constituents[73,74]. Effluent concentrations of As, Cd and Zn were below the detection limit for all water samples, indicating that the DWTRs and other bioretention media components used in this study did not leach these metals during the monitored storms. Effluent concentrations of Mn were also below the detection limit for all water samples, which is noteworthy because Mn leaching from DWTRs has been identified as an environmental concern[43,45,75]. All bioretention cells exhibited higher (but not statistically different) concentrations of Al in effluent than influent (Figure 15a). The observation of minor Al leaching from all four cells suggests that the sand, compost and gravel constituents of the media contribute a small amount of Al to effluent loads. However, effluent concentrations of Al in this study averaged 0.028 mg Al L^{-1}, which is far below the normalized chronic toxicity values for most aquatic species[76], and therefore likely would not threaten aquatic organisms in receiving waters. Overall, these heavy metal results suggest that relatively small quantities of the DWTRs used here (5% of the total media volume above the pea stone layer) can be incorporated into bioretention media to enhance P removal without posing toxicity risks to downstream waterbodies. Further research is needed to determine variability in metals leaching risk among DWTRs from different sources.

3.4.5 Bioretention Media Design Implications

Prior research assessing P removal by DWTRs in field bioretention systems did not report significant reductions in SRP concentrations[17,39], despite effective SRP removal in laboratory column studies[32,38]. The observation of significant SRP concentration reductions by DWTR media in both this study and the preceding column study[40] could provide insight into the media design factors that govern P removal by DWTRs in bioretention systems. In this study, media mixtures were created for two distinct bioretention layers: a 30.5cm deep upper layer composed of 10% low P compost and 90% washed sand (by volume), and a 30.5cm deep lower layer composed of 10% DWTR and 90% washed sand (by volume) (Figure 8). However, Liu and Davis[17] rotated 5% DWTR by mass into the top 40cm of a 50-80cm deep existing sandy loam medium and Houle[39] mixed 10% DWTR by volume into a media blend composed of 50% sand, 10% compost (derive from food and yard waste), and 20% woodchips.

The differences in media composition, layering strategy, and DWTR incorporation techniques among these studies could account for their different SRP removal performances. For example, the bioretention media of previous studies likely contained larger internal P pools than the media used in the current study due to their relative ages[17] or organic matter content[39]. Leaching from these P pools may have prematurely saturated the DWTRs and prevented them from removing SRP from stormwater. Moreover, DWTRs were placed below organic media constituents (e.g. compost, organic sediments, plant litter) in this study, allowing them to bind dissolved P leaching downward from surface layers. Previous field studies either incorporated DWTRs into the top of existing media[17] or mixed them uniformly with organic components within a media blend[39], which may have spatially prevented DWTRs from sorbing all internal sources of P. Finally, previous studies incorporated DWTRs into bioretention media using backhoes[38], and noted that such mixing strategies could have produced clumpy, heterogenous media that facilitated preferential flow paths. Sieving the DWTRs and blending the media layers with motorized cement mixers in this study may have produced a more homogenous media and uniform hydraulic environment that allowed stormwater to come into full contact with the soil media, enabling effective P removal.

Although DWTRs have large P sorption capacities, comparisons between field studies suggest that they must be strategically incorporated into bioretention media to achieve their maximum P removal potential. Compost selection criteria, media layering strategies, and DWTR incorporation techniques appear to exert strong control over the P removal efficacy of DWTRs in bioretention systems.

3.5 Conclusion

This is the first field study to clearly demonstrate that additions of DWTRs to bioretention media can increase dissolved P removal from urban stormwater. Rather than P loads being managed through stormwater volume reductions alone, this research observed P load reductions that were driven largely by P concentration reductions, which played a greater role in P removal for the DWTR cells. The relative P removal effectiveness of DWTR cells compared to the Control cells was most pronounced during large storm events, which contributed disproportionally to annual P loads. Growing differences in SRP removal between the Control and DWTR cells suggests that the demonstrated capacity of DWTRs to enhance P removal is conservative in this study, and that performance gaps between the DWTR media and Control media are likely to expand over time. Notably, the Control media demonstrated excellent P retention capacity relative to other field bioretention studies[10–15], highlighting the importance of compost selection criteria in bioretention media designs. Beyond P removal, the addition of DWTRs to bioretention media had no impact on system hydraulics. Additionally, no significant evidence of heavy metal leaching from, or adsorption by, DWTRs was observed in this study. Media design decisions (e.g. compost amount and type, media layering strategy, DWTR incorporation techniques and placement) appear to strongly influence the hydraulic effects and P removal performance of DWTRs. More laboratory and field studies that examine different DWTR materials and design strategies are needed to reduce uncertainty regarding performance variability and to determine best practices for material testing prior to field use.

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CHAPTER 4: IMPACT OF STORMWATER BIORETENTION SYSTEM DESIGNS ON CATCHMENT-SCALE URBAN PHOSPHORUS LOADS

Abstract

Bioretention systems are increasingly popular tools for managing urban runoff volumes and pollutant loads. However, our understanding of how bioretention system designs influence hydrologic and water quality outcomes at the catchment scale is limited. In this study, we built an urban watershed model using the U.S. EPA Storm Water Management Model (SWMM) to assess the impact of bioretention P removal performance and infiltration capacity (lined versus unlined systems) on watershed phosphorus (P) loads, stormwater volumes, and peak flow rates. We also created scenarios to vary the percentage of impervious surface area managed with bioretention to examine the impact of bioretention design factors at different scales of implementation. Bioretention media P removal performance had significant effects on watershed P loads. The impact of P removal performance increased as the spatial coverage of bioretention increased but was mediated by whether the systems were lined or unlined. Media P removal performance had the largest impact on P loads in lined systems, suggesting that lined systems should be prioritized to receive high performance media, particularly if treating runoff from P hotspots. Lined systems exhibited little ability to reduce runoff volumes and peak flow rates, suggesting that some level of deep infiltration is needed to manage urban hydrology with bioretention. Watershed management strategies that infiltrate stormwater into the soil where appropriate and make strategic use of P-sorbing media have great potential to simultaneously achieve hydrologic and water quality goals with bioretention systems.

4.1 Introduction

Urban population growth and development pressures drive the expansion of impervious surfaces across the globe[1,2]. Impervious surfaces prevent rainfall from infiltrating into the soil and, in turn, dramatically increase stormwater runoff volumes[3]. Large runoff volumes can cause extensive erosion, sewer overflows, flooding, and property damage[4]. Runoff can also threaten water quality by transporting urban contaminants to receiving waters. Many cities are located on large freshwater bodies[5,6] and because urban centers are major sources of pollution, water quality within and downstream of cities and suburbs is often impaired[7,8]. Phosphorus (P) loading from developed areas is particularly problematic because excessive P inputs can cause eutrophication and harmful algal blooms in freshwater ecosystems[9,10], degrading the water resources on which cities rely.

Green stormwater infrastructure (GSI) is increasingly used to mitigate the adverse hydrologic and water quality impacts of urbanization [11,12]. Common examples of GSI include green roofs, pervious pavement, urban trees, bioswales, constructed wetlands, and bioretention systems. In addition to their ability to manage stormwater, GSI can provide pollinator habitat[13,14], reduce urban heat island effects[15], and increase property values[16]. In light of these multiple benefits, many jurisdictions have made considerable investments in GSI[17]. Additional future investments in GSI are also likely, as cities struggle to comply with Total Maximum Daily Load (TMDL) requirements for pollutant reductions and to manage increased stormwater volumes associated with development and climate change[2].

Media-based GSI, such as bioretention, are popular stormwater management tools because they can address hydrologic and water quality goals simultaneously[18,19]. From a hydrologic perspective, bioretention systems are like other GSI in their capacity to reduce peak flow rates by capturing, temporarily storing, and slowly releasing runoff volumes into storm sewers, surface waters, or groundwater, depending on bioretention design. The incorporation of vegetation and soil media also allows bioretention to filter and treat stormwater with physical, chemical, and biological processes absent in most other forms of GSI[18,20,21]. Consequently, bioretention systems have repeatedly demonstrated effective removal of sediments, oils, grease, and heavy metals in field studies[22–25]. However, their capacity to remove P is highly variable and systems often function as net sources of P[23,26–29]. Poor P retention in prior field studies has been attributed to the high P content[28–30] and low P sorption capacity of conventional media blends[20,31], which have historically consisted of a sandy soil mixed with organic amendments (e.g. woodchips, topsoil, compost)[19,32]. Sand has little innate ability to sorb P[33,34] and composts have great potential to leach P, depending on the feedstocks from which they are made[35]. Widespread implementation of bioretention systems filled with conventional media that leaches P could therefore exacerbate P loading in developed watersheds.

Because bioretention systems are increasingly used for meeting water quality goals, researchers have explored various media design strategies to enhance their P retention performance[20,36,37]. For example, substantial improvements in P removal have been achieved in laboratory and field studies by incorporating P-sorbing materials, such as drinking water treatment residuals, into bioretention media as amendments[29,33,38–40]. These materials contain high concentrations of metal hydroxides[41,42] that can bind P though chemical adsorption and precipitation processes[43]. Other research has found that P leaching can be minimized by modifying the type, amount, and location of organic amendments within bioretention media[35,37,44]. For example, Ament *et al*.[33] recommend not exceeding 10% compost by volume in the upper layers of bioretention media using compost derived from "low P" feedstocks, such as leaf litter and yard waste. Such media design strategies have shown considerable potential to improve the P removal performance of bioretention media in lab and field studies of individual sites[33,38,44]. However, few studies have assessed the impact of bioretention P removal performances on catchment-scale P loads, so it is unclear how bioretention media designed for P retention could affect P loading when implemented broadly within a watershed.

