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Balancing Hydraulic Control and Phosphorus Removal in Bioretention Media Amended with Drinking Water Treatment Residuals

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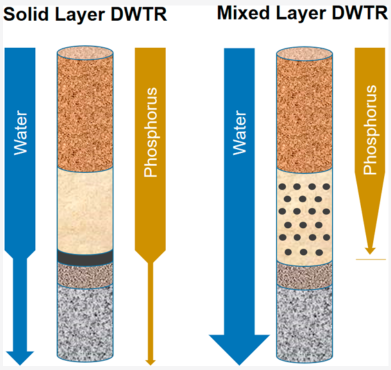
ABSTRACT: Green stormwater infrastructure such as bioretention can reduce stormwater runoff volumes and trap sediments and pollutants. However, bioretention soil media can have limited capacity to retain phosphorus (P) or even be a P source, necessitating addition of P-sorbing materials. We investigated the potential trade-off between P removal by drinking water treatment residuals (DWTRs) and hydraulic conductivity to inform the design of bioretention media. 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 DWTRs were applied to bioretention media, their impact on hydraulic conductivity and P removal depended on the 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.



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

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 particularly important 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 a high P sorption capacity.[11−13] Industrial byproducts, such as steel slag, fly ash, and drinking water treatment residuals (DWTRs), 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 conductivities.[16−19] This trade-off between hydraulic conductivity and P sorption capacity poses a significant challenge for simultaneously achieving stormwater drainage goals and P load reductions with GSI.

The trade-off 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 an 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] and leaching of P from compost,

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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 trade-offs between hydraulic conductivity and P removal is essential for the design of bioretention media. 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 trade-offs 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 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 under 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 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 widespread availability and high P sorption capacity in laboratory studies.[35−39] Our specific study objectives were (a) to quantify the P removal capacity that DWTRs exhibit across a range of P concentrations, contact times, and experimental methodologies, (b) to determine the physicochemical properties of DWTRs that govern hydraulic conductivity and P removal, (c) to determine the hydraulic and P removal impacts of two different DWTR layering strategies in bioretention media, and (d) to offer practical media design recommendations for simultaneously achieving hydrologic control and long-term P removal in bioretention systems.

2. MATERIALS AND METHODS

DWTR Sources. Three different DWTRs were obtained from the Champlain Water District (Burlington, VT), the Portsmouth Regional Water System (Portsmouth, NH), and the University of New Hampshire Water Treatment Plant (Durham, NH). These DWTR sources will henceforth be termed CWD, PORT, and UNH, respectively. The CWD plant uses aluminum sulfate ("alum") along with a 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 being tested.

Material Characterization. *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 (square meters per gram) were obtained using the three-point BET N_2 gas adsorption method (Particle Lab Technologies, Downers Grove, IL). Bulk densities (grams per cubic centimeter) 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}; centimeters per hour) were obtained using a constant head permeameter. Collected water volumes were converted to saturated hydraulic conductivity using Darcy's law.[16]

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: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 $[(P_{ox}/(0.5 \times (Al_{ox} + Fe_{ox})) \times 100]$,[44] with P_{ox}, Al_{ox}, and Fe_{ox} expressed as millimoles per kilogram.

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 μm 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 of P L^{-1}, and samples that measured below that value were set to 0.005 mg of P L^{-1} for statistical purposes.[8,11,26] All P removal values are expressed on an oven-dry mass basis.

Batch Isotherm Experiment. A multipoint batch isotherm technique[46] was used to estimate the maximum P sorption capacity of the DWTRs. Twenty milliliters of eight P concentrations (0, 1, 10, 25, 50, 75, 150, and 300 mg of P L^{-1} in 0.01 M KCl) added as KH_2PO_4 was continuously shaken (∼175 rpm) with 1 g of DWTRs 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 of P L^{-1} were used for the CWD DWTR to ensure saturation of its sorption complex. The maximum P sorption capacity (Q_{max}) was estimated using an optimization program[47] to fit the nonlinear Langmuir adsorption equation:

