Phosphorus removal, metals dynamics, and hydraulics in stormwater bioretention systems amended with drinking water treatment residuals

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ABSTRACT

Drinking water treatment residuals (DWTRs) are a promising media amendment for enhancing phosphorus (P) removal in bioretention systems, but substantial removal of dissolved P by DWTRs has not been demonstrated in field bioretention 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 P removal efficiency of the DWTR cells were greater than those of the Control cells for all P species, particularly during the second monitoring season as P sorption complexes likely began to saturate in the Control cells. The difference in P removal efficiency between the Control and DWTR cells was greatest during large storm events, which transported the majority of dissolved P loads in this study. We also investigated the potential for DWTRs to restrict water flow through bioretention media or leach heavy metals. The DWTRs used in this study did not affect the hydraulic performance of the bioretention cells and no significant evidence of heavy metal leaching was observed during the study period. Contrasting these results with past studies highlights the importance of media design in bioretention system performance and suggests that DWTRs can effectively capture and retain P without affecting system hydraulics if properly incorporated into bioretention media.

KEY WORDS: *bioretention, drinking water treatment residuals, phosphorus removal, hydraulic conductivity, heavy metals, field study*

INTRODUCTION

Urban landscapes contain substantial amounts of phosphorus (P) originating from lawn fertilizer, pet waste, soil particles, plant litter and atmospheric deposition (Hobbie et al. 2017; Müller et al. 2020; U.S. EPA 1999). The transport of urban P sources to surface waterbodies via runoff is a leading cause of eutrophication and harmful algal blooms in freshwater ecosystems (Carpenter et al. 1998; National Research Council 2009; U.S. EPA 2009). Bioretention systems are a form of green stormwater infrastructure increasingly used in developed areas for hydrologic control and water quality improvement (Davis et al. 2009; Taguchi et al. 2020). While bioretention systems have proven effective for reducing peak flow rates, sediment loads, and concentrations of certain pollutants (LeFevre et al. 2015; Liu et al. 2017; Vijayaraghavan et al. 2021), their capacity to remove P from stormwater is highly variable and some studies have even shown net release of P (Cording et al. 2018; Dietz and Clausen 2005; Hatt et al. 2009; Hunt et al. 2006; Shrestha et al. 2018)

Because P does not have a gaseous phase relevant in the context of stormwater (Schlesinger and Bernhardt 2013), 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 (Liu and Davis 2014). While conventional bioretention media constituents (e.g. sand, compost, topsoil) effectively filter particulate P (PP), they have limited capacity to adsorb dissolved P (Li and Davis 2016; Tirpak et al. 2021). 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. 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 (Chahal

et al. 2016; Hurley et al. 2017; LeFevre et al. 2015; Passeport et al. 2009). 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 (Marvin et al. 2020). Many industrial byproducts contain high concentrations of metal hydroxides, which can bind dissolved P through chemical adsorption or precipitation processes (Buda et al. 2012; Cucarella and Renman 2009; Leader et al. 2008). 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 (Babatunde and Zhao 2007). 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 (Babatunde et al. 2009; Ippolito et al. 2011; O'Neill and Davis 2011a). P sorption by aluminum (Al)-based DWTRs is relatively insensitive to soil redox conditions (Penn and Bowen 2018; Zvomuya et al. 2006), 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 (Liu et al. 2014; Lucas and Greenway 2011; O'Neill and Davis 2011b; Palmer et al. 2013; Poor et al. 2018; Yan et al. 2016b), 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. (2020) identified only two unique field

89 installations (results presented in Liu and Davis (2014), Roseen and Stone (2013), and Houle
90 (2017)) that have evaluated the P removal performance of DWTRs in urban bioretention. In both
91 of these installations, the DWTR-amended media failed to significantly reduce stormwater SRP
92 concentrations, despite effective SRP removal in corresponding column experiments (O'Neill
93 and Davis 2011b; Roseen and Stone 2013). Liu and Davis (2014) also investigated the potential
94 for DWTRs to retain DOP but did not observe significant DOP removal. Authors speculated that
95 poor dissolved P removal performance was due to equilibrium adsorption dynamics (Liu and
96 Davis 2014), short-circuiting of the media volume (Roseen and Stone 2013), and non-uniform
97 distributions of DWTRs in the filter media (Roseen and Stone 2013). Further research is needed
98 to establish whether DWTRs can, in fact, enhance dissolved P removal in field contexts and to
99 determine the factors that regulate P removal by DWTRs in urban bioretention systems.
100 Another dimension of adding DWTRs to bioretention media is whether this practice
101 produces unintended consequences. The high P sorption capacity of DWTRs has been linked to
102 their large surface areas and fine-grained texture (Ament et al. 2021; Yang et al. 2006), which
103 could cause flow restrictions in DWTR-amended media. Ament et al. (2021) and Yan et al.
104 (2017) demonstrated that additions of DWTRs to bioretention media can reduce infiltration rates
105 in column experiments. Such hydraulic restrictions in field contexts could produce preferential
106 flow paths that facilitate media short-circuiting or clogging of outlets that lead to excessive
107 ponding or backflow.
108 Additionally, DWTRs can contain high concentrations of heavy metals (Buda et al. 2012;
109 Ippolito et al. 2011), which could potentially leach from bioretention systems amended with
110 these materials and pose risks to surface and ground water resources. Metals, such as Al,
111 manganese (Mn), and zinc (Zn), can be toxic to humans and aquatic life and have been shown to

leach from DWTRs in column studies (Mortula and Gagnon 2007; Novak et al. 2007; Palmer et al. 2013). However, urban runoff can contain heavy metals such as arsenic (As) and cadmium (Cd) (Davis et al. 2001), which some P-sorbing materials can adsorb (Lim et al. 2015; Siswoyo et al. 2014; Zhou and Haynes 2012). The potential leaching of heavy metals from industrial byproducts is a common concern that limits broader use of DWTRs in field applications (Ippolito et al. 2011), yet few studies have investigated heavy metal dynamics in field bioretention systems amended with DWTRs.