Another factor that affects both the hydrologic and water quality performance of bioretention systems is their ability to infiltrate water into surrounding soils and groundwater. Bioretention systems that are designed for deep seepage into the soil (henceforth referred to as infiltration) have been shown to substantially decrease stormwater volumes and flow rates[45]. They have also been shown to significantly reduce mass P loads in stormwater runoff even when the media is net leaching P[46], because P that infiltrates into surrounding soils is often considered lost from the system in field monitoring studies. However, infiltration is not always feasible in highly developed landscapes due to soil compaction, contamination, and perched water tables[17,19]. Excessive water infiltration in concentrated areas can also cause groundwater to mound, which poses structural risks[11,47]. Accordingly, urban bioretention systems are often fitted with impermeable liners that prevent deep infiltration or underdrains that connect to the broader storm sewer network[28]. Understanding how stormwater infiltration interacts with bioretention P removal performances to influence watershed hydrology and water quality outcomes is critical from a management perspective, yet few studies have investigated these dynamics at broad scales.

Here, we developed an urban watershed model using the U.S. EPA Storm Water Management Model (SWMM)[48] to assess the relative impacts of bioretention P removal performance (low and high P removal) and infiltration capacity (lined and unlined systems) on P loads, runoff volumes, and peak flow rates at the catchment scale. We also varied the percentage of impervious surface area managed with bioretention systems (henceforth referred to as spatial coverage) in this analysis to determine how bioretention design factors influence watershed outcomes under varying levels of GSI implementation. The objectives of this study were to:

1) Assess the potential for bioretention systems to meet both hydrology and water quality goals at the watershed scale.
2) Determine the relative importance of bioretention P removal performance and infiltration capacity in achieving those goals.
3) Examine potential tradeoffs between decisions to invest in high performance media (either through initial investment or media retrofits) or construct more bioretention systems with low performance media.

4.2 Methods and Materials

4.2.1 Study Area

The Potash Brook watershed in South Burlington, Vermont (VT), USA is a suburban watershed that encompasses an area of approximately 18 km^2 and drains directly into Lake Champlain at Shelburne Bay (Figure 16). This is one of the most developed watersheds in VT, as 53% of the land area is developed (commercial, industrial, residential)[49] and 22% of the land area is considered impervious[49]. The watershed receives roughly 1000 mm of annual rainfall[50] and has a separate storm sewer system[49]. Runoff volumes are managed with numerous structural best management practices (BMPs), which consist mostly of wet ponds, dry ponds, and infiltration basins[49]. These existing BMPs manage runoff from drainage areas that account for nearly 35% of the total watershed area and 60% of the total impervious surface area (Figure 16).

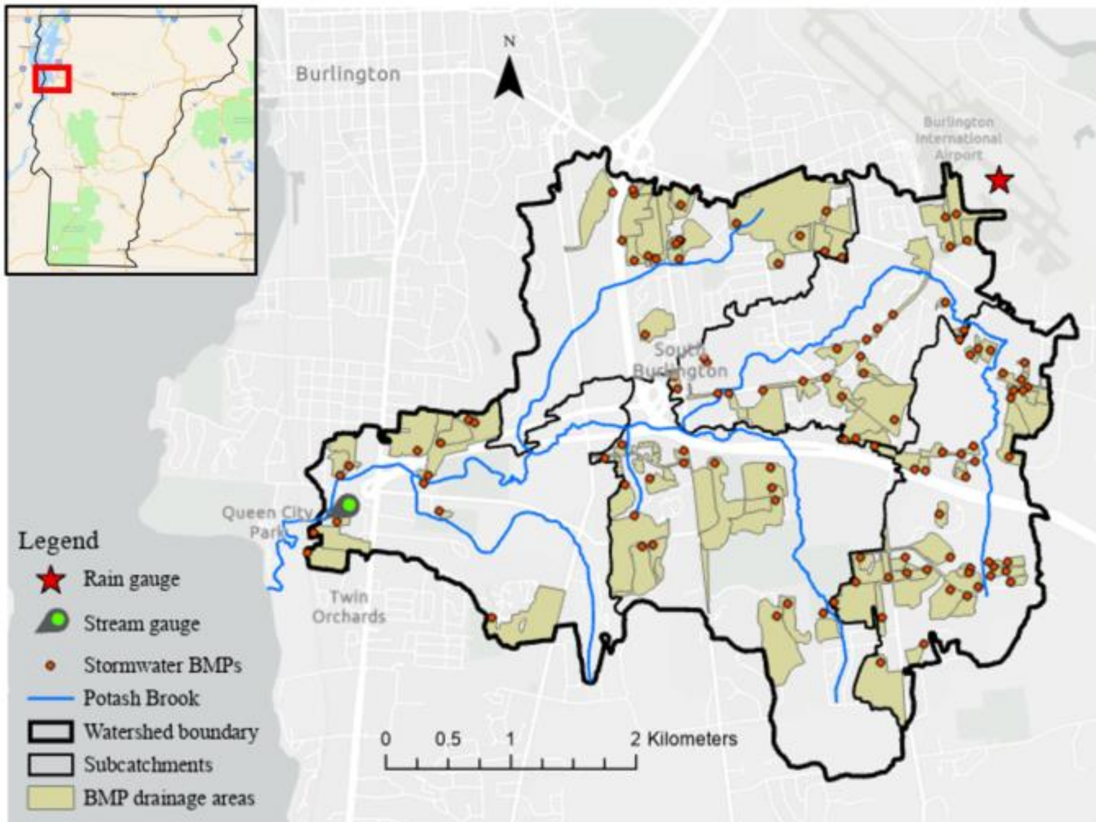

Figure 16. Diagram of Potash Brook watershed in South Burlington, VT. Each BMP drainage area (tan polygon) drains to a stormwater BMP (orange dot), which routes flow from the BMP to the nearest junction on the stream network (blue lines).

Despite the prevalence of stormwater BMPs in the watershed, Potash Brook is on the list of impaired waters due to its failure to comply with the biological water quality standards of Section 303(d) of the Federal Clean Water Act[51]. Consequently, it has established a flow-based Total Maximum Daily Load (TMDL) and the city of South Burlington has created a Flow Restoration Plan to achieve the TMDL's hydrologic goals[49]. Furthermore, Lake Champlain has a P TMDL due to its history with eutrophication and harmful algal blooms[52]. Potash Brook therefore represents a model watershed for exploring how bioretention system designs (e.g. P removal performance and infiltration capacity) affect hydrologic and water quality outcomes in impaired urban and suburban catchments seeking to reduce P loads.

4.2.2 Stormwater Model

4.2.2.1 *Water Quantity*

A watershed model was created in SWMM to simulate hourly runoff volumes in Potash Brook from 2014 to 2019. The watershed was separated into five sub-catchments based on the stream network and the natural topography of the landscape. These sub-catchments were delineated in ArcGIS using digital elevation models (DEM) obtained from the VT Center for Geographic Information[53]. Flow through the existing storm sewer network was not simulated in this model due to data constraints. However, flow through 116 existing BMPs, which treat runoff from 60% of the watershed's impervious surfaces, was modeled. Data on the BMP locations, storage dimensions, outlet structures, and corresponding drainage areas were provided by the Vermont Department of Environmental Conservation and the South Burlington Public Works Department. Stormwater that exited each BMP was modeled to discharge into Potash Brook at the nearest stream junction point within the sub-catchment (stream segments within each of the five sub-catchments were divided into five smaller segments connected by junctions)[49]. Although storm sewer data were not used in this model, an effort was made to account for the impact of storm sewer pipes on the timing of flows. Consequently, runoff volumes from each of the five sub-catchments that were not routed to BMPs were instead routed to a conduit, which drained into Potash Brook at the nearest steam junction point. The length of these conduits was determined through calibration.

Additional model inputs included soil properties, slope, imperviousness, evapotranspiration, and hourly precipitation. Soil data were downloaded from the Soil Survey Geographic Database (SSURGO)[54] and an area-weighted average hydraulic conductivity value was calculated for each sub-catchment (sub-catchment will henceforth refer to drainage areas with and without BMPs) to inform the Green-Ampt method of infiltration[55]. Slope data were obtained from the DEMs and a single area-weighted slope value was calculated for each sub-catchment. Impervious land cover data were downloaded from VT Geographic Information Center[56], and percent imperviousness was calculated for each sub-catchment. Average monthly potential evapotranspiration values for Burlington, VT were obtained from the Northeast Regional Climate Center[57] and converted into an hourly time series. Hourly precipitation data from 2014 to 2019 were downloaded from the Burlington International Airport rain gauge[58] (Figure 16; red star), which is managed by the National Weather Service. Characteristic width values were determined by dividing sub-catchment areas by the average maximum overland flow distance[59] (estimated as half the square root of the sub-catchment area). Hourly runoff volumes were continuously simulated in the watershed using the kinematic-wave flow routing method[60]. Groundwater hydrology was not simulated in this model.

4.2.2.2 *Water Quality*

The event mean concentration (EMC) method was used to simulate P loading in SWMM. This method applies a constant pollutant EMC value to stormwater that runs off a given land use or cover class within a watershed. High-resolution (0.5 m^2) land cover data were downloaded from the VT Center for Geographic Information[56]. Land use washoff concentrations for soluble reactive P (SRP) and total P (TP) were obtained from the National Stormwater Quality Database (NSQD), regionalized to the northeastern U.S.[61] (Appendix J). Land use types were converted to land cover classes using a crosswalk table (Appendix K), which allowed the land cover database and the water quality database to be integrated. SRP and TP removal values of 0% and 50%, respectively, were used to simulate P removal in the existing wet ponds, dry ponds, and infiltration basins[59,62].

