Bioretention Column Studies of Phosphorus Removal from Urban Stormwater Runoff

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ABSTRACT: This study investigated the effectiveness of bioretention as a stormwater management practice using repetitive bioretention columns for phosphorus removal. Bioretention media, with a higher short-term phosphorus sorption capacity, retained more phosphorus from infiltrating runoff after 3 mg/L phosphorus loading. A surface mulch layer prevented clogging after repetitive total suspended solids input. Evidence suggests that long-term phosphorus reactions will regenerate active short-term phosphorus adsorption sites. A high hydraulic conductivity media overlaying one with low hydraulic conductivity resulted in a higher runoff infiltration rate, from 0.51 to 0.16 cm/min at a fixed 15-cm head, and was more efficient in phosphorus removal (85% mass removal) than a profile with low conductivity media over high (63% mass removal). Media extractions suggest that most of the retained phosphorus in the media layers is available for vegetative uptake and that environmental risk thresholds were not exceeded. *Water Environ. Res.,* **79,** 177 (2007).

KEYWORDS: stormwater, phosphorus, bioretention, runoff, leaching, eutrophication, fertility.

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Introduction

Phosphorus is an essential macronutrient for plant growth. Through leaching and transport processes, however, excess phosphorus can endanger the quality of surface waters. Phosphorus inputs to water bodies are under close scrutiny because of the contribution of phosphorus to water eutrophication and algal blooms, which result in the depletion of dissolved oxygen and high turbidity levels in aquatic ecosystems. These impairments ultimately can lead to poor water quality and the loss of biodiversity in water bodies. According to recent surveys (U.S. EPA, 1998), phosphorus is a leading pollutant for impaired surface waters (including rivers, lakes, reservoirs, ponds, estuaries, lake shorelines, and ocean shorelines) and groundwater.

In developed areas, because impervious surfaces result in a significant fraction of impinging rainfall becoming runoff, urban runoff is a major source of non-point-source pollution (U.S. EPA, 1996). Phosphorus found in urban runoff originates from lawn fertilizers, atmospheric deposition, soil erosion, animal waste, and detergents (U.S. EPA, 1999). In runoff, phosphorus is distributed as both dissolved (particle size <0.45 μm as operational definition) and particulate (phosphorus sorbed onto the solids before or after transport in the runoff [Sharpley, 1985], with particle size >0.45 μm). Both dissolved and particulate phosphorus include organic phosphorus components. A considerable total suspended solids (TSS) load is common in urban stormwater runoff (Characklis and Wiesner, 1997). Several pollutants, including phosphorus and many metals (Sansalone and Buchberger, 1997), are commonly associated with particulate matter; TSS is a frequently reported parameter for runoff quality.

Bioretention is a low-impact development best management practice (BMP) for urban stormwater runoff. It is a filtration/infiltration practice with surface vegetation and a mulch layer, sized at approximately 4 to 5% of the drainage area. During rainfall events, runoff is directed into a bioretention facility, with excess runoff temporally held on the ponding surface once the intensity of rainfall exceeds the media infiltration capacity. Bioretention media (typically mixes of soil, sand, and organic matter) can remove infiltrating pollutants through several mechanisms, including filtration, adsorption, ion exchange, and precipitation. Approximately 0.8 m of media are placed over an underdrain, which leads to the traditional storm drain system, or directly to surface waters. By using high-permeability engineered media, bioretention can further promote rapid runoff infiltration to achieve the goals of both runoff quality protection and flood/erosion control. Evapotransporation can also contribute to runoff volume reductions.

Retention of phosphorus in bioretention facilities decreases the phosphorus load to downstream waterways. Retention mechanisms of phosphorus combine physical, chemical, and biological processes. The continuum of chemical phosphorus sorption processes is generally categorized into fast and slow reactions (McGechan and Lewis, 2002). Fast reactions are characterized by the reversible sorption of phosphorus onto media surface sites. Slow reactions include the deposition of phosphorus within iron and aluminum oxide mineral structures and the precipitation of calcium phosphates; slow reactions are strongly pH-dependent. Phosphorus removal depends not only on chemical phosphorus sorption, but also on the geometry of the flow system (Sawhney and Hill, 1975); diffusion processes in the soil matrix (Reddy et al., 1999); filtration processes (Heathwaite and Dils, 2000); vegetative uptake; microorganism degradation processes; and sedimentation and entrainment (Reddy et al., 1999; Van Cuyk et al., 2001). Previous work has shown that approximately 80% of dissolved phosphorus was removed by a sandy loam soil in two laboratory-scale pilot bioretention cells (Davis et al., 2001). Similar studies have demonstrated 70 to 85%

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Table 1—Bioretention media chemical and mechanical analyses (Hsieh and Davis, 2005).

	d_{10}*	d_{60}*			mg/100 g				Organic matter content	Cation exchange capacity	Sand	Clay	Silt	
	mm	mm	d_{60}/d_{10}*	pH	Magnesium	Phosphorus	Potassium	Calcium	%	meq/100 g soil	%	%	%	Classification
Sand I	0.30	0.84	2.8	5.0	2.5	4	0.8	0.8	0.10	0.4	92	5	3	Sand
Sand II	0.17	0.30	1.8	7.1	9.5	5	3	2.8	0.15	1.1	95	3	2	Sand
Soil I	0.09	0.29	3.2	6.7	28	7.5	35	No data collected	4.40	No data collected	71	17	12	Sandy loam
Soil II	0.09	0.20	2.2	7.8	29	12	21	>44	2.20	19	66	19	15	Sandy loam
Soil III	0.10	0.32	3.2	7.1	27	9.9	18	68	3.50	15	71	14	15	Sandy loam
Mulch	0.15	2.31	15.4	7.1	28	56	35	>44	29.8	34				

* d_{10} = effective size (10th percentile diameter); d_{60} = 60th percentile diameter.

phosphorus removal, correlated with media depth, in pilot- and full-scale bioretention facilities (Davis et al., 2006).