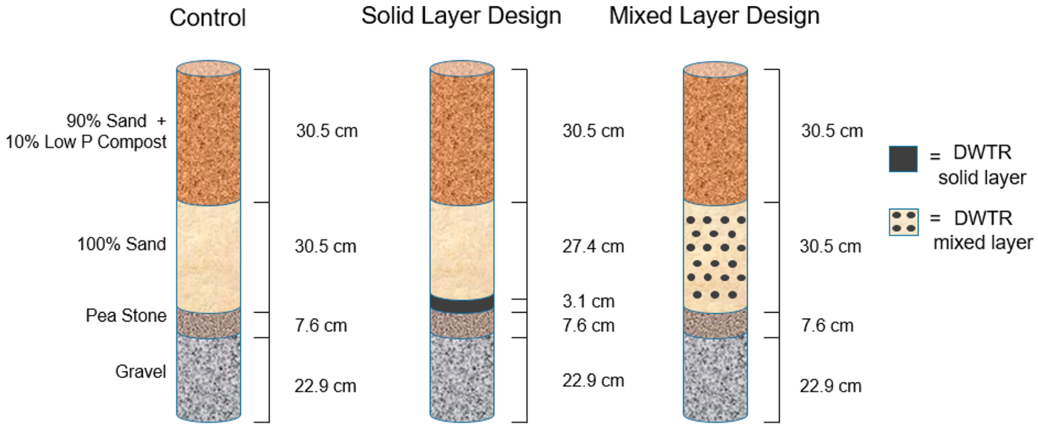

Figure 1. Profile of designs of bioretention media used in a large column experiment. Columns were 1.3 m in length and 15 cm in diameter. Drinking water treatment residuals (DWTRs) were added to offset 10% of the sand layer volume in both the solid and mixed layer designs. This amount of DWTR represents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

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

where Q_e is the quantity of P bound to the adsorbent at equilibrium (milligrams of P per kilogram), Q_{max} is the maximum P sorption capacity of the adsorbent (milligrams of P per kilogram), K is the Langmuir binding strength constant, and C_e is the equilibrium P concentration (milligrams of P per liter).

Flow-Through Column Experiments. Two continuous vertical upflow column experiments were conducted to determine P retention for each DWTR under 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, and prolonged media contact time), while the second assessed P retention under field-like conditions (i.e., low P concentration, neutral pH, and short media contact time). These experiments will henceforth be termed the "high-P/low-flow" experiment and the "low-P/high-flow" experiment, respectively.

In the high-P/low-flow experiment, 500 g of each DWTR was 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 of P L^{-1} in 0.01 M KCl, pH 4.6) vertically through the columns at a hydraulic loading rate of 1.5 L day^{-1} (~5−9 h media contact time). In the low-P/high-flow experiment, 5 g of each DWTR was mixed with 15 g 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 of P L^{-1} in 0.01 M KCl, pH 7) vertically through the columns at a hydraulic loading rate of 4.5 L day^{-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 °C for 2 weeks. To quantify the effects of prolonged dry periods on potential regeneration of P sorption capacity, dried columns were re-fed a P solution until the DWTRs returned to a state of P saturation. Finally, the P-free 0.01 M KCl solution was continuously fed through the columns for 1 week to measure P desorption.

P Removal Kinetics. A batch kinetic 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. Twenty milliliters of a P solution (10 mg of P L^{-1} in 0.01 M KCl) was added to 1 g of DWTR in centrifuge tubes and shaken continuously for variable lengths of time (1, 10, 60, and 360 min). P removal was calculated by subtracting effluent P concentrations from influent P concentrations. A flow-through kinetic experiment was also performed to determine P removal rates under more realistic conditions (influent P concentration of 0.2 mg of P L^{-1}, contact times of 1, 2, 4, 8, and 16 min), where P ions have limited contact opportunities with media surfaces (see the Supporting Information).

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 vs mixed (Figure 1)] were assessed among the three DWTR sources and compared to a non-amended control.

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). Then, 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).

Experimental Setup and Design. Test columns were composed of bioretention media in clear polycarbonate tubes (1.3 m in length, 15 cm in diameter) held in place by PVC end-caps (15 cm in 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). On the basis of the design assumptions of a 20:1

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Table 1. Summary of the Physical Properties for Each Drinking Water Treatment Residual Source

DWTR	effective grain size (d_{10}, μm)	uniformity coefficient (d_{60}/d_{10})	specific surface area (m^2 g^{-1})	bulk density (g cm^{-3})[a]	porosity[a]	K_{sat} (cm h^{-1})[a]
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] Values are means ± one standard deviation ($n = 3$).