4.2.3 Model Calibration and Validation

Long-term stream flow and water quality data were provided by Vermont EPSCoR's Basin Resilience to Extreme Events (BREE) project[63], which manages the Potash Brook stream gauge (Figure 16; green and black pin). The dataset obtained from the BREE project includes 15-minute stream flow values during non-winter months from 2014 to present, so the model simulations only reflect non-winter dynamics. It also includes 15-minute SRP and TP concentrations during the same time period, obtained from optical water quality sensors[50]. The 15-minute flow and water quality data were aggregated to an hourly time series that matched the rainfall dataset. Years 2014-2016 were used for model calibration and years 2017-2019 were used for model validation. Flow data beyond October 30th, 2019 were omitted due to potential damage to the stream gauge following an extreme rainfall event.

4.2.3.1 *Water Quantity*

The proportion of stream flow attributable to base flow versus surface runoff was determined using a standardized Lyne-Hollick recursive digital filter[64,65]. This base flow separation technique was selected due to its simplicity and demonstrated ability to provide satisfactory base flow estimates in small to mid-sized catchments[66,67]. The Nash-Sutcliffe Efficiency (NSE; described in Appendix L) metric was used to assess the predictive power of the water quantity model. Although NSE was prioritized for model calibration and validation[68], the percent bias (PBIAS; description in Appendix L) and root-mean-square-error-observations standard deviation ratio (RSR; description in Appendix L) metrics were also calculated. A multiparameter autocalibration technique was executed in R[69] using the swmmr package[70] to determine the calibration parameter values that maximize NSE and minimize the difference between the cumulative observed and simulated flow volumes measured at the stream gauge location (Figure 16) for years 2014 to 2016. The hydrologic parameters used for calibration in this model included Manning's *n* values, depressional storage, soil hydraulic conductivity, and percent imperviousness. These parameters were selected for calibration due to their high sensitivity[68,71,72] and the lack of detailed parameterization data[73]. The numerical boundaries within which each parameter was calibrated are summarized in Appendix M. The calibrated parameter values were then validated for years 2017 to 2019. Base flow and dry periods (identified as the periods when base flow × 1.1 > stream flow) were removed during the calibration process to isolate surface runoff volumes[74]. According to Moriasi *et al.*[73] , a stream flow model can be deemed satisfactory if NSE ≥ 0.5, if PBIAS is ± 25%, and if RSR is ≤ 0.7.

4.2.3.2 *Water Quality*

Observed P loads were calculated by multiplying hourly flow volumes by the corresponding stream concentrations of SRP and TP. NSE was used to assess the agreement between observed P loads and the simulated P loads at the stream gauge location. The EMC values for each land cover class were calibrated using the swmmr package[70] to maximize NSE values and minimize the difference between observed and simulated P loads for years 2014-2016. EMC values were allowed to vary between one standard deviation of the mean SRP and TP concentrations for each VT land cover class (Appendix K). Base flow, dry periods, and periods without water quality data were removed during the calibration and validation processes.

4.2.4 Simulation Scenarios

The validated SWMM model was used to assess the relative effects of bioretention P removal performance, infiltration capacity, and spatial coverage (i.e. percent of impervious surface area managed with bioretention) on P loads, runoff volumes, and peak flow rates. Low P removal (SRP removal = 25%; TP removal = 45%) and high P removal (SRP removal = 75%; TP removal = 95%) bioretention media—henceforth referred to as “Low Removal” and “High Removal”, respectively—were simulated in this model. The Low Removal media represents, for example, a media comprised of sand and low-P organic amendments (e.g. leaf compost, sphagnum peat, reed sedge peat)[33,37] and the High Removal media represents, for example, a media containing low-P organic materials and P-sorbing amendments (e.g. iron-coated sand, steel slag, drinking water treatment residuals)[33,75,76]. Conventional media blends (e.g. mixtures of sand and high-P compost or topsoil in 60:40 proportions) could not be simulated in this model because SWMM cannot model P leaching (i.e. negative pollutant removal), which is routinely observed in field bioretention studies that use conventional media[23,26–29].

Table 4. Unique identifications for each of the thirteen modeling scenarios

Infiltration	**Media design**	**Percent of impervious surface area in watershed managed with bioretention**			
		0	***30***	***60***	***90***
	Low Removal	No BMPs	30_Lined_Low	60_Lined_Low	90_Lined_Low
Lined	*High Removal*	-	30_Lined_High	60_Lined_High	90_Lined_High
	Low Removal	-	30_Unlined_Low	60_Unlined_Low	90_Unlined_Low
Unlined	*High Removal*	-	30_Unlined_High	60_Unlined_High	90_Unlined_High

Scenarios in which all bioretention systems were lined or unlined were also simulated in this model. Lined systems were represented in SWMM by setting the bioretention seepage rate to 0 and unlined systems were represented by setting the seepage rate equal to the conductivity of the surrounding soil. Finally, different spatial coverage scenarios in which 0%, 30% 60% and 90% of the impervious surface areas are managed with bioretention systems were simulated in this study. Descriptions of the spatial coverage scenarios are provided in Appendix N and the naming scheme used to refer to the thirteen modeled scenarios are presented in Table 4. All simulated bioretention systems were sized such that their surface areas were 5% of the impervious surface area they manage, which is consistent with designs from bioretention field and modeling studies conducted in the eastern U.S.[23–25,28,46,77]. All additional bioretention design dimensions used in this model are summarized in Appendix O.

4.2.5 Stochastic P Generation and Removal

A Monte Carlo simulation method was used to account for uncertainty associated with P washoff concentrations from the VT land cover classes (*n*=6) and P removal by the Low Removal and High Removal media[78]. For each of 500 model simulations, P EMC washoff values and P removal percentage values were determined by random sampling from assigned probability distributions (EMC washoff parameter values provided in Appendix K and bioretention P removal parameter values provided in Appendix P). The assigned probability distributions were truncated to ensure non-negative EMC values and to bound removal percentage values between 0 and 100, as required by SWMM. Each model simulation was evaluated for its average monthly SRP loads, TP loads, stormwater volumes, and peak flow rates. Hydrologic parameters were not varied in the simulations.

4.2.6 Statistics

Statistical analyses were performed to determine the relative impact of bioretention P removal performance, infiltration capacity, and spatial coverage on average monthly SRP and TP loads. The individual and interactive effects of these factors on SRP and TP loads were evaluated using a 3-way ANOVA. The P load results for each modeling scenario were compared using post hoc pairwise comparisons with the Tukey HSD test. All analyses were performed in R[69].

4.3 Results

4.3.1 Model Calibration and Validation

The calibrated hydrologic model produced an NSE value of 0.59, a PBIAS value of -1.1% and an RSR value of 0.64 (Table 5). These calibration results indicate that the hydrologic model is effectively predicting the observed runoff hydrographs (NSE ≥ 0.5) without a consistent bias toward overestimation or underestimation (PBIAS ± 25%) and with a relatively small margin of error (RSR ≤ 0.7).

Table 5. Summary of the watershed model performance metrics for hourly stormwater volumes, SRP loads, and TP loads during the calibration and validation periods

Modeling Period	Constituent	NSE	PBIAS	RMSE	RSR	Observed Totals	Simulated Totals	Days with surface runoff data
Calibration (2014-2016)	*Stormwater*	0.59	-1.1%	6.9	0.64	2,070,069 (m^3)	2,093,627 (m^3)	282
	SRP Load	0.31	-7%	1.3	0.83	121.4 (kg)	130.5 (kg)	271
	TP Load	0.21	-0.3%	4.6	0.89	273.1 (kg)	273.8 (kg)	263
Validation (2017-2019)	*Stormwater*	0.42	3.8%	10.3	0.75	3,784,323 (m^3)	3,647,115 (m^3)	289
	SRP Load	0.27	-10.5%	0.9	0.92	91.9 (kg)	102.7 (kg)	128
	TP Load	0.15	38.3%	4.7	0.92	291.3 (kg)	210.6 (kg)	128

For the validation period, the hydrologic model exhibited an NSE value of 0.42, a PBIAS value of 3.8%, and an RSR value of 0.75 (Table 5). These performance metrics were slightly weaker than those of the calibration period and the NSE and RSR values were just outside of the range of satisfactory values established by Moriasi *et al*.[73]. However, given that the model used hourly timesteps and produced simulated total flow volumes within 4% of the observed total flow volumes for both the calibration and validation period (Table 5), the calibrated hydrologic model was deemed satisfactory for further water quality assessments.

The 15-minute SRP and TP concentration data obtained from the optical water quality sensors in this study allowed water quality to be calibrated and validated at hourly time steps consistent with the hydrologic model. Although the NSE, PBIAS, and RSR values for SRP and TP were weaker than those obtained for the hydrologic model, all PBIAS values were far less than the ± 70% deemed satisfactory by Moriasi *et al*.[73]. Furthermore, simulated total SRP and TP loads were similar to observed total SRP and TP loads for both the calibration and validation periods (Table 5). Given that the primary goal of this model was to assess the relative impact of bioretention system designs on watershed hydrology and water quality, the calibrated water quantity and quality models were considered acceptable for achieving study objectives.