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. (2021), 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)

MATERIALS AND METHODS

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 (Cording et al. 2018). 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 contains a perforated underdrain raised approximately 12 cm above the bottom of the cell, which creates a small internal water storage zone.

Experimental Design

A field bioretention experiment was conducted to compare differences in water quality improvement between a DWTR-amended treatment media and a non-amended control media (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 media, while the remaining two cells were retrofitted with the DWTR media. 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 media. One group of cells consisted of 43 m^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 59 m^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).

158 The Control media contained washed gravel (3-5 cm diameter), washed pea stone (1-2
159 cm diameter), washed sand (< 2 mm diameter) and compost (Figure 1a). Previous research has
160 shown that conventional bioretention media (e.g., 60% sand, 40% compost) and composts
161 derived from manure feedstocks leach nutrients into bioretention effluent (Cording et al. 2017,
162 2018; Mullane et al. 2015). Accordingly, the Control media in this study contained reduced
163 quantities (10% compost by volume in the top 30.5 cm of media) of a low-P compost (derived
164 from leaf litter feedstocks; 0.19% P by dry mass) (Shrestha et al. 2020) to limit the internal P
165 content of the media. The DWTR media was identical to the Control, except that 10% of the
166 sand layer (located 30.5 cm – 71 cm below the media surface) volume was replaced with
167 DWTRs (Figure 1b), which Ament et al. (2021) determined to be enough for long-term (> 10
168 years) P removal. The DWTRs were passed through a 5 mm sieve to remove coarse debris and
169 mixed into the sand with cement mixers. The DWTRs used in this study were obtained from the
170 University of New Hampshire Water Treatment Plant (Durham, NH), which uses polyaluminum
171 chloride as a treatment coagulant and processes its DWTRs via freeze-thaw cycling. This
172 material exhibited the lowest P retention capacity of the three DWTR sources evaluated in
173 Ament et al. (2021) and was selected for this study to provide a conservative estimate of the P
174 removal performance of DWTRs in field bioretention systems. A summary of the physical and
175 chemical properties of this DWTR material is provided in Table S1.

176 After retrofit, all four cells were planted with an identical assemblage of species, which
177 consisted of *Asclepias tuberosa* (Butterfly Milkweed, *n*=1 plant per bioretention cell), *Echinacea*
178 *purpurea* (Echinacea Sp., *n*=2), *Helenium autumnale* (Sneezeweed 'Sombrero', *n*=1), *Iris*
179 *versicolor* (Harlequin Blueflag, *n*=3), and *Symphyotrichum nova-angliae* (New England Aster,
180 *n*=2). Vegetation was watered every other day for three weeks to ensure plant establishment. The

181 *Helenium autumnale* cultivar did not survive the first season of study and was replaced with
182 *Zizia aurea* (Golden Alexander) in May of 2020.

183 **Stormwater Sampling**

184 Stormwater inflows and outflows from the four bioretention cells were simultaneously
185 monitored with eight autosamplers (Teledyne ISCO 6712, Lincoln, NE). A cedar box equipped
186 with a 90^{o} v-notch weir was placed at the inlet of each bioretention cell to capture runoff being
187 conveyed from the road (Figure 2, left). Inflow volumes were determined using submerged probe
188 flow modules (ISCO 720) to measure the stage height of water within the weir boxes (Cording et
189 al. 2017) every minute. Stage height measurements were converted to flow rates using the
190 equation (Dunne and Leopold 1978):

191 $$L/s = 1380 \text{ (stage height m)}^{2.5}$$

192 Outflow volumes were determined similarly. However, instead of using a weir box to
193 measure flow, a sealed sump was used, which drained into a 15 cm diameter PVC pipe equipped
194 with a Thel-Mar weir (Thel-Mar, LLC, Brevard, NC) (Figure 2, right). Submerged probes
195 secured to the bottom of the sumps were used to measure stage heights, which were converted to
196 flow rates using conversion charts provided by Thel-Mar, LLC.

197 Flow-based composite sampling (fifteen 200 ml water samples per bottle) was used to
198 monitor inflow and outflow stormwater quality for the bioretention cells. For a given rainfall
199 event, a maximum of four composite water sampling bottles were obtained from each of the
200 inflow and outflow autosamplers, roughly targeting the rising, peak, and falling limbs of the
201 storm hydrograph. The volumetric sampling intervals (L) needed to capture the entire storm
202 event were calculated from rain forecasts before every storm using unique linear relationships
203 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. The water quality data therefore represent the P removal performance of newly constructed bioretention cells (data from approximately 0.5- and 1.5- years post media retrofit). Furthermore, runoff produced from snowmelt or winter rainfall events was not monitored in this study, so the water quality data only reflects warm weather performance. Every storm forecasted to produce > 5 mm of rainfall was monitored with the autosamplers, but only storms that generated outflow in all bioretention cells were analyzed in this study. Twenty-one captured storm events generated outflow during the 2019 and 2020 field monitoring seasons (Table S2).

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 .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 (Table S3) (APHA et al. 2005). PP and DOP were calculated as TP minus TDP and TDP minus SRP, respectively (Table S3). 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 (Davis 2007; Liu and Davis 2014). To investigate the effects of data below detection limits, results were assessed assuming concentrations of 0, 0.5, and 1 × detection limits when sample concentrations registered below detection. Results assuming 0.5 × detection limits are presented in all tables and figures in the main article. Results assuming 0 and 1 × detection limits are presented briefly in

Tables S4 and S5 and used to provide an estimate of uncertainty driven by low sample concentrations. 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. These metals were selected due to their potential prevalence in DWTRs and urban stormwater (Grebel et al. 2013; Ippolito et al. 2011; Steele et al. 2015; Zhao and Yang 2010), 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).

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 expressed in percentage were calculated as:

$$\text{Removal efficiency (\%)} = ((M_{in} - M_{out})/M_{in}) \times 100$$

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 (Barfield et al. 1981). 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 (Davis 2008). Hydraulic detention time and R_{peak} values were used to assess bioretention system hydraulics.