After being retained, captured phosphorus can be used as a nutrient for plant growth in bioretention facilities, which possibly would allow a removal pathway via harvesting the vegetation (Davis et al., 2006). For vegetative purposes, dissolved inorganic phosphorus is typically considered as bioavailable and can be used for plant nutrition (Rechcigl, 1995; Reddy et al., 1999). With respect to environmental concerns, the mobility of phosphorus compounds in soils determines the potential of retained phosphorus to present detrimental risk to ground and surface water quality. Overall, high plant availability and low mobility are preferred for environmental phosphorus management.

Two issues regarding phosphorus removal in bioretention were addressed in this study. Various bioretention media possess different short- and long-term phosphorus sorption capacities. Soil phosphorus sorption capacities can vary widely (Sawhney and Hill, 1975). Similarly, sands with a high metal content (calcium, aluminum, or iron) demonstrated much higher phosphorus-removal capacity than those with lower concentrations of these metals (Arias et al., 2001). Also, the chemical properties of a media do not fully predict the mobility of phosphorus through media with macroporosity (Cox et al., 2000), because phosphorus removal in columns may not occur by simple sorption processes alone (Van Cuyk et al., 2001). Previous studies with various media columns and existing bioretention facilities have indicated variable phosphorus removals that do not correlate well with the measured media properties (Hsieh and Davis, 2005).

The first objective of this work was to investigate correlations between media short-term phosphorus sorption characteristics and total phosphorus removal through bioretention columns. The short-term phosphorus sorption capacity of sands, soils, and mulch used as bioretention media was examined, with three continuous-flow bioretention columns, with media consisting of different soil-to-sand ratios.

Second, two bioretention columns configurations were tested for phosphorus removal and accumulation over multiple-loading periods (80 to 120 days). The study objectives were to investigate the effect of two media layer configurations (media with low hydraulic conductivity overlaying one with high hydraulic conductivity, and media with high hydraulic conductivity overlaying one with low hydraulic conductivity) on runoff infiltration rate and to evaluate the effectiveness of these two columns for phosphorus removal. Three-layer media, with different media components and configurations, were used in each column to maximize the runoff infiltration rate and phosphorus and TSS removal efficiencies. Effects of capillary barriers between two media layers were examined, with corresponding phosphorus removal efficiency as a function of time, resulting from the consumption of phosphorus sorption capacity of the media. Environmental and agronomic soil tests were conducted on the media from one column before and after repetitive experiments to examine the potential for phosphorus leaching from the bioretention media and to quantify available phosphorus for future plant growth.

Materials and Methods

Materials. Two types of sand (sand I and II); three soils (soil I, II, and III); and one mulch material were used. The sands, with different mean particle sizes, were obtained from a local home supply store. Before all experiments, both sands were washed using the silica sand washing procedure (Kunze and Dixon, 1989). All soils were obtained locally from the Prince George's County Department of Public Works and Transportation (Maryland). Mulch used in the experiments was obtained from the College Park City Department of Public Works (College Park, Maryland). Characteristics of these media are summarized in Table 1 (Hsieh and Davis, 2005).

Batch Phosphorus Sorption Tests. To determine the short-term phosphorus sorption capacity of different media, different masses (0.2 to 70 g) of each medium were shaken in 100-mL plastic bottles containing 3 mg-P/L sodium phosphate, dibasic (Na_2HPO_4) (J.T. Baker, Phillipsburg, New Jersey). The suspension was equilibrated at laboratory temperature (22°C) for 24 hours. The initial pH was controlled at 7.0 ± 0.3. After 24 hours, an aliquot of the suspension was centrifuged and filtered through Pall Gelman GF/C filters (0.2 μm) (Pall Corporation, East Hill, New York), and the concentration of dissolved phosphorus was determined (section 4500-P of *Standard Methods*, APHA et al., 1995). Another unfiltered aliquot was used for measuring the pH value (final pH ranged from 6.7 to 7.4). The amount of phosphorus sorbed was calculated from the decrease in the solution phosphorus concentration. Solutions without any added media served as controls.

Continuous Column Tests. Three small columns (Plexiglas, 40 cm long × 6.4 cm inner diameter), with different ratios of sand-to-soil, were used to investigate phosphorus uptake. The media compositions (soil I/sand I, percent mass basis, total mass = 1350 g) for these three columns were 30/70, 50/50, and 70/30. The flowrate was held constant, at 3.1 mL/min (0.97 mm/min loading). The influent contained 3 mg-P/L Na_2HPO_4, maintained at pH 7.0 ±

Table 2—Characteristics of synthetic urban runoff used in repetitive column studies (Hsieh and Davis, 2005).

Water quality parameter	Unit	Value	Source
pH	—	7.0	HCl or NaOH
Total dissolved solids	mg/L	120	$CaCl_2$
Phosphorus	mg/L as P	3	Na_2HPO_4
Nitrate	mg/L as N	2	$NaNO_3$
Ammonium	mg/L as N	2	NH_4Cl
Lead	mg/L	0.1	$PbCl_2$
Suspended solids	mg/L	150	Local soil sieved through a 0.59-mm opening
Motor oil	mg/L	20	Used oil from local garage

0.3. During the experiment, influent was pumped continually to the top of the column, and effluent was collected from the bottom of the column every day, for a total of 29 days. Effluent samples were filtered through Pall Gelman GF/C filters (0.2 µm) and analyzed for phosphorus concentration.