4.3.2 SRP Loads

All twelve bioretention scenarios significantly reduced average monthly SRP loads relative to the No BMPs scenario (Figure 17; Tukey's post hoc contrasts; $p < 0.01$). Bioretention P removal performance, infiltration capacity, and spatial coverage all exhibited significant individual effects on watershed SRP loads ($p < 0.01$). Other factors equal, the High Removal media reduced SRP loads more than the Low Removal media, Unlined bioretention systems reduced SRP loads more than Lined systems, and SRP loads decreased as spatial coverage increased (Figure 17). However, bioretention P removal performance, infiltration capacity, and spatial coverage exhibited a significant 3-way interaction ($p < 0.01$), in which the SRP load impacts of a particular factor depended on the other factors. For example, although increased spatial coverage of bioretention tended to decrease SRP loads, SRP loads for the 30_Lined_High and 60_Lined_Low scenarios were not statistically different (Tukey's post hoc contrasts; $p > 0.1$) and the 60_Lined_High scenario exhibited lower SRP loads than the 90_Lined_Low scenario (Tukey's post hoc contrasts; $p < 0.01$). Such exceptions were not observed in the unlined systems, however, as increased spatial coverage resulted in lower SRP loads regardless of media P removal performance (Tukey's post hoc contrasts; $p < 0.01$).

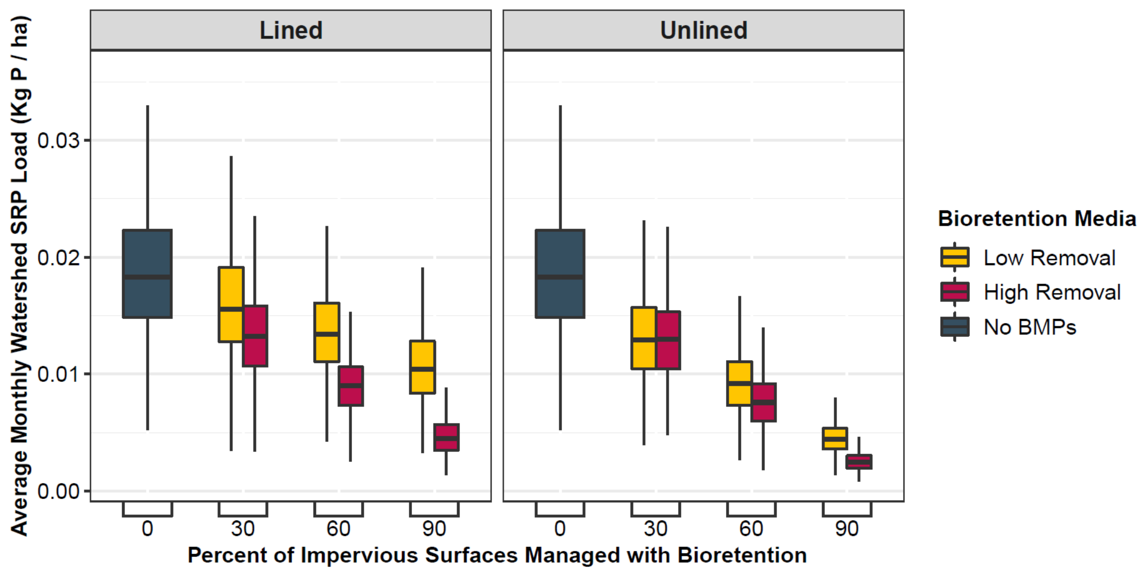

Figure 17. Simulated average monthly watershed soluble reactive phosphorus (SRP) load results for 13 different modeling scenarios. Each box and whisker plot represents the distribution of simulated SRP loads generated from 500 stochastic model simulations.

4.3.3 TP Loads

Trends in average monthly TP loads were similar to those for SRP loads across all modeling scenarios (Figures 2 and Figure 18) and a significant 3-way interaction was also observed between P removal performance, infiltration, and spatial coverage ($p < 0.01$). However, because average TP removals were 20 percentage points higher than average SRP removals for both media designs, the relative impacts of media design and infiltration on TP loads were less pronounced than for SRP loads (Figures 2 and Figure 18). Unlike SRP loads, no statistical differences in TP loads were observed between the 30_Lined_High and 30_Unlined_High scenarios or the 60_Lined_High and 60_Unlined_High scenarios (Tukey's post hoc contrasts*;* $p > 0.1$). Moreover, increased spatial coverage of lined systems significantly improved TP removal irrespective of media design at 30% and 60% spatial coverage (Tukey's post hoc contrasts*;* $p < 0.01$), which was not observed for SRP.

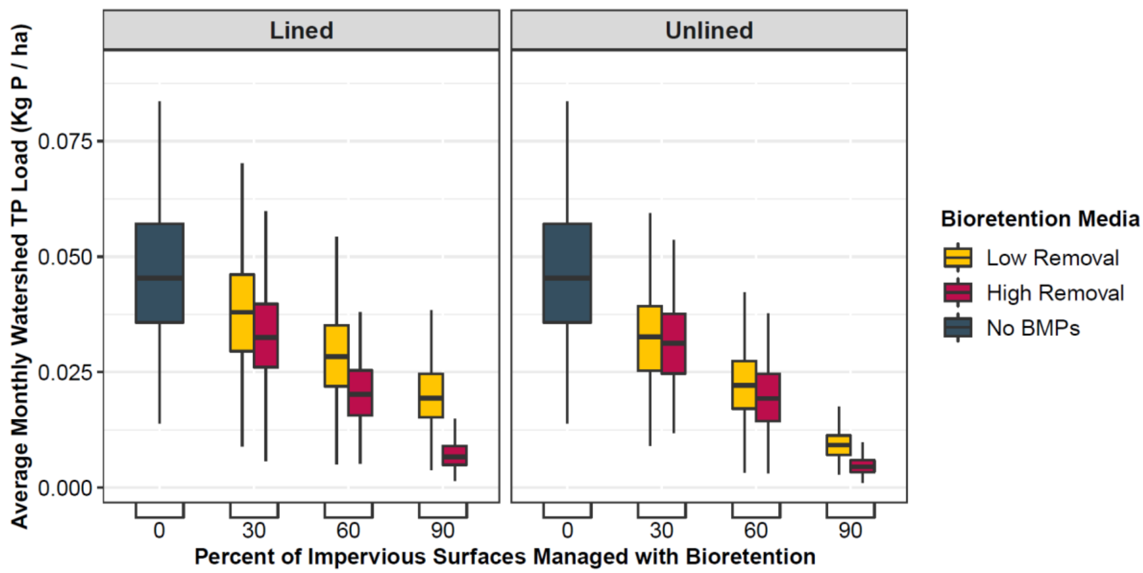

Figure 18. Simulated average monthly watershed total phosphorus (TP) load results for 13 different modeling scenarios. Each box and whisker plot represents the distribution of simulated TP loads generated from 500 stochastic model simulations.

4.3.4 Stormwater Volumes and Peak Flow Rates

The impact of bioretention systems on average monthly runoff volumes and peak flow rates in Potash Brook depended on whether the systems were lined or unlined. Lined bioretention systems had virtually no impact on runoff volumes, as routing runoff from 90% of the watershed's impervious surfaces to lined bioretention systems reduced runoff volumes by only 3.5% relative to 0% of impervious surfaces (Table 6). However, lined bioretention did reduce average monthly peak flow rates for the 30% and 60% coverage scenarios, relative to the 0% coverage scenario (Table 6). Interestingly, routing runoff from 90% of the impervious surfaces to lined bioretention systems resulted in monthly peak flow rates higher than those of the 30% and 60% coverage scenarios.

Table 6. Summary of the average monthly stormwater volumes and peak flow rates for simulated lined and unlined bioretention systems across the spatial coverage scenarios.

Infiltration	Hydrologic metric	Percent of watershed impervious surfaces routed to bioretention			
		0	*30*	*60*	*90*
Lined Bioretention	*Average monthly stormwater volume (m^3)*	211,362	206,356	205,291	204,149
	Average monthly peak flow rate (m^3/h)	8,735	7,605	6,843	8,180
Unlined Bioretention	*Average monthly stormwater volume (m^3)*	211,362	160,254	129,418	81,814
	Average monthly peak flow rate (m^3/h)	8,735	6,594	5,163	3,869

Unlined bioretention systems, however, reduced average monthly peak flow rates in Potash Brook by a much larger margin than the lined systems and produced substantial reductions in stormwater volumes (Table 6). Stormwater volumes and peak flow rates decreased as a linear function of bioretention spatial coverage, with the 90% coverage scenario exhibiting stormwater volumes and peak flow rates 62% and 56% lower than those of the 0% coverage scenario, respectively. Even the 30% spatial coverage scenario reduced stormwater volumes and peak flow rates by 25% and 24%, respectively, compared to the 0% coverage scenario.

4.4 Discussion

4.4.1 Impact of Bioretention P Removal Performance on Watershed P Loads

The design of bioretention systems influences their hydrologic and water quality performance[18–20], yet we lack an understanding of how different system designs and spatial configurations of bioretention interact to affect watershed outcomes. In this modeling study, bioretention P removal performance had a significant impact on SRP loads, with the High Removal media exhibiting consistently lower average monthly SRP loads than the Low Removal media (Figure 17). The model outputs likely underestimate the water quality impacts of bioretention media designs that target P retention (e.g. media containing low-P organic amendments and P-sorbing materials), as they do not consider conventional media designs, which can leach substantial amounts of SRP over long time periods[28,29]. These results demonstrate that the P removal performance of bioretention systems can reduce catchment-level dissolved P loads and that media designed for P retention can significantly improve urban and suburban water quality, even at modest levels of implementation (Figure 17, Lined).