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 (Shrestha et al. 2018; Winston et al. 2013) and were identified by inter-storm dry periods of at least 12 hours. Storm events were only included in this analysis when inflow and outflow volumes were accurately measured in all four bioretention cells. 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 (Shrestha et al. 2018). 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 (R Core Team 2016).

RESULTS

Captured Storms and Flow Volumes

Eight and thirteen distinct storm events were captured in the 2019 and 2020 field monitoring seasons, respectively (Table S2). 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 1). Although the experimental groups (Control and DWTR) received similar aggregate inflow volumes, 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 1). 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 1).

Stormwater P Species Composition and Removal

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 lower than the SRP, PP and TP values typically reported in urban bioretention studies (Dietz and Clausen 2005; Hunt et al. 2006; Komlos and Traver 2012; O'Neill and Davis 2011a; Shrestha et al. 2018). 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 nearly an order of magnitude lower than those reported by Liu and Davis (2014) and Song et al. (2015). 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}).

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 5; Table 1). The 2-year total mass removal efficiency 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 1). This difference in TP removal between the Control and DWTR cells was driven primarily by a major drop in SRP mass removal efficiency for the Control cells relative to the DWTR cells in the second (2020) monitoring season (Figure 5). During this period, the Control cells retained 30%-80% of SRP loads, while the DWTR cells retained 91%-93% of SRP loads (Table 1). Differences in P removal performance between the Control and DWTR cells also grew for PP during the 2020 monitoring season (Table 1).

In this study, water quality samples considered below the detection limits ranged from 20%-29% of the data, depending on the P species (Table S6). Outflow samples accounted for the majority (>80%) of samples below detection and non-detects accounted for a larger proportion of outflow samples for DWTR cells than Control cells. Compared to assigning non-detects a value of 0.5× detection limits, the 0 or 1× detection limits approaches slightly altered the 2-year mass removal efficiency values for SRP, PP, and TP by 0.5% – 2.0% across all bioretention cells (Tables S4 and S5). Further, statistical outcomes were uniform across the 0, 0.5, and 1× detection limits scenarios for these P species. However, for DOP, detection limit assumptions altered the 2-year mass removal efficiency values by 12%-42% and changed statistical outcomes for all bioretention cells, likely because DOP concentrations were extremely low in this study (Tables S5 and S6). Accordingly, future study is needed to confirm whether these low concentrations are typical and assess DOP removal performance of bioretention.

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

341 The observed P load reductions were due to both stormwater volume reductions (LR_{vol})
342 and P concentration reductions (LR_{conc}). However, LR_{conc} values far surpassed LR_{vol} values for
343 all bioretention cells and P species (Table S7), indicating that P concentration reductions were
344 the primary driver of P load reductions. Although the proportion of total load reductions
345 attributable to concentration reductions were high for both media treatments (63% - 99%), the
346 DWTR cells exhibited higher LR_{conc} values than the Control cells for all P species (Table S7).

347 Storm size also influenced P removal dynamics in this study. Both the Control and
348 DWTR cells exhibited uniformly high mass removal efficiency for all P species during small
349 storm events (rainfall < 25 mm; n=17) (Figure S1). However, removal efficiency values dropped
350 substantially for the Control cells during the few large storms (rainfall > 2.5 mm; n=4) but
351 remained relatively consistent across storm sizes for the DWTR cells (Figure S1).

352 **Hydraulic Detention Times and Peak Flow Ratios**

353 The addition of DWTRs to bioretention media did not affect system hydraulics in this
354 study. Hydraulic detention times for the bioretention cells were not statistically different from
355 one another ($p > 0.1$), exhibiting median values of 60-65 minutes for the Control cells and 49-67
356 minutes for the DWTR cells. Peak flow ratios (R_{peak}) for the bioretention cells were also not
357 statistically different from one another ($p > 0.1$), exhibiting median values of 0.15-0.19 for the
358 Control cells and 0.17-0.19 for the DWTR cells. The hydraulic detention time and peak flow data
359 are displayed in Figure 6 and Figure 7, respectively.

360 **Stormwater Heavy Metal Composition and Removal**

361 No evidence of heavy metal leaching from, or adsorption by, DWTRs was observed
362 during the study period. 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 8). 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 8a; $p > 0.1$). 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.

DISCUSSION

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 5, Table 1). The difference in P mass removal efficiency between the Control and DWTR cells was greater for dissolved P than particulate P (Table 1), which suggests that the enhanced P sorption capacity of the DWTR media was responsible for the improved P removal performance. While SRP removal efficiency values dropped by 16% and 59% between the 2019 and 2020 sampling seasons for the Small and Large Drainage Area Control cells, respectively, SRP removal efficiency 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 1). These results suggest that the P sorption complexes of the Control cells became saturated much faster than those of the DWTR cells. Additionally, these results 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 Control and DWTR 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 mass removal efficiency 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 1). 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 removal efficiency 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 1). DOP retention by DWTRs has been demonstrated in previous laboratory column studies (Yan et al. 2016a), but not in field bioretention studies (Liu and Davis 2014). The greater DOP removal efficiency values of the DWTR cells compared to the Control cells is likely due to increased P binding site availability in the DWTR media. However, inflow and outflow concentrations of DOP were very low in this study (Table 1), possibly due to the scarcity of organic matter in the bioretention media as well as 100% paved drainage areas with little surrounding vegetation or sediment sources. Statistically significant DOP removal was not found in any of the bioretention cells (Figure 3) and assumptions regarding below detection limit samples strongly influenced the magnitude of DOP loads. Consequently, strong conclusions regarding the impact of DWTRs on field DOP removal cannot be made. 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 (Cording et al. 2018; Davis 2007; Liu and Davis 2014; Roseen and Stone 2013; Shrestha et al. 2018). Nevertheless, the DWTR cells exhibited higher PP mass removal efficiency than the Control cells, particularly in 2020 (Table 1). 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 (Cording et al. 2018; Dietz and Clausen 2005; Hunt et al. 2006; Shrestha et al. 2018). Over the course of the study, the Control cells exhibited combined mass removal efficiency of 84% and 82% for TP and SRP (Table 1), respectively, and never released effluent that exceeded 0.025 mg SRP L^{-1} (Figure 3). 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 (Dietz and Clausen 2005; Hatt et al. 2009; Hunt et al. 2006), including two studies previously conducted in the exact hydrologic locations of the Control cells (Cording et al. 2018; Shrestha et al. 2018). 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 30.5 cm of media) and used compost derived from low P feedstocks (leaf litter), rather than higher P feedstocks (food and animal waste) (Cording et al. 2018; Shrestha et al. 2018). 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.