Repetitive Bioretention Column Tests. Two bioretention columns were tested for phosphorus removal and accumulation over multiple loading periods (80 to 120 days). The two columns were designated as RP1, media with low hydraulic conductivity overlaying one with high hydraulic conductivity; and RP2, media with high hydraulic conductivity overlaying one with low hydraulic conductivity. A 110-cm bioretention column and synthetic runoff were prepared as described previously (Hsieh and Davis, 2005) to investigate effects of media component and configuration on runoff infiltration and phosphorus removal. The media used in RP1 included a top mulch layer (5 cm and 0.82 kg), a middle porous soil II layer (15 cm and 8.17 kg), and a bottom sand II layer (75 cm and 30.9 kg). According to previous work using identical column conditions (Hsieh and Davis, 2005), sand II is more permeable (0.83 cm/min at 15 cm head) than the mulch (0.28 cm/min) or soil II (0.28 cm/min). Therefore, less permeable mulch and soil layers were designed to overlay the high-permeability sand layer in this testing column, which is also a typical configuration used in surface, organic, and pocket sand filters. An alternative three-layered media design was used for RP2. A composite media was synthesized homogeneously, by mixing 3.06 kg mulch, 3.06 kg soil III, and 6.13 kg sand I, and placed at the top (30 cm). The middle layer was 23.2 kg sand II (55 cm), and the bottom was 5.9 kg soil III (10 cm). The mulch and soil material should provide sufficient organic matter to serve as plant growth media (Table 1). The organic matter also should serve as an energy source for microorganisms involved in phosphorus (and nitrogen) cycling. Sand I should increase porosity, allowing greater infiltration to treat larger volumes of runoff.

During the experiment, runoff was applied to the RP1 bioretention column 12 times, each after a 4- to 14-day dormant period. Similarly, 16 RP2 tests were completed. The characteristics of simulated runoff used in the repetitive columns are summarized in Table 2. For every run, the simulated runoff was stored in a 200-L plastic container with a large mixer. At the start of the experiment, runoff was pumped into the column from the top, and the first sample was collected. Over a 6-hour period, samples were collected every hour from the column effluent and taken to calculate the flowrate and measure the phosphorus concentration. The water head was maintained constant, at 15 cm, by controlling the pumping rate during the experiment.

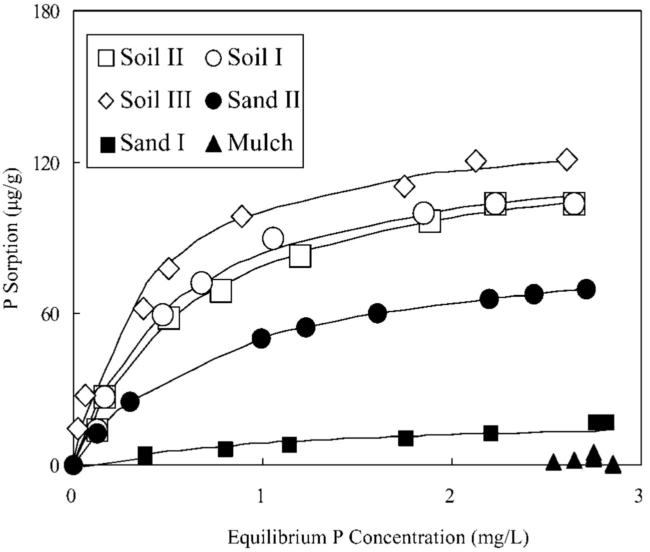

Figure 1—Phosphorus sorption isotherms for different media (pH = 7, initial phosphorus = 2.85 mg/L). Line is fit of Langmuir isotherm (eq 1).

Media Phosphorus Analyses. Media samples were collected from different depths in RP2 before and after the total runoff application and analyzed for water-soluble phosphorus (WSP), calcium chloride phosphorus ($CaCl_2$-P), Mehlich-I extractable phosphorus, and Mehlich-III extractable phosphorus. Water-soluble phosphorus and $CaCl_2$-P have been used to predict the leaching potential or bioavailability of phosphorus retained in soils (Maguire and Sims, 2002; McDowell et al., 2001; Sims et al., 2001). Mehlich-I and Mehlich-III extractable phosphorus are agronomic soil tests. The WSP was determined by mixing 2.5 g media with 25 mL deionized water for 1 hour (Maguire and Sims, 2002). The $CaCl_2$-P was analyzed by shaking 5 g media with 20 mL 0.01-M calcium chloride ($CaCl_2$) for 24 hours (Maguire and Sims, 2002). Mehlich-I extractable phosphorus was determined by shaking 2.5 g media with 10 mL Mehlich-I reagent (0.05-M hydrochloric acid [HCl] + 0.0125-M sulfuric acid) for 5 minutes (Sims and Heckendorn, 1991). Mehlich-III extractable phosphorus was determined by shaking 2.5 g media with 25 mL Mehlich-III reagent (0.2-N glacial acetic acid + 0.25-N ammonium nitrate + 0.015-N ammonium fluoride + 0.013-N nitric acid + 0.001 M ethylenediaminetetraacetic acid) for 15 minutes (Mehlich, 1984). Phosphorus in all extractants was analyzed using the method of Murphy and Riley (1962). The absorbance of the molybdophosphate complex was measured via spectrophotometry at 712 nm.