Bioretention P removal performances also affected average monthly TP loads in this study, but to a lesser extent than SRP loads (Figure 17 and Figure 18). Bioretention systems effectively filter particulate P irrespective of media design[21,46,79], so the dampened effect of P removal performance on TP loads may be due to the inclusion of particulate P removal in performance calculations. State and municipal governments often focus water quality efforts on improving TP loads and could interpret these results to indicate that bioretention P removal performances are less important from a TP perspective. However, this interpretation may be inaccurate for two reasons. First, as was the case for SRP loads, the model results were not compared to conventional media blends, which can exhibit much lower TP removal than that of the Low Removal media used in this model. While the difference in average monthly TP loads between the Low Removal and High Removal media were relatively small in this study, TP load differences could be substantial if compared to conventional media designs modeled to leach P[28,29]. Second, mineralization of trapped particulate P can occur within bioretention systems over time[21,80] and influence TP removal performance. These lagged P cycling dynamics are rarely included in watershed models, but may diminish TP removal performances in field settings over time. Although P removal media reduced TP loads less than SRP loads in this model, long-term trends in TP and SRP removal performances may be similar in field settings for a given media design. Future research is needed to better parameterize rates of P mineralization in bioretention media and to incorporate this aspect of the P cycle into watershed models.

4.4.2 Interactive Effects of Spatial Coverage and Infiltration Capacity on P loads

The difference in watershed P loads between the High Removal and Low Removal media scenarios increased with bioretention spatial coverage in this study (Figure 17 and Figure 18). However, infiltration capacity (lined versus unlined systems) mediated the effect of P removal on P loads, such that the difference in P load reductions achieved by the Low Removal and High Removal media were largest in the lined systems (Figure 17 and Figure 18). These interactions between bioretention P removal performance, infiltration, and spatial coverage produced water quality outcomes that may have important implications for watershed P management. For example, prioritizing lined systems to receive high performance media may be an efficient way to manage urban P loads because media P removal performance had a much larger impact on watershed P loads when bioretention systems were lined (versus unlined) in this study. The use of high P removal media may be particularly effective when constructing lined bioretention systems that treat runoff from P hotspots (e.g. lawns[6,81] and golf courses[82]) or are located near impaired waterways, and when replacing the media of lined bioretention systems that were originally filled with P-rich media or are P-saturated from years of P inputs[83,84]. Furthermore, the model showed that greater P load reductions can sometimes be achieved in lined systems by managing a smaller portion of the watershed with high performance media than by managing a larger portion of the watershed with low performance media (Figure 17, 60_Lined_High versus 90_Lined_Low). These results indicate that, depending on the hydraulic context, it may be more effective to invest in media designed for P retention than in new bioretention systems filled with conventional media.

The modeling results also show that infiltrating water into the surrounding soil can substantially reduce P loads and even compensate for poor P removal performance by bioretention media (Figure 17 and Figure 18). These results suggest that stormwater pollutant loads can be effectively managed by infiltrating stormwater at sites that have high permeability soils. This practice has been adopted by many state and municipal governments and incorporated into permitting frameworks that award pollutant removal credits for stormwater infiltration into surrounding soils[62]. However, caution is warranted pursuing infiltration-based P management strategies. Infiltrating P into soils does not necessarily guarantee its permanent removal from a watershed and infiltrated P loads could still migrate to surface waters via subsurface hydrologic pathways in some settings.

Although soils can immobilize P through chemical adsorption and precipitation, they can also release previously bound P when exposed to anoxic conditions, high pH, and dissolved organic matter[85,86]. In fact, numerous studies have reported exceptionally high groundwater P concentrations in human-dominated landscapes[87–90] and modeling efforts suggest that groundwater can be a major contributor to external P loads in urban and agricultural watersheds[91–93]. These results call into question the long-term benefits of P control strategies that neglect to decrease the total amount of mobile P within a watershed. Furthermore, the soils that are most conducive to infiltration (e.g. coarse sands) may have low surface areas and P sorption capacities[33,34,94], so urban P loads could be particularly mobile in these subsurface environments. Additional research is needed to determine the fate of groundwater P in urban watersheds of varying topographies, soil types, and proximity to surface waters[91,93]. However, infiltration-based P management strategies may simply delay P transport to surface waters under certain conditions and therefore should not be considered a perfect substitute for media-based P removal, which can permanently remove dissolved P from the watershed during media replacement.

4.4.3 Hydrologic Impacts of Infiltration

In addition to influencing P loads, bioretention systems had significant impacts on watershed hydrology. The extent to which bioretention systems affected average monthly stormwater volumes and peak flow rates, however, depended mostly upon whether the systems were lined or unlined (Table 4). Lined systems had virtually no impact on stormwater volumes across all spatial coverage scenarios and had inconsistent effects on peak flow rates, such that increasing lined bioretention coverage from 60% to 90% actually increased average peak flow rates (Table 6). This increase in peak flow rates could be due to flow convergences that arose from omitting the storm sewer network from the model. It may also be due to the replacement of stormwater drainage areas that provided moderate infiltration with lined bioretention systems that prevented deep infiltration of stormwater. Thus, widespread implementation of lined bioretention systems could conceivably increase watershed peak flow rates and may be insufficient for achieving watershed hydrology goals. Conversely, unlined systems substantially decreased stormwater volumes and peak flow rates, even at modest levels of implementation. For example, the 30_Unlined scenario produced stormwater volumes and peak flow rates 22% and 19% lower, respectively, than the 90_Lined scenario (Table 6). These results demonstrate that relatively small investments in GSI on highly permeable soils can have large impacts on urban water quantities and suggest that both lined and unlined (infiltrating) systems may be needed to simultaneously manage watershed hydrology and water quality with bioretention[77].

The impact of bioretention systems on stormwater volumes and peak flow rates in this model may have alternative explanations. For example, although lined systems are incapable of infiltrating stormwater, they have been shown to significantly reduce stormwater volumes via media absorption in field studies[28,29]. Evapotranspiration during inter-storm dry periods can reduce the volumetric water content of the bioretention media and therefore increase its water holding capacity[28]. Improved representations of media adsorption and evapotranspiration processes within watershed models may therefore produce better hydrologic outcomes by lined bioretention systems than suggested by these model results. Furthermore, it is unclear whether the soil conductivity values provided by SSURGO could be achieved in the field, particularly in situations where infiltrating bioretention systems are replacing formerly lined wet ponds. If SSURGO conductivity values are in fact higher than field conductivity values, then infiltration would have less of an impact on watershed hydrology and water quality outcomes, and media P removal performance would be of even greater significance. Infiltration would also have relatively less impact if cities use drainage to treatment area ratios greater than the 20:1 ratio used in this study.

4.4.4 Watershed Management Implications

This modeling study shows that bioretention P removal performances can have large effects on urban P loads, particularly in lined systems, and that bioretention systems designed for deep infiltration can have substantial water quantity and quality impacts by reducing total runoff volumes and associated P loads. According to modeling efforts associated with the P TMDL for Lake Champlain, Shelburne Bay (the receiving waterbody of Potash Brook watershed and other watersheds) received 3.4 mt of TP annually from developed land during the 2001-2010 base period and requires a 20.2% reduction in annual TP loads from developed lands to comply with TMDL allocations[52]. In this study, Potash Brook discharged a median 0.98 mt of TP to Shelburne Bay annually under the No BMPs scenario. Compared to the No BMPs scenario, all of the modelling scenarios generated TP load reductions of at least 20.2% except the 30_Low_lined scenario. Furthermore, the unlined bioretention scenarios exhibited significant ability to reduce stormwater volumes and peak flow rates (Table 6). Although the model used in this study differed from the model used for the P TMDL for Lake Champlain, these results demonstrate that bioretention systems with high P removal performance and infiltration capacity have potential to reduce P loads at the catchment scale and to achieve compliance with P and flow-based TMDL requirements.

However, the resources needed to implement P-retaining bioretention systems (e.g., low-P organic amendments, P-sorbing materials, public financing) are often limited, as are opportunities for stormwater infiltration into subsoils, especially in clay soils and highly developed areas. Accordingly, bioretention systems that treat P hotspots, are located near impaired waters, or are filled with P-saturated media should receive priority to receive high P removal performance media. Lined systems that are hydrologically connected to surface water bodies pose the most immediate eutrophication risk, but unlined systems should also be considered for high performance media because infiltration may not be an effective long-term P removal strategy in some contexts. New bioretention systems should be built on permeable soils when appropriate to reduce stormwater volumes and peak flow rates, but should receive media that, at the very least, does not leach P (e.g. uses relatively small amounts of low-P organic amendments)[33,37]. When resources are limited, decisions to invest in high performance media or additional bioretention systems should consider both the media design and soil conductivity of the existing and proposed bioretention sites. This type of nuanced approach to watershed management may be the most effective way to leverage bioretention system designs to simultaneously manage urban hydrology and water quality with limited resources.

4.5 Conclusion

Few studies have used a watershed modeling framework to assess the relative impacts of different bioretention P removal performances on urban P loads at the catchment scale. Our results show that the P removal performance of bioretention media can significantly affect watershed SRP and TP loads, especially in lined systems, which are common in urban and suburban environments. These results likely provide a conservative estimate of the impact of bioretention media designed for P removal, as our model did not consider conventional media that has been shown to leach substantial amounts of P[23,24,28,32]. The effect that media P removal performance had on P loads increased with the spatial coverage of bioretention, but was modified by whether the systems were lined or unlined. Unlined bioretention systems demonstrated the capacity to infiltrate large volumes of runoff and P loads into the subsoil. Consequently, infiltration masked the impact of media design, particularly at low levels of spatial coverage. Overall, these results suggest that bioretention media designed for P retention have potential to reduce urban P loads and help municipalities comply with P TMDLs. For maximum P load reductions, however, use of media designed for P retention should prioritize lined systems that treat runoff from P hotspots, are hydrologically connect to impaired water bodies, or contain P saturated media. Highly permeable soils have major potential to reduce stormwater volumes and should be prioritized for construction of new bioretention systems. However, measures should be taken to ensure that infiltrated P is not posing long-term eutrophication risks to receiving waters. Through a combination of P retaining media and strategic infiltration, bioretention systems can be used to simultaneously manage watershed hydrologic and water quality goals.