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, both mechanisms must be accounted for to isolate the impact of media designs on system performance (Liu and Davis 2014). Unlike other bioretention studies that have achieved P load reductions through stormwater volume reductions (Li and Davis 2009; Liu and Davis 2014), 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 1) and LR_{conc} values were higher (Table S7) 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 (Ament et al. 2021).

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 between storms by reducing the volumetric water content and thus increasing the water holding capacity of the soil media (Mullane et al. 2015; Zinger et al. 2021). Although total stormwater volume reductions were fairly high in this study (26%-52%) (Table 1), LR_{vol} values were relatively low (1%-37%) (Table S4). 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 1).

Storm size also influenced P removal performance of the bioretention cells, as Control cells exhibited lower removal efficiency values than DWTR cells during large storms for all P

454 species (Figure S1). Large storms can contribute disproportionately to annual urban P loads
455 (Shrestha et al. 2018), with four large storms (17% of the captured storms) transporting 59% of
456 total inflow SRP loads in this study. P removal also tends to be worse in bioretention systems
457 during large storms than small storms, with some systems exhibiting substantial dissolved P
458 export during large events (Shrestha et al. 2018). The capacity of DWTR-amended media to
459 effectively remove dissolved and particulate P via P concentration reductions during large storm
460 events is particularly relevant for stormwater practitioners seeking to reduce the required areal
461 footprint of bioretention systems, while maintaining P removal performance, in urban areas
462 where compacted soils and liners prevent infiltration.

463 Despite high P removal by the DWTR cells in this study, P retention was not as effective
464 as in prior column studies (Ament et al. 2021). The small discrepancy between lab and field
465 results in this research may be due to a variety of environmental factors. First, the lab experiment
466 did not include plants, which can facilitate preferential flow along their root networks (Muerdter
467 et al. 2016, 2018) and allow a portion of the stormwater to bypass the media. Second, prolonged
468 antecedent dry periods in the field can reduce media contact times by increasing the hydraulic
469 conductivity of bioretention media (Blecken et al. 2009; Hatt et al. 2009). Antecedent dry
470 periods and wetting and drying cycles were not simulated in the Ament et al. (2021) column
471 study, so it is unclear whether these factors affect P removal by DWTRs. Finally, field SRP
472 inflow concentrations exhibited a median value of 0.022 mg P L^{-1} compared to the 0.2 mg P L^{-1}
473 used in the column study. Because sorption processes are driven by equilibrium dynamics
474 (Ament et al. 2021; Li et al. 2016), very low influent P concentrations could suppress P sorption
475 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 improvement.

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 (Ament et al. 2021; Yan et al. 2017). 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. (2021). Additionally, the UNH DWTRs exhibited higher hydraulic conductivity and coarser texture than sand in Ament et al. (2021), so incorporating them into a sand-based media would place minimal restrictions on water flow. Nevertheless, hydraulic concerns can limit the use of P-sorbing amendments in bioretention systems (Liu and Davis 2014; Marvin et al. 2020; Penn and Bowen 2018; Poor et al. 2018; Yan et al. 2017) 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 (Barfield et al. 1981). 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

499 do reflect the relative differences in hydraulic detention time between the bioretention cells
500 monitored in this study and demonstrate that the DWTR used did not produce prolonged
501 detention times that can lead to excessive ponding and flooding.

502 **Impact of DWTRs on Heavy Metal Dynamics**

503 The presence of DWTRs did not affect heavy metal adsorption or leaching dynamics in
504 this bioretention study. Influent concentrations of all heavy metals were very low, which
505 prevented assessments of DWTR adsorption for As and Cd. Some evidence of Zn removal was
506 observed in this study, but these results were not unique to the DWTR cells and may be due to
507 Zn adsorption by organic media constituents (Davis et al. 2003; Li and Davis 2008). Effluent
508 concentrations of As, Cd and Zn were below the detection limit for all water samples, indicating
509 that the DWTRs and other bioretention media components used in this study did not leach these
510 metals during the monitored storms. Effluent concentrations of Mn were also below the detection
511 limit for all water samples, which is noteworthy because Mn leaching from DWTRs has been
512 identified as an environmental concern (Ippolito et al. 2011; Novak et al. 2007; Wang et al.
513 2014). All bioretention cells exhibited higher (but not statistically different) concentrations of Al
514 in effluent than influent (Figure 8a). The observation of minor Al leaching from all four cells
515 suggests that the sand, compost and gravel constituents of the media contribute a small amount
516 of Al to effluent loads. However, effluent concentrations of Al in this study averaged 0.028 mg
517 Al L^{-1}, which is far below the normalized chronic toxicity values for most aquatic species (U.S.
518 EPA 2018), and therefore likely would not threaten aquatic organisms in receiving waters.
519 Overall, these heavy metal results suggest that relatively small quantities of the DWTRs used
520 here 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.

Bioretention Media Design Implications

The observation of significant SRP concentration reductions by DWTR media in both this study and the preceding column study (Ament et al. 2021) highlight critical media design factors for achieving P removal with DWTRs in bioretention systems. In this study, media mixtures were created for two distinct bioretention layers: a 30.5 cm deep upper layer composed of 10% low P compost and 90% washed sand (by volume), and a 30.5 cm deep lower layer composed of 10% DWTR and 90% washed sand (by volume) (Figure 1). However, Liu and Davis (2014) rotated 5% DWTR by mass into the top 40 cm of a 50-80 cm deep existing sandy loam media and Houle (2017) 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 performance. 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 (Liu and Davis 2014) or organic matter content (Houle 2017). 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 (Liu and Davis 2014) or mixed them uniformly with organic components within a media blend (Houle 2017), which may have spatially prevented DWTRs from sorbing all internal sources of P. Finally, previous studies

incorporated DWTRs into bioretention media using backhoes (Roseen and Stone 2013), 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 that enabled effective P removal by allowing stormwater to fully contact the soil media.