Results and Discussion

Initial batch and small-column studies were completed with only dissolved phosphorus to evaluate soluble phosphorus interactions with the media. Large-column experiments contained a more realistic matrix of pollutants, and phosphorus was present in both soluble and particulate forms.

Short-Term Phosphorus Sorption. Phosphorus sorption isotherms were determined for all media used in this study at pH 7 (Figure 1). Apparent short-term phosphorus sorption capacity for each medium was calculated using the Langmuir isotherm equation, as follows (Sparks, 1995):

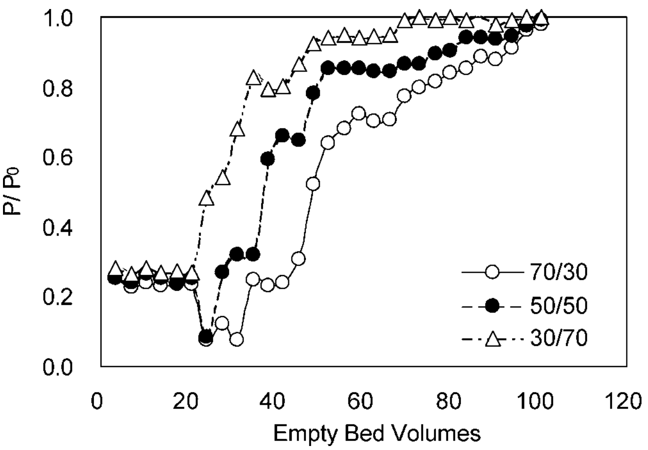

Figure 2—Phosphorus effluent from continuous flow columns, soil/sand ratio (pH = 7, initial phosphorus = 3 mg/L, flowrate = 3.1 mL/min). One empty bed volume = 1290 mL.

$$q = \frac{QKC}{1 + KC} \tag{1}$$

Where

C = equilibrium aqueous phosphorus concentration (mg/L),
q = amount of phosphorus sorbed (sorbate mass per unit mass of sorbent) (μg/g),
Q = short-term phosphorus sorption capacity of the media (μg/g), and
K = constant related to the phosphorus binding strength (L/mg).

Except for the mulch, the Langmuir equation provided a good fit ($p < 0.05$) to all data. Short-term phosphorus sorption capacities (Q in eq 1) were 20 μg/g for sand I and 89 μg/g for sand II. The sorption capacities of the soils were higher and showed little variability, with soil I at 128 μg/g, soil II at 130 μg/g, and soil III at 137 μg/g. The mulch sorbed less than 5 μg/g phosphorus. The greater sorption capacity of sand II compared with sand I is likely a result of the formation of calcium phosphate surface precipitates as a result of the higher calcium and magnesium concentration in sand II (Table 1; Sparks, 1995).

The results of the 29-day continuous-flow columns with 30/70, 50/50, and 70/30 soil I/sand I percentages are shown in Figure 2. During the first 6 days, all columns demonstrated similar phosphorus effluent levels at 23 to 28% of influent, corresponding to concentrations of 0.69 to 0.84 mg/L as phosphorus. After 20 (more sand) to 43 (more soil) empty bed volumes, higher phosphorus concentrations sequentially broke through the columns. By 100 empty bed volumes, every column was saturated with phosphorus ($P_{in} = P_{out}$).

Based on the results of batch phosphorus sorption data, the short-term phosphorus sorption capacity for each of the three continuous columns was calculated as follows:

$$m = \sum_{i=1}^{\text{all media}} q_i \times M_i \tag{2}$$

Where

m = sorptive mass of phosphorus by each continuous column (mg),
q_i = short-term phosphorus sorption capacity of each medium at initial 3.0 mg P/L, obtained from isotherm data (mg/kg),
M_i = mass of media used (kg), and the summation includes both the soil and sand in the column.

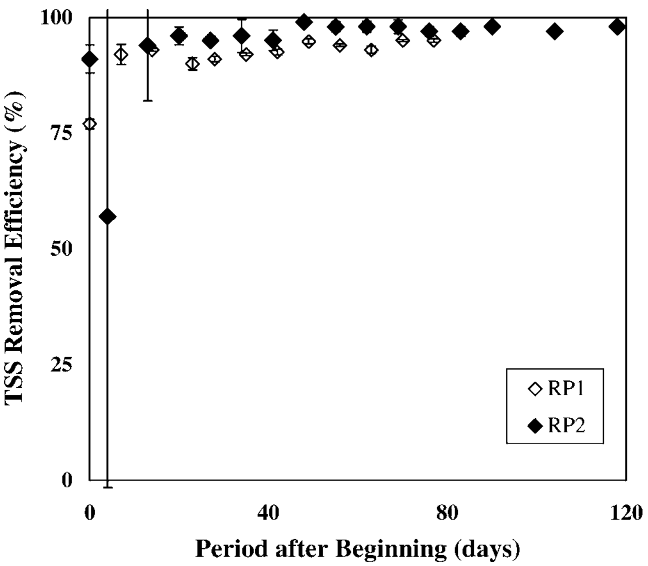

Figure 3—Total suspended solids removal during repetitive experiments with columns at 15-cm head (TSS input = 150 mg/L). Error bars represent ±1 standard deviation over the 6-hour runoff application study period.

Total phosphorus sorption, m_a, was calculated for each continuous column, as follows:

$$m_a = \int_{t=0}^{t=29} (C_{in} - C_{out})\, Q\, dt \tag{3}$$

Where

C_{in} and C_{out} = input and output phosphorus concentrations, respectively (mg/L);
Q = flowrate (L/d); and
t = experimental period (days).