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CHAPTER 5: CONCLUSION

The overarching goal of this research was to provide a systematic assessment of the potential for drinking water treatment residuals (DWTRs) to reduce urban phosphorus (P) loads by enhancing P retention within bioretention media. Although the high P sorption capacity of DWTRs has been recognized for decades, significant questions related to their practical use in bioretention systems still remain, and span multiple scales. This research started by investigating the foundational mechanisms governing P sorption at fine scales and used the knowledge generated from these investigations to inform broader scale inquires. This step-wise research approach allowed for strong mechanistic interpretations of study results and for information to be integrated across scales. In addition to advancing our basic understandings of P transport in urban environments, this research offers practical guidance to stormwater practitioners seeking to use local DWTR sources within municipal bioretention systems. The following sections summarize the critical knowledge gaps addressed by this research at different scales.

5.1 Key Research Findings

5.1.1 Micro-Scale

The amount of DWTR to add to bioretention media is a critical design parameter, but recommended application rates vary among studies and are rarely based on quantitative metrics (e.g. P sorption capacity). Additionally, several methods for quantifying P sorption capacities exist, but these methods can yield very different values and a standardized method for stormwater contexts has not been established. This research determined that DWTR application rates should be based on P sorption capacity values obtained from flow-through column studies that closely resemble field bioretention conditions (e.g. the Low P/High Flow experiment conducted in this research). Batch isotherms were also shown to provide reasonable approximations of the P sorption capacity of DWTRs in stormwater contexts, which provides a scientific justification for a method that practitioners may otherwise use out of convenience. A standardized method for quantifying the P sorption capacity of P-sorbing amendments is needed to ensure effective P removal in field applications and this research suggests two potential standard methods for estimating long-term P removal potentials (i.e., the Low P/High Flow experiment conducted in this research and batch isotherms).

Using these P sorption capacity values and estimates of annual P loading, 5% DWTR by total media volume was determined to be a sufficient quantity for long-term (10+ years) P removal. This research therefore recommends that other studies use 5% DWTR by total media volume, provided that a given DWTR source has physicochemical properties similar to those of the DWTRs studied here. If physicochemical properties differ substantially from the DWTRs studied in this research, DWTR application rates should be based on estimates of the total amount of dissolved P a bioretention system will receive over its operational lifespan as well as estimates of the P sorption capacity of the DWTRs using batch isotherm experiments or experiments similar to the Low P/High Flow experiment used in this study.

Although DWTRs are known to be heterogeneous materials, standard screening metrics for DWTR source selection have not yet been established. The batch isotherm and flow-through column experiments demonstrated that the P sorption capacity of DWTRs is highly variable, confirming the fact that DWTR source matters. Variability in

P sorption capacity was driven mostly by differences in specific surface area and effective particle size, since amorphous metal hydroxide contents were largely uniform across the DWTR sources. These results show that physical properties can have strong influence on the P sorption capacity of materials and suggest that specific surface area and effective particle size could be useful criteria for selecting between DWTR sources.

Finally, a major question that limits broader use of DWTRs in bioretention systems is whether these fine-textured amendments will restrict water flow when added to media and undermine the primary hydraulic functions of bioretention systems. This research provided strong evidence of a tradeoff between P sorption capacity and hydraulic conductivity in DWTRs, such that DWTRs with the highest P sorption capacity exhibited the lowest hydraulic conductivity and vice versa. Furthermore, some of the hydraulic conductivity values exhibited by the DWTRs were substantially lower than that of sand, suggesting that they could cause hydraulic issues if used as amendments. This tradeoff has not been explicitly demonstrated in past research and poses a significant challenge for achieving P removal in bioretention systems without sacrificing hydraulic control.

5.1.2 Meso-Scale

Several column experiments have investigated the potential for DWTRs to remove P from stormwater but have not provided clear guidance on how best to incorporate DWTRs into bioretention media. From a media design perspective, there is particular need to determine how to incorporate DWTRs within bioretention media for effective P removal and hydraulic control.

The micro-scale DWTR analyses indicated that 5% DWTR by total media volume could provide long-term P removal, but also suggested the DWTRs could cause hydraulic issues. The large column experiment confirmed that DWTRs can restrict water flow when added as a solid layer within bioretention media. These flow restrictions also created preferential flow paths that led to incomplete P removal, illustrating the connection between hydraulic and water quality outcomes. However, mixed layers of sand and DWTR alleviated the hydraulic restrictions imposed by DWTRs in the large column experiment and improved P removal by allowing water to contact the full media volume. These results provide an important first step in documenting the potential hydraulic impacts of fine-grained P-sorbing amendments and also offer a simple design solution (e.g. mixing DWTRs with sand) to reconcile the often competing goals of hydrologic control and water quality improvement.

5.1.3 Field-Scale

Although DWTRs have improved P removal performances in numerous laboratory column experiments, there is little evidence that they significantly reduce dissolved P concentrations in field experiments. This discrepancy between lab and field results raises fundamental questions about whether DWTRs can actually improve P retention in real-world scenarios and thus reduce urban P loads. In the field portion of this research, the bioretention cells that received DWTR-amended media consistently reduced soluble reactive P (SRP) and particulate P (PP) concentrations over two years of inflow and outflow monitoring. The DWTR cells also had higher SRP removal efficiencies than the Control cells and the difference in SRP removal performance increased substantially from the first to the second year of monitoring. These results provide critical field validation of the capacity of DWTRs to enhance P retention in bioretention systems. They also demonstrate that DWTRs can effectively sorb P even when exposed hydraulic variation, competing anions, and very low dissolved P concentrations.

Successful observations of P removal in both the lab and field components of this research may have important media design implications. First, the DWTRs in this study were placed in a layer beneath a surface layer of sand and compost. This positioning of DWTRs within the media profile would allow them to sorb P leaching downward from organic substrates at the surface, thereby improving P retention. Second, the amount of DWTRs added to the media was based on measured P sorption capacity values, which confirms that the media had sufficient capacity for long-term P removal. The failure of DWTRs to significantly reduce P concentrations in past studies may be due to limited P sorption capacities, which is particularly possible if the DWTRs were not sieved or overwintered (e.g. exposed to a freeze-thaw cycle) prior to use. Finally, the DWTRs were thoroughly mixed into the bioretention media using cement mixers in this study, whereas previous studies have used backhoes and manual shoveling. Such technical details may be essential for replicating laboratory results in the field.

The DWTRs used in this study were not shown to cause hydraulic issues or to significantly leach heavy metals. The hydraulic impacts of DWTRs have not been evaluated in previous field bioretention studies and the potential for DWTRs to leach heavy metals has only been investigated in one previous study. These results suggest that DWTRs have potential to improve P removal in bioretention systems without causing hydraulic or toxicity issues if properly incorporated into bioretention media, but continued testing for metals leaching is recommended.

5.1.4 Catchment-Scale

Watershed models are needed to simulate the effects of different management practices on large-scale hydrologic and water quality outcomes. The laboratory and field results of this research demonstrate that DWTRs have significant potential to enhance P retention within bioretention systems and that media design strongly influences P removal performance. However, few studies have evaluated the impact of bioretention P removal performance on catchment-scale P loads, so the potential effects of installing DWTR-amended bioretention broadly within a watershed is unknown. The watershed model used in this research demonstrated that the P removal performance of bioretention systems can have a substantial impact on watershed P loads, even at relatively low presence of bioretention on the landscape. The model results also showed that in some cases it can be more effective from a catchment-scale P management perspective to treat a smaller fraction of the watershed with high P removal media than to treat a larger fraction of the watershed with low P removal media. Bioretention systems that contain DWTR-amended media therefore have great potential to reduce urban P loads and may be an effective tool for combatting eutrophication and complying with TMDL requirements.

5.2 Remaining Questions and Future Research Directions

This research significantly advanced our understanding of the DWTR-amended bioretention media technology, but significant questions remain. The following sections summarize those questions at the aforementioned scales.

5.2.1 Micro-Scale

The laboratory results presented in this work were only based on three DWTR sources. Therefore, more research is needed to determine if other DWTR sources exhibit tradeoffs between P sorption capacity and hydraulic conductivity. P-sorbing materials other than DWTRs also need to be tested to establish whether batch isotherms can consistently produce P-sorption capacity values similar to those of the Low P/High Flow Column study used in this study. Furthermore, the Low P/High Flow experiment used an influent P concentration of 1.0 mg P L^{-1}, which is still relatively high by stormwater standards. Future flow-through column experiments should quantify P sorption capacities using influent P concentrations common in stormwater (e.g. 0.1 mg P L^{-1}) to determine the impact of very low P concentrations on P sorption capacity values.

5.2.2 Meso-Scale

Mixing DWTRs with sand was shown to be an effective strategy for mitigating the hydraulic impacts of fine-grained DWTRs in this research. However, more research is needed to determine if this strategy is effective across a broader range of DWTR textures. It is also unclear whether DWTRs that are mixed with sand will migrate out of the media over time as the media experiences repeated drying and wetting cycles. Future column studies should investigate these dynamics over long time periods. Despite the impressive P removal performance observed by the media in this research, layered media designs present greater practical challenges for stormwater practitioners than a single media blend. Future research should therefore examine whether similar P removal performances can be achieved using single media blends and whether additional organic amendments would be needed to support plant establishment in these blends. Future research should also assess the potential for DWTRs to both leach and adsorb various species of heavy metals.