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.

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 by P concentration reductions, which played a greater role in P removal for the DWTR cells. Differences in P removal performance between the Control and DWTR cells were 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 (Cording et al. 2018; Dietz and Clausen 2005; Hunt et al. 2006; Paus et al. 2014; Shrestha et al. 2018), 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 lab 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.

DATA AVAILABILITY STATEMENT

All data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPLEMENTAL MATERIALS

Figure S1 and Tables S1-S4 are available online in the ASCE Library (ascelibrary.org).

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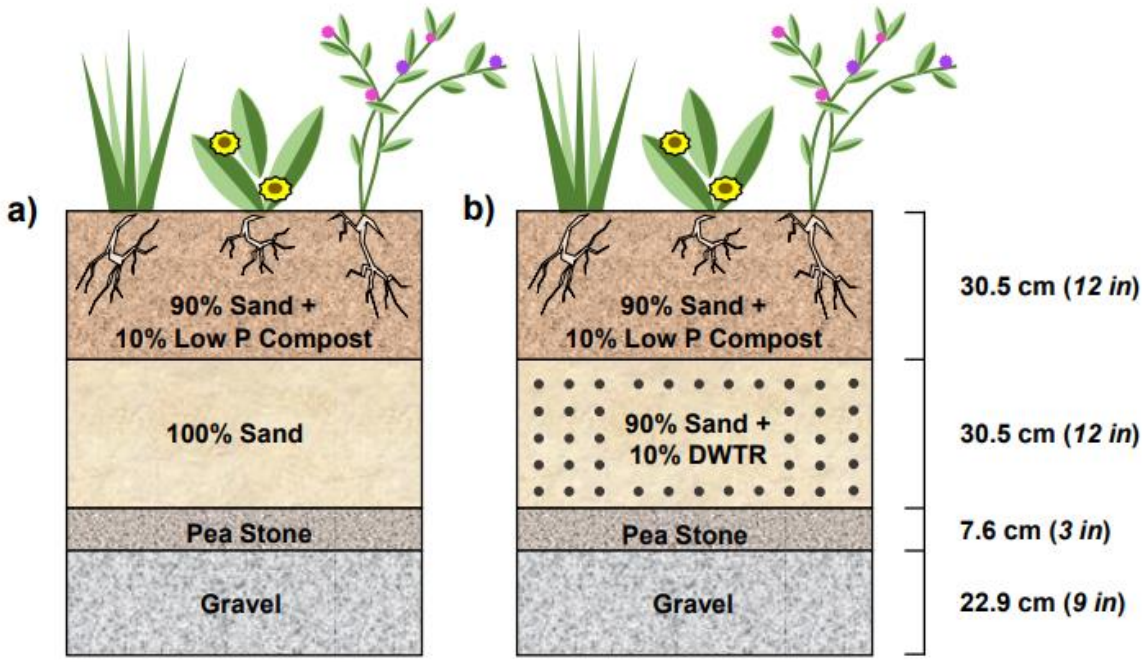
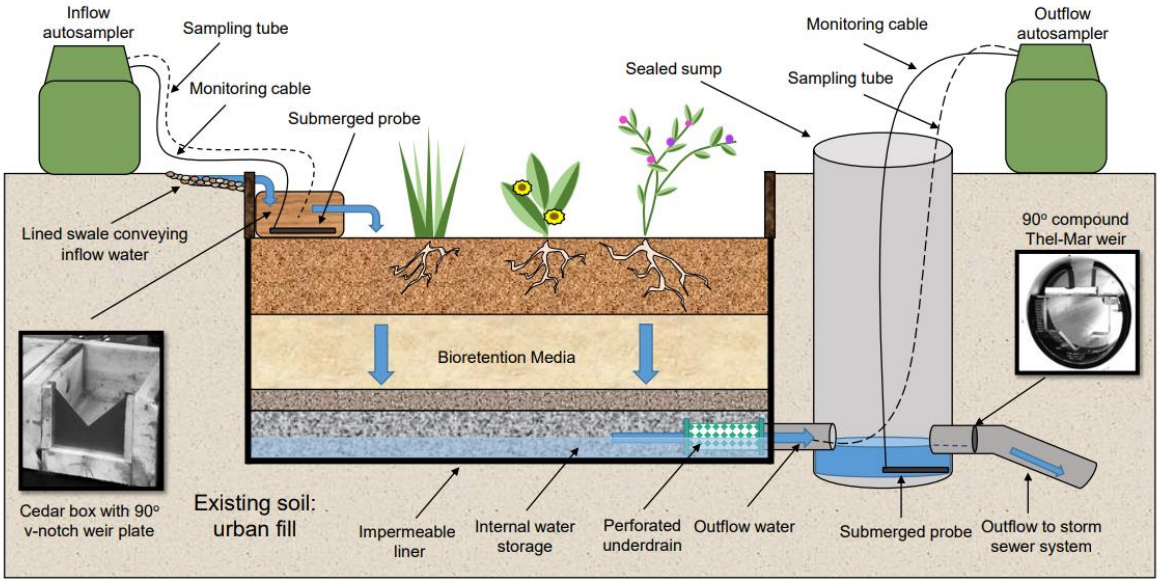
822 FIGURES