Table 2. Summary of the Chemical Properties for Each Drinking Water Treatment Residual Source

DWTR	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	oxalate-extractable (mmol kg^{-1})[a]			P saturation ratio (%)[b]
					Al_{ox}	Fe_{ox}	P_{ox}	
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 ± one standard deviation ($n = 3$). [b] The P saturation ratio was calculated as $[(P_{ox}/(0.5 \times (Al_{ox} + Fe_{ox}))) \times 100]$.

catchment:treatment area ratio, 100 cm of annual rainfall, a runoff coefficient of 1.0, and an average dissolved P concentration of 0.1 mg of 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 United States[5,7,8,13,50,51] and assume a 100% impervious drainage area typical of parking lot and roadside environments. Before the experiment began, 15 L of reverse osmosis water was passed through each of the columns to remove potential air pockets within the media and weaken the influence of capillary suction forces.

The daily simulated storm 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 1 min 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 the 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.

Statistical Analyses. Statistical analyses were performed in R.[52] For the P sorption and retention experiments, one-way analyses of variance 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 the DWTR source and layering strategy on hydraulic conductivity and P removal. Linear models were fit to the data that regarded the 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 a layering strategy combination using varIdent. To assess how the DWTR source and layering strategy affected the hydraulic conductivity and P removal, post hoc pairwise comparisons were performed using the Tukey HSD test.

3. RESULTS AND DISCUSSION

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 the material texture and particle size exert strong control over hydraulic conductivity. CWD and PORT exhibited K_{sat} values that were 41% and 34% lower 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 the 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.

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 lower percentage of their amorphous metal oxides was already occupied by P. The 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.

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] The total Al oxide contents range from 2.9% to 16.9%, and the amorphous Al oxide contents range from 516 to 6133 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 h^{-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 study 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]

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 (flow-through column experiments) or retention values (column experiments) of the DWTR sources showed significant differences ($p < 0.001$), with CWD exhibiting values much higher than those of 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 11675 ± 440, 1347 ± 645, and 1479 ± 35 mg of 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 9576 ± 50, 1463 ± 13, and 1284 ± 49 mg of 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 40026 ± 1069, 10019 ± 3702, and 8668 ± 662 mg of 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 13−78% of their initial P retention capacities (Tables S1 and S2). Furthermore, DWTRs desorbed only 3−8% of the total P they retained in the column experiments, suggesting that the P sorbed by DWTRs is largely stable (Tables S1 and S2).

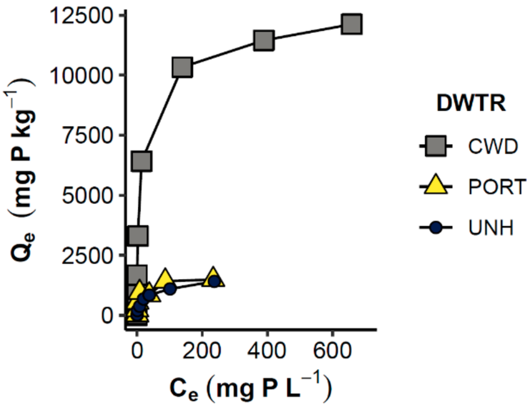

Figure 2. Phosphorus (P) sorption results from batch isotherm experiments. The points on the graph represent the mean ($n = 3$) quantity of P retained at equilibrium (Q_e) and the corresponding mean equilibrium concentrations (C_e) across a range of influent concentrations (0, 1, 10, 25, 50, 75, 150,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

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 4 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, the specific surface area was the best indicator of P sorption capacity, as CWD exhibited by far the largest surface area and the highest sorption capacity. These results suggest that the 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.

The results from this study clearly illustrate a trade-off between hydraulic conductivity and P removal for DWTRs. CWD was the finest material and had the lowest K_{sat} and highest P sorption capacity. UNH was the coarsest material and had the highest K_{sat} and the lowest P sorption capacity. However, the 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 small (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.

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 a level of 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 1400 to 55300 mg of P kg^{-1} amendment.[15] Similarly, the DWTRs in this study varied >4-fold in their P sorption capacity or retention values across experimental methods (batch isotherms, 1347−11675 mg of P kg^{-1}; low-P/high-flow, 1284−9576 mg of P kg^{-1}; high-P/low-flow, 8668−40026 mg of 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.

Intermethodological differences in P removal values may account for some of the variation in the literature and have implications for bioretention media design recommendations. While most column studies use synthetic stormwater with P concentrations of <5 mg of P L^{-1},[15] some have used very high P concentrations (5−400 mg of 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 designs of media 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 of P L^{-1}) (Table S3).