5.2.3 Field-Scale

Although DWTRs were not shown to directly affect the hydraulic functions of bioretention media when mixed with sand in this research, they could indirectly cause clogging in the field by improving particulate capture. Conversely, large plant roots could combat such hydraulic restrictions by promoting preferential flow but may reduce P contact with DWTRs. Assessments of the hydraulic and P removal performance of established, DWTR-amended bioretention systems are needed to determine the real-world efficacy of this practice over time. The DWTRs used in this field study were also sieved and thoroughly mixed into the sand using electric cement mixers. Such practices may not be feasible for large-scale operations, so successful demonstrations of P removal by DWTR-amended media using typical field installation practices are needed to confirm real-world effectiveness.

5.2.4 Catchment-Scale

The watershed modeling results from this research showed that bioretention P removal performances have large effects on catchment-scale P loads. However, P removal performances are not static through time as represented in this model, but rather depend on the P saturation ratio of the media, the concentration of P inputs, among other factors. P release from organic media amendments and trapped sediments can further complicate P removal performances within bioretention systems. Future modeling efforts that better represent P cycling dynamics within bioretention systems are needed to provide more realistic watershed outcome predictions. Moreover, DWTRs and other P-sorbing amendments are a limited resource. Additional research is needed to determine rates of DWTR production in various localities and the corresponding area of land that could be managed with DWTR-amended bioretention.

5.3 Summary

Overall, this research provides an important bridge between our theoretical understanding of P sorption and our practical application of P-sorbing amendments to bioretention media for watershed P management. It offers many generalizable recommendations for how to use a generic DWTR source within bioretention media to simultaneously achieve hydraulic control and effective P removal. It shows that bioretention media design matters and has significant influence on P removal performances. It also provides a critical validation of enhanced P removal by DWTRs in a controlled field context. Finally, this research demonstrates that bioretention P removal performances can have substantial impacts on catchment-scale P loads at various levels of GSI implementation. This multiscale approach links fine-scale physicochemical processes to large-scale water quality outcomes and showcases the potential for DWTRs and other P-sorbing amendments to reduce P loads and mitigate eutrophication risks.

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APPENDICES

Appendix A:

Flow-Through Kinetics Experiment Methods

Rates of P sorption were determined in a flow-through scenario by measuring P removal across a range of media contact times (1, 2, 4, 8, and 16 min). 10 mL of each drinking water treatment residual (DWTR) were added to miniature columns (10 cm-length; 2.5 cm-diameter) and a peristaltic pump was used to feed a synthetic P solution (0.2 mg P L^{-1} in 0.01 *M* KCl) vertically through the DWTRs at different flow rates. The flow rates needed to achieve each contact time were calculated by the porosity of each DWTR such that, for example, 10 mL of a media with 50% pore volume would need a flow rate of 5 mL min^{-1} to achieve 1 min of media contact. After 100 mL of solution had passed through the DWTRs for each flow rate, one sample was collected to represent P removal for that contact time.

Appendix B:

Table 1. Summary of phosphorus (P) retention capacity, regeneration of P retention capacity, and P desorption results for each drinking water treatment residual (DWTR) source in the High P/Low Flow column experiment.

DWTR	P retention (mg P kg^{-1})	Additional P retained (mg P kg^{-1}) and (%)		P desorption (mg P kg-1) and (%)	
CWD	40,026 ± 1,069	5209 ± 146	13	2,227 ± 62	5
PORT	10,019 ± 3,702	5117 ± 809	51	1226 ± 188	8
UNH	8,668 ± 662	4201 ± 468	48	686 ± 29	5

Appendix C:

Table 2. Summary of phosphorus (P) retention capacity, regeneration of P retention capacity, and P desorption results for each drinking water treatment residual (DWTR) source in the Low P/High Flow column experiment.

DWTR	P retention (mg P kg^{-1})	Additional P retained (mg P kg^{-1}) and (%)		P desorption (mg P kg-1) and (%)	
CWD	9,576 ± 50	1,787 ± 128	19	373 ± 18	3
PORT	1,463 ± 13	1,124 ± 34	77	105 ± 7	4
UNH	1,284 ± 49	996 ± 52	78	87 ± 16	4

Appendix D:

Table 3. Comparison of column study P retention values at P saturation to the isotherm Qe values predicted by the Langmuir adsorption models at Ce values equal to the column study influent concentrations (i.e., 1 or 300 mg P L-1). Values are means ± 1 standard deviation.

DWTR	Predicted Q_e @ C_e = 1 mg P L^{-1} using Langmuir models	Cumulative P retention in Low P/High Flow column study (C_i = 1 mg P L^{-1})	Predicted Q_e @ C_e = 300 mg P L^{-1} using Langmuir models	Cumulative P retention in High P/Low Flow column study (C_i = 300 mg P L^{-1})
CWD	1,163.8 ± 335.1	9,576 ± 50	11,304.3 ± 295.2	40,026 ± 1,069
PORT	513.7 ± 289.0	1,463 ± 13	1,333.8 ± 298.0	10,019 ± 3,702
UNH	56.3 ± 6.1	1,284 ± 49	1,363.0 ± 25.2	8,668 ± 662

Appendix E

Table 1. Summary of the physical and chemical properties of the University of New Hampshire (UNH) drinking water treatment residuals (DWTR). Data from Ament *et al*.[40].

Physical Properties	**UNH DWTR**
Specific surface area ($m^2 g^{-1}$)	3.2
Effective grain size (d_{10})	211.6
Hydraulic conductivity (cm hr^{-1})	98.5
Chemical Properties	
Al_2O_3 (%)	28.4
Fe_2O_3 (%)	1.8
M_nO (%)	0.5
As (ppm)	38
Cd (ppm)	> 0.5
Zn (ppm)	65
Isotherm Q_{max} (g P kg^{-1})	1,479

Appendix F

Table 2. Summary of storm events captured during the 2019 and 2020 field monitoring seasons. Precipitation depths were obtained from the Burlington International Airport rain gauge. This rain gauge is located approximately 4km from the UVM Bioretention Laboratory and managed by the National Weather Service.

2019			**2020**		
Storm Number	**Date**	**Precipitation Depth (mm)**	**Storm Number**	**Date**	**Precipitation Depth (mm)**
1	9/7/2019	14	1	6/30/2020	17
2	9/23/2019	17	2	7/1/2020	6
3	9/26/2019	11	3	7/11/2020	6
4	10/1/2019	22	4	7/12/2020	7
5	10/7/2019	29	5	7/27/2020	17
6	10/17/2019	41	6	8/4/2020	63
7	10/23/2019	10	7	8/29/2020	19
8	10/27/2019	18	8	9/30/2020	50
			9	10/2/2020	12
			10	10/7/2020	13
			11	10/10/2020	10
			12	10/16/2020	18
			13	11/15/2020	11

Appendix G

Table 3. Summary of the methods used for phosphorus analyses. Detection limit differences between 2019 and 2020 were due to the use of a new flow injection analyzer.

Nutrient Species	Standard Method Procedure	2019 Detection Limit (mg/L)	2020 Detection Limit (mg/L)
Total P (TP)	4500-PJ[a] Combined Persulfate Digestion	0.015	0.01
Total Dissolved P (TDP)	4500-PJ[a] Combined Persulfate Digestion	0.015	0.01
Soluble Reactive P (SRP)	4500-PE Ascorbic Acid Reduction	0.01	0.005
Particulate P (PP)	PP = TP - TDP	N/A	N/A
Dissolved Organic P (DOP)	DOP = TDP - SRP	N/A	N/A
[a] Determined as PO_4^{3-} by 4500-PE			

Appendix H

Table 4. Summary of the phosphorus (P) load reductions attributable to volume reductions (LR_{vol}) and concentration reductions (LR_{conc}).

Bioretention Cell	P Species	Total Load Reduction (mg)	LR_{vol} (mg)	LR_{conc} (mg)	LR_{vol} (%)	LR_{conc} (%)
Small Drainage Area Control	SRP	329	35	294	11	89
	DOP	28	10	18	37	63
	PP	305	13	292	4	96
	TP	662	58	604	9	91
Small Drainage Area DWTR	SRP	821	27	794	3	97
	DOP	127	9	118	7	93
	PP	764	12	752	2	98
	TP	1712	48	1664	3	97
Large Drainage Area Control	SRP	430	45	385	10	90
	DOP	37	10	27	28	72
	PP	541	61	480	11	89
	TP	1007	115	892	11	89
Large Drainage Area DWTR	SRP	390	30	360	8	92
	DOP	36	11	25	30	70
	PP	430	6	424	1	99
	TP	856	47	809	5	95