During the testing period, the total mass input of phosphorus for each column was 391 mg. As calculated from eq 2 using the batch isotherm data, the short-term sorbable phosphorus capacity was 107 mg phosphorus for the column with 70% soil I. Total phosphorus sorption was 184 mg phosphorus (eq 3). The net difference (77 mg) estimates phosphorus sorbed through slow reactions and physically protected fast sorption sites (slow reaction phosphorus). For the column with 50% soil I, 82 mg of short-term phosphorus sorption was estimated, whereas 139 mg of phosphorus was retained in the column; thus, an estimated 57 mg of slow-reaction phosphorus was retained through the experiment. For the column with 30% soil I, 57 mg of short-term phosphorus sorption was estimated, and 92 mg of phosphorus was retained, giving an estimated 35 g of slow-reaction phosphorus. Short-term phosphorus sorption capacity and slow-reaction phosphorus sorption were positively correlated, with the 70% soil I media mixture retaining the greatest quantities of both fast- and slow-reaction phosphorus.

Repetitive Bioretention Column Tests. *Total Suspended Solids Removal and Infiltration Rate.* A total of 12 (RP1) and 16 (RP2) repetitions were completed to test the performances of the

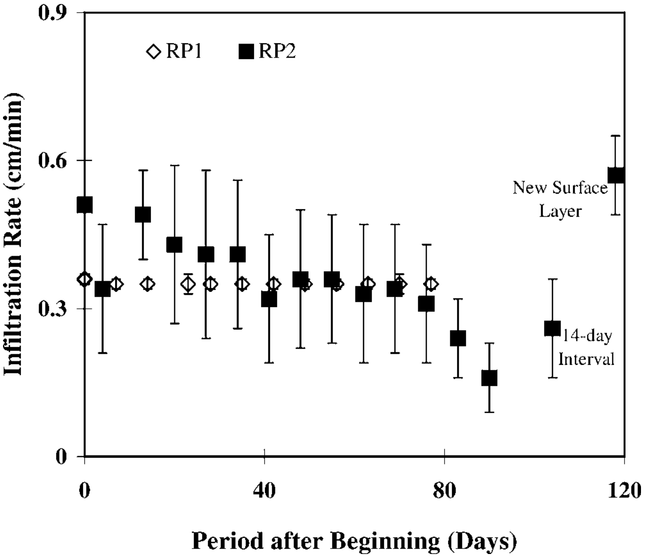

Figure 4—Runoff infiltration rate during repetitive experiments at 15-cm head. Error bars represent ±1 standard deviation over the 6-hour runoff application study period.

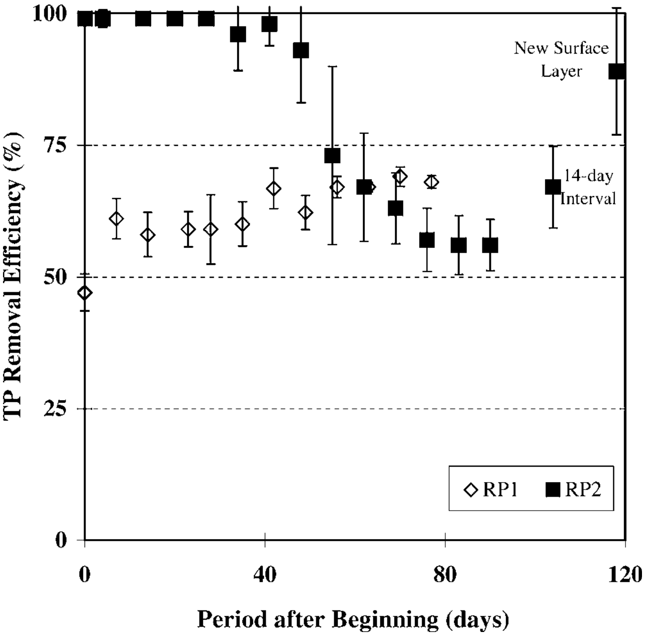

Figure 5—Total phosphorus (TP) removal during repetitive experiments at 15-cm head (input TP concentration = 3 mg/L; input TP mass = 1.62 g for RP1 and 2.0 g for RP2). Error bars represent ±1 standard deviation over the 6-hour runoff application study period.

bioretention media, with specific focus on the infiltration rate and removals of TSS and phosphorus. Cumulatively, for all repetitions, 87 g of TSS were applied to RP1 and 88 g to RP2. The first repetition of RP1 and the first two repetitions of RP2 demonstrated highly variable and inefficient TSS removal by the bioretention media (Figure 3). Similar to the results from studies conducted in newly constructed bioretention facilities (Hsieh and Davis, 2005), some suspended solids washed out from the soil media and resulted in net low TSS removal efficiencies during the first two repetitions. Afterward, the media stabilized, and the TSS removal efficiency was consistently >94% (effluent <12 mg/L TSS) throughout the remaining experiments. Overall, both media provided effective solids filtration throughout the repetitive studies, indicating that bioretention can be very effective in TSS management.

The results for the runoff infiltration rate at a 15-cm head are presented in Figure 4. The infiltration rate throughout all 12 repetitions in RP1 remained constant, at 0.35 cm/min, which was near that for runoff flowing through soil I only (0.28 cm/min) (Hsieh and Davis, 2005). Runoff did not enter the lower sand layer until the head was sufficiently built up in the soil to overcome the capillary tension between layers (Stormont and Anderson, 1999). Afterwards, runoff rapidly flowed through the bottom sand layer. It was apparent that runoff infiltration was controlled by the top soil layer, and flow variability was minor during each 6-hour experiment at a 15-cm fixed water head.