823

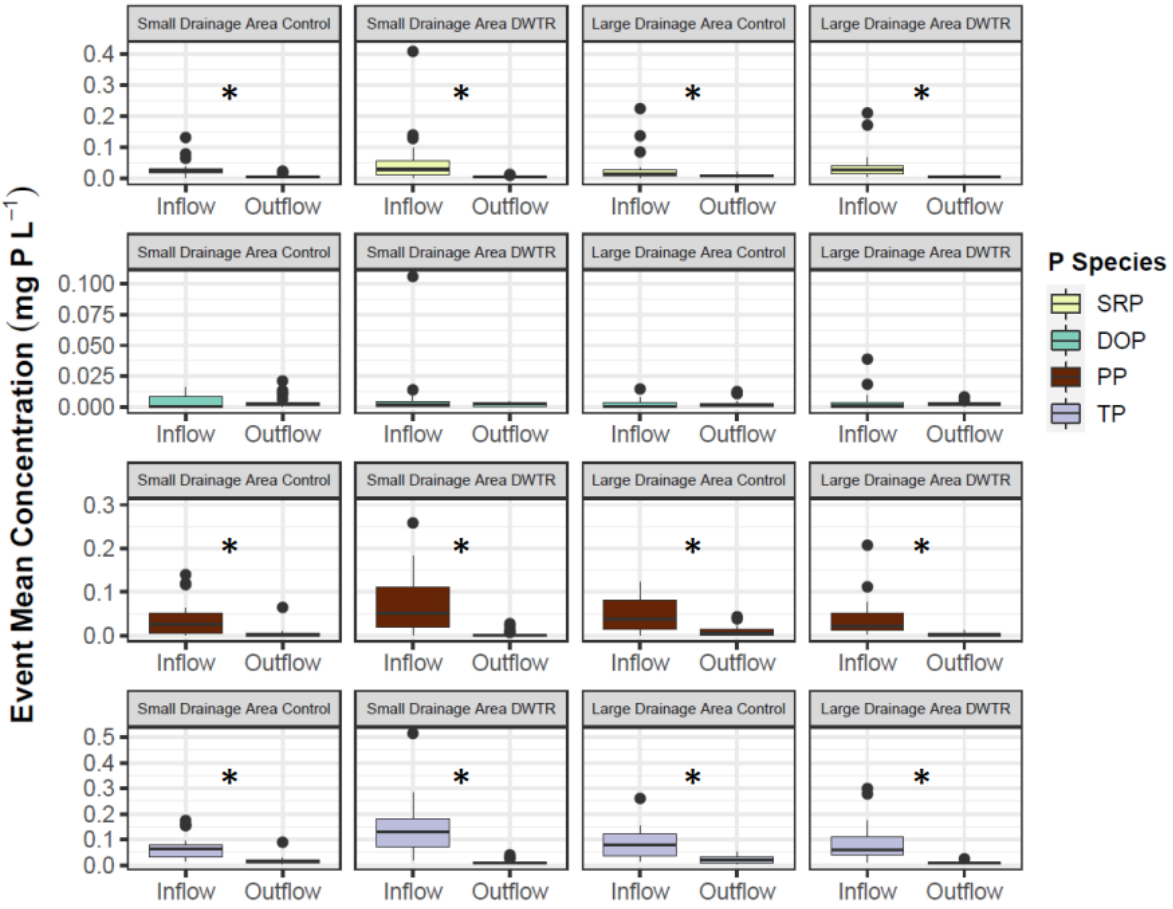
824 **Fig. 1.** Bioretention media profiles: **a)** Control media **b)** DWTR media



825

826 **Fig. 2.** Stormwater inflow and outflow monitoring systems. Weir photos are from Cording *et al*.

827 (2017).



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829 **Fig. 3.** Phosphorus (P) inflow and outflow event mean concentrations (EMC) for each

830 bioretention cell and P species. Box and whisker plots represent the distribution of EMC inflow

831 and outflow data for soluble reactive P (SRP), dissolve organic P (DOP), particulate P (PP), and

832 total P (TP) during all storm events captured during the 2019 and 2020 monitoring seasons (*n* =

833 21). Asterisks (*) between bars denote significant differences between inflow and outflow

834 EMCs ($\alpha = 0.05$). Note that the y-axes differ between P species.

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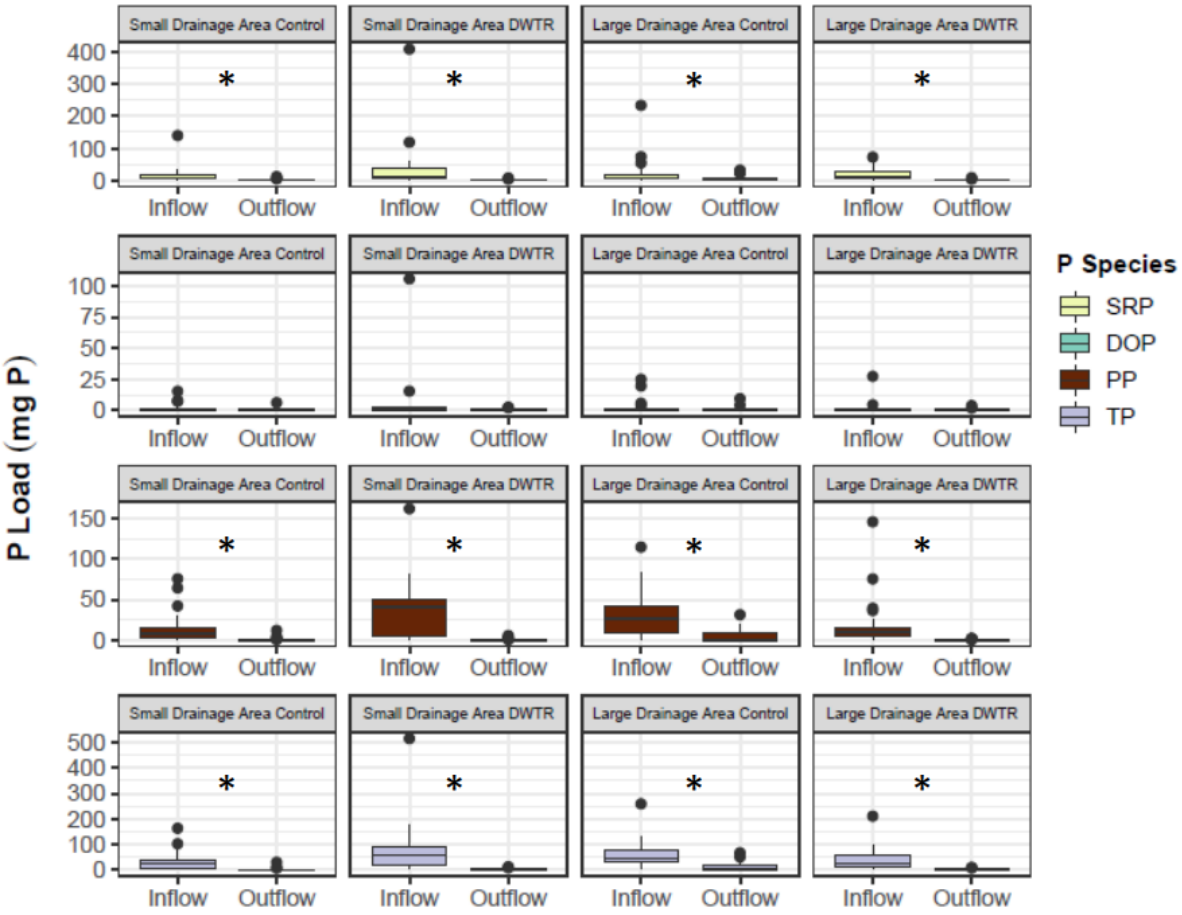