Appendix I

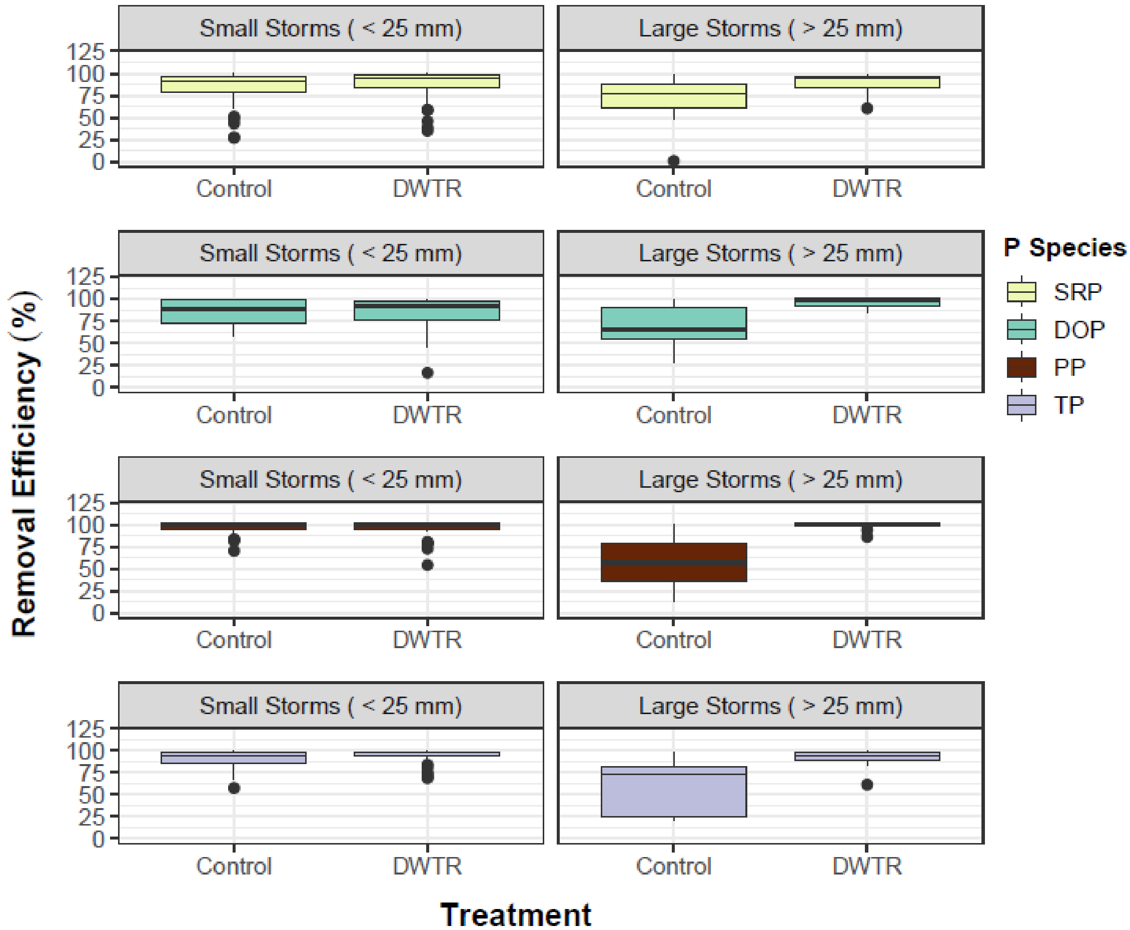

Figure 1. Phosphorus (P) mass removal efficiency (RE) percentages for the Control and DWTR bioretention cells during small storms (defined as < 25 mm) and large storms (defined as > 25 mm). Box and whisker plots represent the distribution of RE values for soluble reactive P (SRP), dissolved organic P (DOP), particulate P (PP), and total P (TP) for the Control media (2 bioretention cells) and DWTR media (2 bioretention cells) during small storms (*n*=17) and large storms (*n* = 4).

Appendix J

Table 1. Event mean concentration (EMC) washoff concentrations (mg/L) for soluble reactive P (SRP) and total P (TP) from six land cover classes derived from the National Stormwater Quality Database (NSQD), regionalized to the northeastern US. Data from Bell *et al*. 2021.

NSQD Land Use Types	Mean SRP (μ)	Standard Deviation SRP (σ)	Mean TP (μ)	Standard Deviation TP (σ)
Commercial	0.16	0.24	0.24	0.27
Freeway	0.11	0.12	0.32	0.34
Industrial	0.24	0.22	0.3	0.5
Institutional	0.08	0.2	0.22	0.16
Open Space	0.13	0.06	0.3	0.35
Residential	0.1	0.11	0.44	0.95

Appendix K

Table 2. Crosswalk table used to convert the VT High Resolution Land Cover Classes to the National Stormwater Quality Database (NSQD) Land Use Types. Soluble reactive P (SRP) and total P (TP) values represent the average of the event mean concentration (EMC; mg/L) values of the NSQD land use types contained within each VT land cover class.

2016 VT High Resolution Land Cover Classes	**Conversion to NSQD Land Use Types**	**Mean SRP (μ)**	**Standard Deviation SRP (σ)**	**Mean TP (μ)**	**Standard Deviation TP (σ)**
Bare Soil	*Industrial/ OpenSpace*	0.19	0.15	0.30	0.43
Buildings	*Residential/ Commercial*	0.13	0.17	0.34	0.61
Grass/Shrubs	*Open Space/ Residential/ Institutional*	0.11	0.12	0.32	0.49
Other Impervious	*Commercial/ Institutional/ Industrial*	0.16	0.22	0.25	0.31
Roads/Railroads	*Freeway*	0.11	0.12	0.32	0.34
Tree Canopy	*Open Space*	0.13	0.06	0.30	0.36
Water	*N/A*	0.00	0.00	0.00	0.00

Appendix L

Table 3. Hydrologic metrics used to evaluate model performance.

Metric	Equation	Description
Nash-Sutcliffe Efficiency (NSE)	$\text{NSE} = 1 - \frac{\sum_{i=1}^{n}\left(Y_i^{obs} - Y_i^{sim}\right)^2}{\sum_{i=0}^{n}\left(Y_i^{obs} - Y_i^{mean}\right)^2}$	Indicates how well the plot of observed versus simulated data fits the 1:1 line. NSE values range from -∞ to 1.0. An NSE < 0 indicates that the mean observed value is a better predictor of observed flow than the model. A value of 0.5 for flow is considered satisfactory (Moriasi *et al.* 2007)
Percent Bias (PBIAS)	$\text{PBIAS} = \frac{\sum_{i=1}^{n}(Y_i^{obs} - Y_i^{sim}) \times 100}{\sum_{i=1}^{n}(Y_i^{obs})}$	Measures the average tendency of the simulated data to deviate from the observed data. Positive values indicate model underestimation and negative values indicate model overestimation, with 0 being the optimal value. Values < ± 20% for flow are considered satisfactory (Moriasi *et al.* 2007)
Root Mean Square Error - observations standard deviation ratio (RSR)	$\text{RSR} = \frac{RMSE}{STDEV_{obs}} = \frac{\sqrt{\sum_{i=0}^{n}\left(Y_i^{obs} - Y_i^{sim}\right)^2}}{\sqrt{\sum_{i=0}^{n}\left(Y_i^{obs} - Y^{mean}\right)^2}}$	RMSE is a measurement of the amount of error between the observed and simulated data and lower RMSE values indicate better model performance. RSR standardizes RMSE by dividing it by the observed standard deviation. RSR values range from the optimal value of 0 to large positive values and values < 0.7 for flow are considered satisfactory (Moriasi *et al.* 2007)

Appendix M

Table 4. Hydrologic model calibration parameter bounds.

Parameter	Default	Bounds
Depressional storage impervious	0.01	.05-.1[a]
Depressional storage pervious	0.1	.2-.4[a]
Imperviousness	N/A	75% - 125% of imperviousness from land cover data
Manning's *n* impervious	0.05	0.01 - 0.04[a]
Manning's *n* pervious	0.05	.1-.4[a]
Soil Conductivity	N/A	Lower and upper bounds of the SSURGO conductivity values

[a] Parameter bounds obtained from Table 3.5 of SWMM hydrology manual and citations therein.

Appendix N

Table 5. Summary of the spatial cover scenarios evaluated in this study and their implementations within SWMM.

Spatial coverage scenarios	Impervious land area routed to non-bioretention BMPs (%)	Impervious land area routed to bioretention (%)	Total land area occupied by bioretention (%)	Description
No BMPs	0	0	0	Remove all existing BMPs from model
30% treatment of impervious areas with bioretention	0	30	0.33% (12.5 acres)	Remove all existing BMPs from model and add bioretention to drainage areas that contain 30% of the impervious surfaces within the watershed. Select drainage areas to receive bioretention based on drainage area size, given that soil conductivity values exceed 0.2 cm/hr
Baseline	60	0	0%	Existing stormwater BMP infrastructure. Mostly wet ponds, dry ponds, and infiltration basins
60% treatment of impervious areas with bioretention	0	60	0.66% (25 acres)	Replace all existing BMPs with bioretention
90% treatment of impervious areas with bioretention	0	90	1% (38 acres)	Replace all existing BMPs with bioretention and treat 75% of remaining impervious surfaces with bioretention

Appendix O

Table 6. Parameter values used to simulate bioretention systems in the SWMM model. A seepage rate of 0 was used for lined systems, but seepage rates were set to the conductivity of the surrounding soil for unlined systems.

Surface	
Berm height (in)	9
Vegetation Volume (fraction)	0.1
Surface roughness (Manning's *n*)	0.05
Surface slope (%)	0.5
Soil	
Thickness (in)	24
Porosity (volume fraction)	0.45
Field Capacity (volume fraction)	0.2
Wilting point (volume fraction)	0.1
Conductivity (in/hr)	5
Conductivity slope	50
Suction head (in)	3
Storage	
Thickness (in)	12
Void ratio (voids/solids)	0.75
Seepage rate (in/hr)	0
Clogging factor	0
Underdrain	
Drain coefficient (in/hr)	1.5
Drain exponent	0.5
Drain offset height (in)	0
Open level (in)	0
Closed Level (in)	0

Appendix P

Table 7. Soluble reactive P (SRP) and total P (TP) removal parameters for the Low P removal and High P removal biorention media designs.

Bioretention media design	**Mean SRP removal (μ)**	**Standard deviation of SRP removal (σ)**	**Mean TP removal (μ)**	**Standard deviation of TP removal (σ)**
Low Removal	25%	10%	45%	10%
High Removal	75%	10%	95%	10%