In this study, the high-P/low-flow experiment yielded P retention values that were 4−7 times greater than those of the low-P/high-flow experiment. The P retention values from the

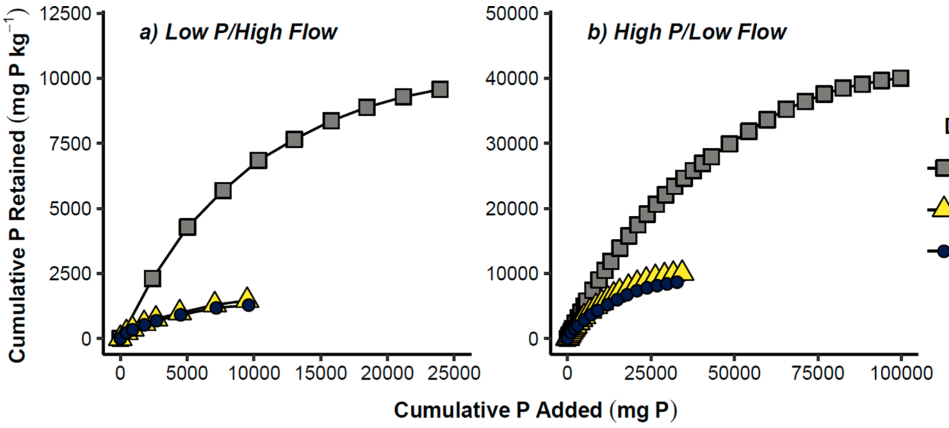

Figure 3. Phosphorus (P) retention results from (a) low-P/high-flow column experiment (influent concentration of 1 mg of P L^{-1}, contact time of 3 min) and (b) high-P/low-flow column experiment (influent concentration of 300 mg of P L^{-1}, contact time of 5−9 h). The points on the graph represent the mean cumulative P retained (n = 3) by drinking water treatment residuals (DWTRs) at different levels of cumulative added P on an oven-dry mass basis. DWTRs from the Champlain Water District (CWD), Portsmouth Regional Water System (PORT), and the University of New Hampshire Water Treatment Plant (UNH) were analyzed. Note that the x- and y-axes differ between panels a and b.

high-P/low-flow experiment represent the theoretical P retention capacity of the DWTRs under conditions ideal for P removal, where a high P concentration with prolonged medium contact drives increased adsorption, diffusion of P 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 represent 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 being 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 isotherm 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, and 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.

Sorption Kinetics. The rate of P sorption was rapid for all DWTRs in the batch kinetics (Figure 4) and flow-through kinetic (Figure S1) experiments. After 1 min of shaking in the batch experiment, CWD, PORT, and UNH removed approximately 90%, 67%, and 62% of the added P, respectively (Figure 4). After 360 min 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 min), though the influent concentration was 0.2 mg of P L^{-1} instead of the value of 10 mg of P L^{-1} used in the batch

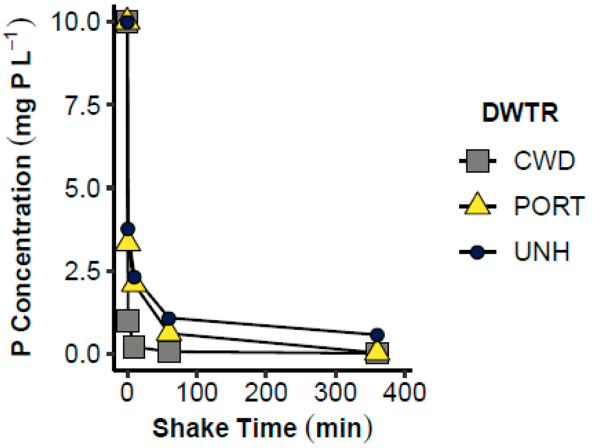

Figure 4. Batch kinetic experiment results. Graph points represent the mean phosphorus (P) concentration (n = 3) of the supernatant across shake times of 1, 10, 60, and 360 min. The initial P concentration of the added solution was 10 mg of P L^{-1}. Drinking water treatment residuals (DWTRs) from the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

experiment. These results indicate that P sorption is rapid enough to be effective in relatively high-flow bioretention contexts but can be improved with an extended contact time. They also indicate that sorption processes are highly effective, even at low P concentrations common in stormwater runoff.