839

840 **Fig. 4.** Phosphorus (P) inflow and outflow mass loads for each bioretention cell and P species.
841 Box and whisker plots represent the distribution of inflow and outflow P load data for soluble
842 reactive P (SRP), dissolved organic P (DOP), particulate P (PP), and total P (TP) for all storm
843 events captured during the 2019 and 2020 monitoring seasons (n = 21). Asterisks (*) between
844 bars denote significant differences between inflow and outflow P loads ($\alpha = 0.05$). Note that the
845 y-axes differ between P species.

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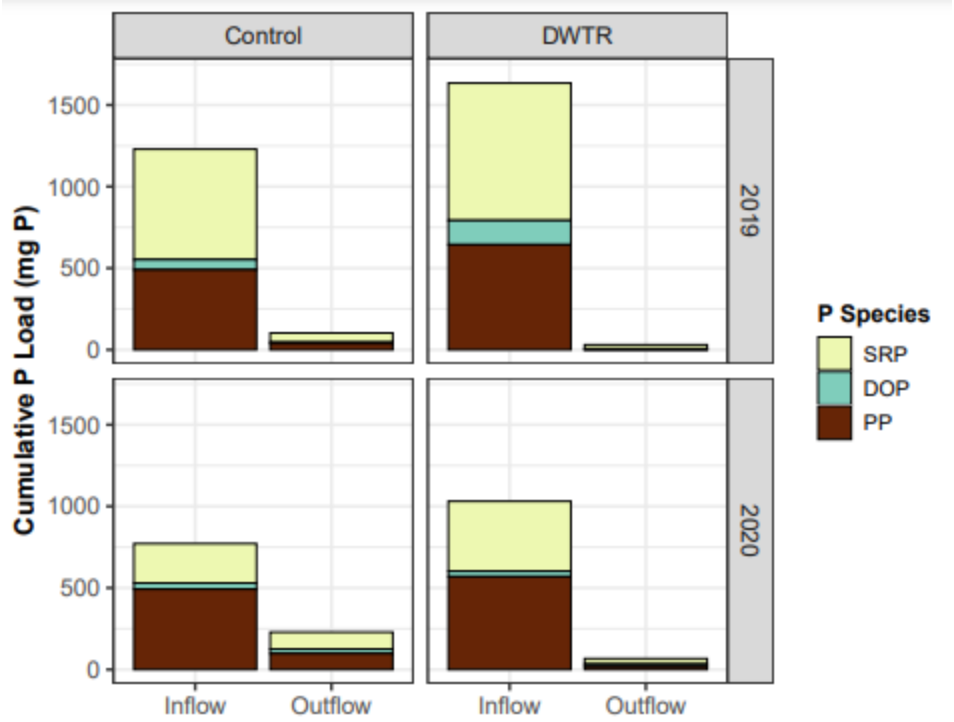
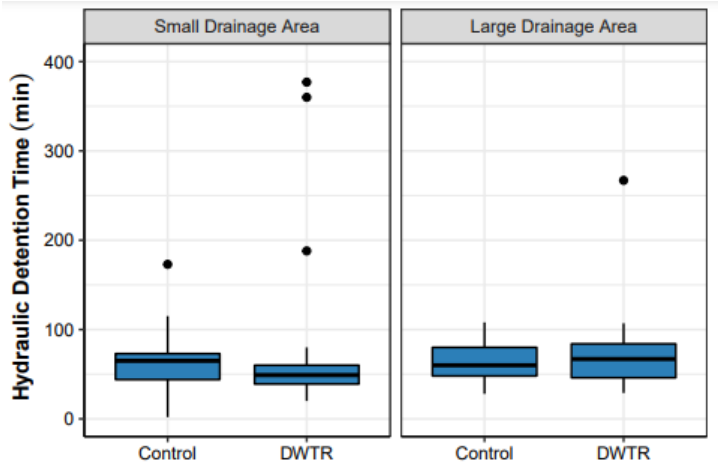


Fig. 5. Phosphorus (P) inflow and outflow loads for the Control media (2 bioretention cells) and drinking water treatment residual (DWTR) media (2 bioretention cells) cells. Bars represent the cumulative sum of loads captured in each of the media treatments during the 2019 (September-November; *n*=8 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.