The RP2 used a high-hydraulic-conductivity media over one with low hydraulic conductivity. As expected, runoff infiltrated RP2 faster than RP1 during the first few repetitions, confirming the importance of the surface layer to runoff infiltration (Pitt et al., 2002). However, the runoff infiltration rate showed significant variability throughout each 6-hour experiment, increasing from the beginning to the end. This variability results from the lower-permeability bottom soil layer. Runoff would not flow immediately through this layer. As a result, the water head within the permeable upper media layers gradually built up and eventually increased the overall runoff infiltration rate. In addition, the infiltration rate gradually decreased from 0.51 to 0.16 cm/min throughout the first 14 repetitions, with suspended solids in the runoff appearing to clog the media surface.

To simulate a field condition without rain for a longer period, the 15th repetition was started 14 days after the 14th, which was twice as long as the dry period between each of the first 14 repetitions. Because the moisture content of the surface layer is expected to be less because of the longer interval (Hillel, 1998), runoff could be absorbed more readily. Accordingly, the infiltration rate increased from 0.16 to 0.26 cm/min during the 15th repetition. Also, to test a possible remediation method for addressing surface clogging, after the 15th repetition, the top 5 cm of medium was removed and replaced with new original material. In response, the runoff infiltration rate recovered to the same level as the initial (approximately 0.5 cm/min).

Comparing RP1 with RP2, the surface mulch layer prevented the column from clogging throughout 12 repetitions in RP1. Because this mulch layer has a high uniformity coefficient (d_{60}/d_{10}= 15.6) with many large pores, input TSS can migrate into this mulch layer via a depth filtration process. However, the surface media mixture of RP2 provided more straining of particulates, forming a surface mat, which eventually restricted water flow (Vinten et al., 1983) and led to compromised infiltration rates.

Total Phosphorus Removal. Particulate phosphorus in the input runoff comprised only approximately 3% of the total added phosphorus, which partitioned to the TSS (Hsieh and Davis, 2005), and a small amount of phosphorus that was originally affiliated with the TSS (38.5 mg-P/100 g TSS, equal to 0.06 mg-P/L), resulting in a distribution of 3.06 mg/L total phosphorus, 2.91 mg/L dissolved phosphorus, and 0.15 mg/L particulate phosphorus. Total phosphorus removal results for RP1 and RP2 are presented in Figure 5. The total phosphorus removal efficiency in RP1 ranged from 47 to 68%, gradually increasing. The initial jump in phosphorus removal in

Table 3—Soil tests for bioretention media after 16 runoff applications (RP2) and recommend values of soil phosphorus leaching potential and soil phosphorus fertility. Approximately 2 g phosphorus was input, and 0.3 g phosphorus passed through the column.

	Media		WSP		$CaCl_2$-P		Mehlich I- P		Mehlich III- P	
Type	Depth (cm)	Mass (kg)	mg-P/ kg-media	ΔP (mg)	mg-P/ kg-media	ΔP (mg)	mg-P/ kg-media	Δ P (mg)	mg-P/ kg-media	Δ P (mg)
Media mixture	Initial condition before runoff application		<0.05		0.2		20.8		48.1	
	0 to 15	6.1	7.2	44	2.6	15	54.7	207	95.5	289
	15 to 30	6.1	5.0	31	0.8	4	47.2	161	87.5	240
Sand II	Initial condition before runoff application		<0.05		<0.05		3.6		5.1	
	30 to 53	9.7	2.7	26	<0.05	0	14.4	105	24	184
	53 to 85	13.5	4.8	65	<0.05	0	15.8	165	25	270
Soil III	Initial condition before runoff application		<0.05		<0.05		17.7		51.3	
	85 to 95	5.9	5.1	30	<0.05	0	42.0	143	118	394
Accumulated phosphorus	Mass			196 mg		19 mg		781 mg		1377 mg
	Fraction of total removed from water			12%		1%		46%		81%

the second repetition may be related to media stabilization and the similar increase noted in TSS removal. However, the reason for the gradual phosphorus removal increases in later repetitions is unclear. With RP2, total phosphorus was nearly all removed in the first 7 repetitions (41 days of operation). After this period, however, the total phosphorus removal efficiency gradually decreased and finally reached only 56% in the 14th repetition. The phosphorus uptake capacity of the media was not reached during these multiloading studies. Although a number of soil/vegetation-based BMPs have demonstrated phosphorus export, this was not seen in the present study. The use of compost (or any organic matter component) as part of the bioretention media, as per several guidelines, should increase the amount of phosphorus within a bioretention system. Care should be taken when using organic media in nutrient-sensitive areas. While the use of compost may be beneficial for removing some pollutants (i.e., metals and oils), its decomposition may prove detrimental in addressing phosphorus runoff concerns.

On a mass basis, input/output total phosphorus mass, *m*, for each column during repetitive periods, was calculated as follows:

$$m = \sum_{1}^{n} \sum_{i=1}^{t_d} Q\, C \Delta t \tag{4}$$

Where

Q = runoff flowrate (L/h),
C = input/output total phosphorus concentration (mg/L),
Δt = measurement time increment over a single trial (hours),
i = specific time increment throughout the duration (t_d= 6 hours), and
n = number of trials (12 for RP1 and 16 for RP2).