Large Column Experiment. The effect that DWTRs had on the hydraulic performance of the designs of media 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 decreased the 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 5; Tukey's post hoc contrasts; $p > 0.1$).

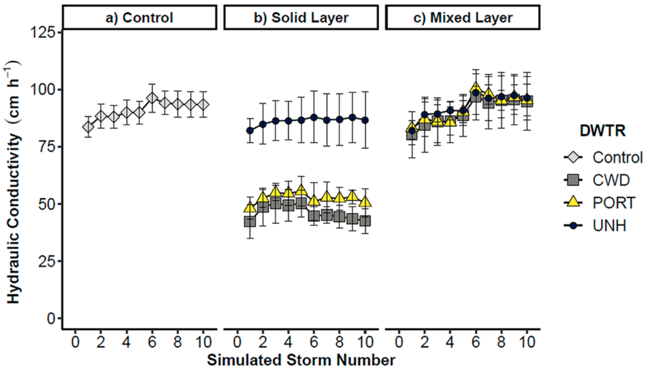

Figure 5. Large column hydraulic conductivity results. The points on the graph represent the mean hydraulic conductivity ± one standard deviation (n = 3) for each simulated storm event. Drinking water treatment residuals (DWTR) from the Champlain Water District (CWD), the Portsmouth Regional Water System (PORT), and the University of New Hampshire Water Treatment Plant (UNH) were analyzed.

These results correspond with the K_{sat} values from Table 1, which show that the hydraulic conductivities of CWD and PORT were lower than that of sand and the hydraulic conductivity of UNH is slightly higher than that of 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 5a,b). 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 5a,c). These results demonstrate that fine-textured amendments such as DWTRs can restrict water flow when amendment K_{sat} values are lower than that of the surrounding media. However, these hydraulic restrictions can be alleviated by mixing DWTRs with slightly coarser constituents like sand.

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 6; 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 6b,c). The P sorption capacity of the added DWTRs (2670, 690, and 535 mg of 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 of 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 nearly complete P removal. The mixed layer design therefore achieved better hydraulic and P removal results than the solid layer design.

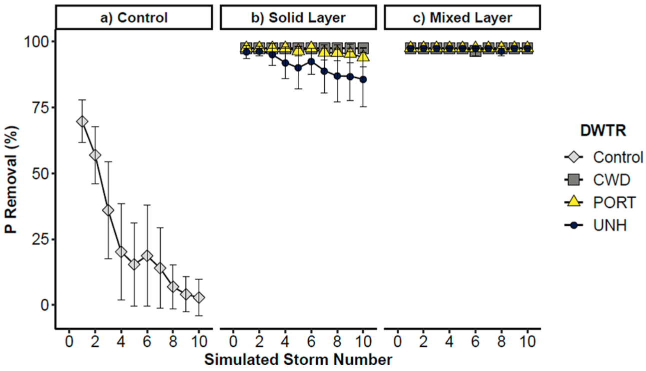

Figure 6. Large column phosphorus (P) removal results. The points on the graph represent the mean P removal (%) ± one standard deviation (n = 3) for each simulated storm event. The initial P concentration of added solution was 0.2 mg of P L^{-1}, so a maximum of 97.5% removal was possible due to analytical detection limits. Drinking water treatment residuals (DWTRs) from the Champlain Water District (CWD), the 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.

On the basis of 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 (Tables S1 and S2). On the other hand, P removal efficiencies decrease rapidly as P-sorbing materials are saturated (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 above the pea stone layer may be a sufficient quantity for high-performance materials like CWD, larger proportions may be required for DWTR amendments with lower P sorption capacities, or in cases in which P-rich compost is included in the bioretention media.

4. CONCLUSION

This is the first study to clearly document the possible trade-off 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. The 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 those of the DWTRs used in this study. However, field data are required to confirm long-term performance. Finally, the hydraulic and P removal performance in the mixed layer design in our large column experiment was better than that of the solid layer design. We therefore suggest mixing fine-textured P-sorbing materials with slightly coarser materials, such as washed sand, to mitigate potential trade-offs between hydraulic conductivity and P removal in bioretention media designs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.0c00178.

> Flow-through kinetics experiment (Supplementary Methods), phosphorus retention, binding site regeneration, and desorption results from flow-through column experiments (Table S1 and S2), isotherm and column study comparisons at matching equilibriums (Table S3), and results of flow-through kinetic experiments (Figure S1) (PDF)

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Notes

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