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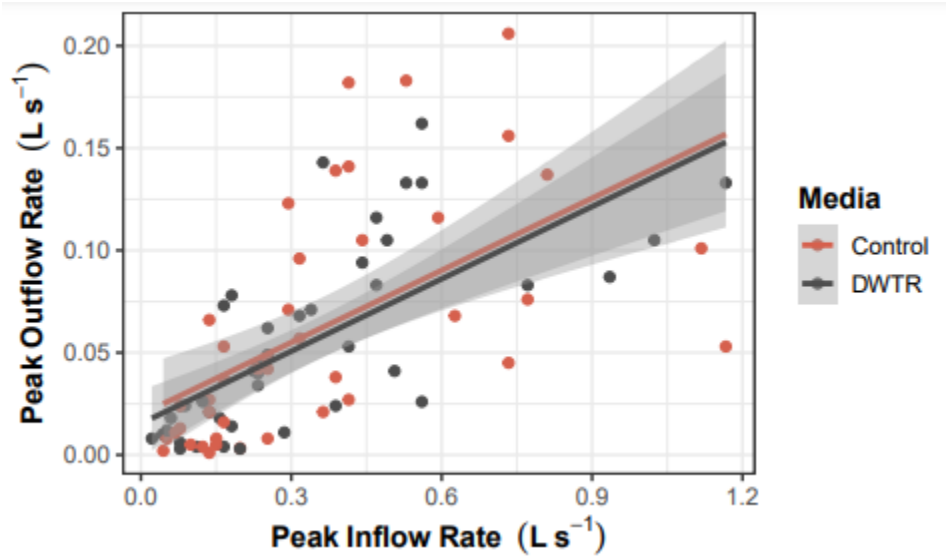
864 **Fig. 6.** Hydraulic detention times for each bioretention cell. Box and whisker plots represent the
865 distribution of detention times observed during all storms captured in the 2019 and 2020
866 monitoring seasons (n = 21).



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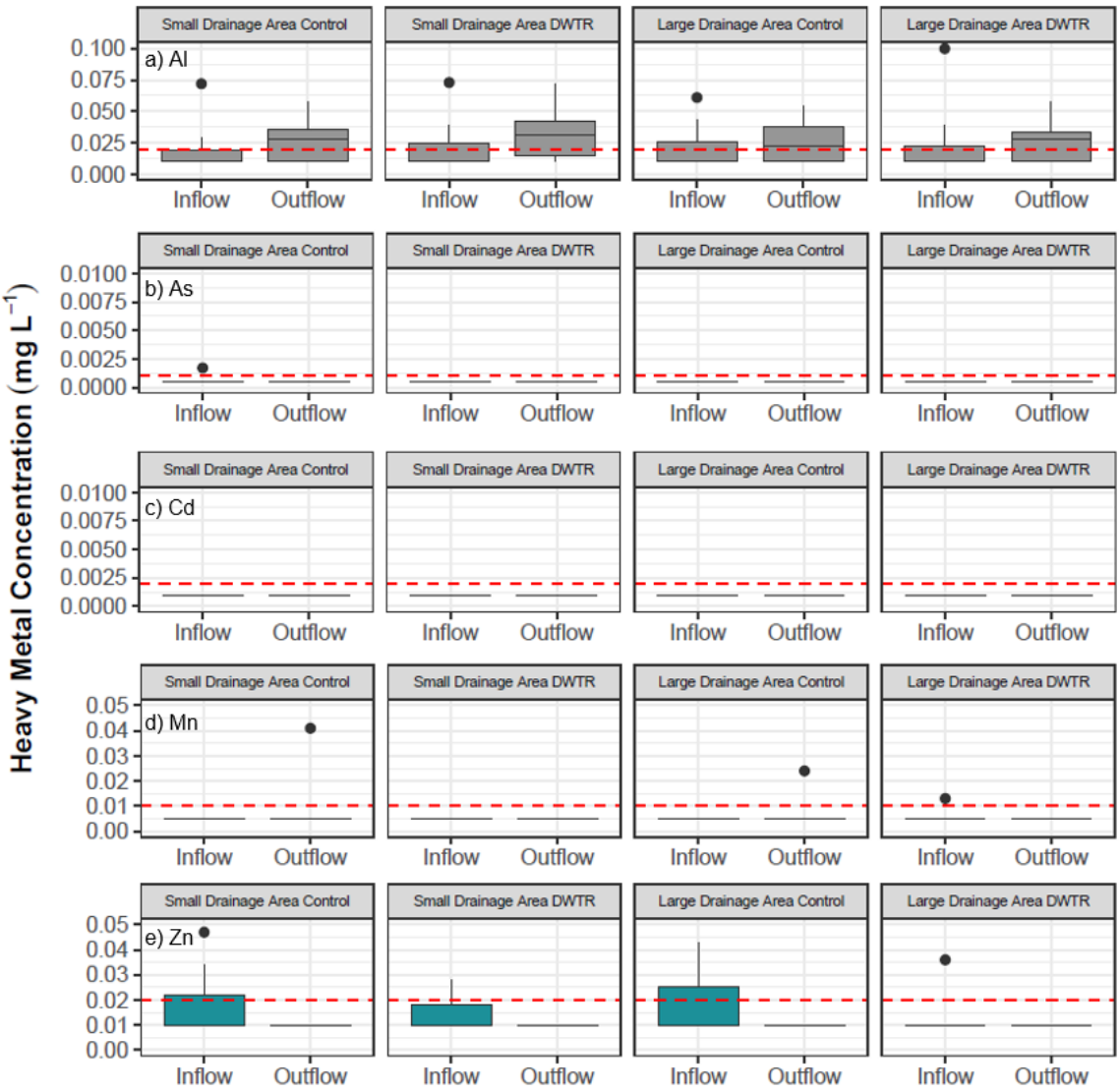
868 **Fig. 7.** Peak inflow and peak outflow rates from the Control media (2 bioretention cells) and
869 drinking water treatment residual (DWTR) media (2 bioretention cells) for all storm events
870 captured in the 2019 and 2020 monitoring seasons (n = 21). Shaded lines represent the least
871 squares regression line and 95% confidence interval for each media treatment.



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873 **Fig. 8.** Heavy metal inflow and outflow event mean concentrations (EMC) for each bioretention
874 cell. Box and whisker plots represent the distribution of inflow and outflow EMC data for
875 aluminum (Al), arsenic (As), cadmium (Cd), manganese (Mn), and zinc (Zn) during four storms
876 captured in 2019 and six storms captured in 2020. Red dashed lines indicate the detection limit
877 for each heavy metal specie. Note that the y-axes differ between metal species.

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TABLES

Table 1. 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) values 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

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