Based on eq 4, total phosphorus effluent mass was 0.6 g from 1.62 g input for RP1 and 0.3 g output from 2.0 g input for RP2. The percent mass removal for RP1 (63%) was lower than that for RP2 (85%), although greater short-term dissolved phosphorus sorption was predicted for RP1 (3.8 g) than RP2 (3.4 g) when applying eq 2 and the isotherm data for the specific media used.

In these columns, particulate phosphorus was filtered by the media as TSS. In addition to the sorption processes, chemical precipitation and biological uptake are expected to contribute to dissolved phosphorus removal. In RP1, the less permeable surface soil layer limited the runoff infiltration rate, and the highly permeable bottom sand layer decreased the overall retention time of runoff in the bioretention column, limiting the water–soil contacting period. In contrast, larger volumes of runoff entered RP2 because of the highly permeable upper media layers. This runoff stayed longer in contact with the column media because of the less permeable bottom soil layer. This less permeable soil possessed high phosphorus removal capacity (based on isotherm data), with the expectation to enhance phosphorus removal efficiency by increasing phosphorus contact time with the bioretention media. Therefore, during each repetition and during dormant periods, dissolved phosphorus had more time to partition to the media of RP2 through sorption, precipitate formation, and biological uptake processes (Cox et al., 2000; Reddy et al., 1999; Sawhney and Hill, 1975; Van Cuyk et al., 2001), all leading to the higher dissolved phosphorus accumulation in RP2 compared with RP1.

Similar to the runoff infiltration rate, total phosphorus removal efficiency recovered somewhat after 14 days of drying (instead of the typical 7), increasing from 56 to 67%. As reported by others (Reddy et al., 1999; Sawhney and Hill, 1975), soils that had been successively treated with phosphorus solution showed reduced phosphorus sorption capacity, but regained the capacity to sorb dissolved phosphorus after drying and wetting cycles. This change can be attributed to dissolved phosphorus being initially adsorbed on the exterior media surfaces, subsequently diffusing via the slow reactions into the media matrix, thereby freeing new short-term sorption sites. Additionally, the removal efficiency of total phosphorus was further increased to 89% after replacing the top 5-cm medium, which provided fresh sorption surfaces for dissolved phosphorus.

Phosphorus Affiliation and Distribution in Bioretention Media Profile. Understanding the distribution of captured phosphorus in the bioretention column assists in interpreting phosphorus movement within and out of the media and media selection for optimum phosphorus accumulation. The phosphorus distribution was investigated by determining the phosphorus concentration in media at different depths using different phosphorus extraction processes before and after repetitive column experiments. Results for column RP2 are summarized in Table 3.

Environmental and Agronomic Phosphorus Soil Tests. The phosphorus concentrations in all media layers increased after repetitive applications, indicating that the applied phosphorus migrated throughout the whole column and did not stay only on the surface layer, in contrast to that noted for metals (Davis et al., 2001, 2003). The WSP and $CaCl_2$-P extractions were developed to simulate the ionic strength of the soil solution, predicting the potential of easily desorbable phosphorus leaching from the soil. Mehlich-I phosphorus and Mehlich-III phosphorus are soil tests that were originally designed to optimize crop production, but have recently been applied to non-point-source phosphorus-pollution management (Sims et al., 2001). The level of WSP in the column increased from <0.05 mg-P/kg for all media before runoff application to between 2.7 and 7.2 mg/kg after 16 repetitions. For $CaCl_2$-P, only that in the top medium increased (from 0.2 to 2.6 mg $CaCl_2$-P/kg for the upper top medium and to 0.8 mg $CaCl_2$-P/kg for the lower zone). The distribution of WSP through the media depth was relatively uniform, with slightly less phosphorus held by the sand compared with the soil. No measurable $CaCl_2$-extractable phosphorus was accumulated in the bottom two layers.

The Mehlich-I phosphorus levels for both zones in the top medium did not demonstrate significant differences, and the increase averaged 30 mg Mehlich-I P/kg (range 26 to 33 mg Mehlich-I P/kg). The average increase in Mehlich-I phosphorus was 11.5 mg P/kg for the middle sand medium and was a 24.3 mg Mehlich-I P/kg increase in the bottom soil layer; again, greater accumulation was noted with the soils. As expected, larger amounts of phosphorus were extracted by the Mehlich-III extractant for all media. The average increase for each layer was 43.5 mg Mehlich-III P/kg for the top medium (39 to 47 mg Mehlich-III P/kg), 19.4 mg Mehlich-III P/kg for the middle medium, and 66.9 mg Mehlich-III P/kg for the bottom layer.

The soils ranged from 42 to 54.7 mg Mehlich-I P/kg. Similar results were noted for Mehlich-III phosphorus, where the soil layer values ranged from 88 to 118 mg Mehlich-III P/kg. For both extractions, the sand values were less than for the soils. The optimum phosphorus ranges to support agricultural production, while minimizing environmental risk, suggested by Sims et al. (2001), are 25 to 50 mg P/kg for Mehlich-I and 50 to 100 mg P/kg for Mehlich-III. The surface media mixture showed values near the top of this range for Mehlich-I after the 16 runoff applications. The Mehlich-III values were just below the proposed optimum values. Overall, the leaching potential of bioretention media after treating a total of 2 g phosphorus in 16 runoff applications remained below recommended environmental values, but still should allow phosphorus uptake to vegetation. Nonetheless, if phosphorus concentrations in runoff influent remain high, removal of phosphorus via some process must be performed to prevent long-term leaching from phosphorus-saturated media.

Phosphorus Mass Distributions. The mass of phosphorus captured by each layer, m_r, was calculated as follows:

$$m_r = M \times \Delta q_p \tag{5}$$

Where

M = media mass used, and
Δq_p = phosphorus retained per unit mass of each media, calculated as the difference before and after the column runs, found using each phosphorus extraction method.

Phosphorus Accumulated Throughout the Column. Of the 1.7 g phosphorus removed from the runoff input, approximately 1.38 g phosphorus was extracted via Mehlich III (81%). Of the Mehlich-III phosphorus extracted, 38% was found in the upper media mixture layer, 33% in the middle sand layer, and 29% in the lower soil layer. On a unit media mass basis, the greatest phosphorus accumulations were noted in the top and bottom soil layers, as compared with the sand layer. As expected, the weaker extractants recovered smaller fractions of phosphorus. Specifically, values for WSP, $CaCl_2$-P, and Mehlich I were 12, 1, and 46%, respectively.

Phosphorus Capacities. The short-term phosphorus capacity of the bioretention media of RP1 and RP2 can be estimated based on the adsorption results. At an assumed phosphorus input of 0.35 mg/P, the specific capacity of each media component is estimated from Figure 2 data (mulch, approximately 0; sand I, 5 mg/kg; sand II, 28 mg/kg; soil II, 28 mg/kg; and soil III, 66 mg/kg). Multiplying these capacities by the mass of each component (eq 2) and dividing by the column surface area (0.029 m^2) provides the phosphorus capacity of the bioretention media, equal to 38 g-P/m^2 for RP1 and 45 g-P/m^2 for RP2.

Using runoff assumptions discussed previously (Davis et al., 2006), at 81 cm/y runoff, 0.35 mg-P/L, and 30:1 drainage:bioretention area, the phosphorus loading is 8.5 g-P/m^2-y. Dividing the column capacities by the phosphorus loading gives a conservative media phosphorus lifetime of only approximately 5 years. However, a number of factors will contribute to increasing this lifetime. First, a fraction of the phosphorus will be affiliated with TSS and not be dissolved; this phosphorus will not contribute to the use of adsorption capacity. Second, this loading assumes 100% adsorption and removal during infiltration, which typically has not been found in bioretention phosphorus studies. Third, these calculations account only for short-term phosphorus capacity, as noted in the continuous column studies of Figure 2, where 60 to 70% more dissolved phosphorus was removed than predicted by batch adsorption data. Integrating phosphorus into soil mineral structures, precipitation of phosphorus minerals, and vegetative uptake will all regenerate phosphorus sorption capacity. On the other hand, higher phosphorus influent concentrations will reduce media phosphorus lifetime because of the nonlinearity of the isotherm relationship noted in Figure 2. Regardless, without a planned management course of action, phosphorus saturation of bioretention media should be expected.

Summary and Recommendations

Phosphorus removal from synthetic urban stormwater runoff by soil media was investigated using batch and column adsorption experiments and pilot-scale layered column studies. Overall, the medium with a higher short-term dissolved phosphorus sorption capacity retained more dissolved phosphorus from the infiltrating runoff after a high phosphorus loading. Short-term dissolved phosphorus sorption capacity was positively correlated with slow reaction phosphorus sorption.

Mulch with large pore sizes was effective in preventing media from clogging from TSS input. A specially designed column, RP2 (a high hydraulic conductivity media overlaying one with low hydraulic conductivity), resulted in a high runoff infiltration rate. Placing a media with a higher hydraulic conductivity in the upper filtration layer will prevent the formation of a capillary barrier, restricting infiltrating runoff. By using the less permeable bottom soil layer to increase the contact time between dissolved phosphorus and media, RP2 was more efficient in total phosphorus removal than RP1, which used more traditional media design. Incorporating a bottom fine sand layer (5 cm) is recommended to prevent soil particles from leaching and clogging. This configuration provided optimum phosphorus removals that ranged from 67 to >98%, with effluent phosphorus equal to 1.2 to <0.55 mg/L.

Without exceeding environmental thresholds for each phosphorus extraction test, the effectiveness of bioretention in decreasing the phosphorus loading from infiltrating runoff was confirmed. Based on extraction data, most of the retained phosphorus in all media layers should be available for future vegetation use through nutrient cycling, and vegetation possibly can be used as a phosphorus-removal mechanism in bioretention facilities (Davis et al., 2006).

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References

American Public Health Association; American Water Works Association; Water Environment Federation (1995) *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; American Public Health Association: Washington, D.C.

Arias, C. A.; Bubba, M. D.; Brix, H. (2001) Phosphorus Removal by Sands for Use as Media in Subsurface Flow Constructed Reed Beds. *Water Res.,* **35** (5), 1159–1168.

Characklis, G. W.; Wiesner, M. R. (1997) Particles, Metals, and Water Quality in Runoff from Large Urban Watershed. *ASCE J. Environ. Eng.,* **123** (8), 753–759.

Cox, J. W.; Kirby, C. A.; Chittleborough, D. J.; Smythe, L. J.; Fleming, N. K. (2000) Mobility of Phosphorus through Intact Soil Cores Collected from the Adelaide Hills, South Australia. *Aust. J. Soil Res.,* **38** (5), 973–990.

Davis, A. P.; Shokouhian, M.; Sharma, H.; Minami, C. (2001) Laboratory Study of Biological Retention for Urban Stormwater Management. *Water Environ. Res.,* **73,** 5–14.

Davis, A. P.; Shokouhian, M.; Sharma, H.; Minami, C. (2006) Water Quality Improvement Through Bioretention Media: Nitrogen and Phosphorus Removal. *Water Environ. Res.,* **78** (3), 284–293.

Davis, A. P.; Shokouhian, M.; Sharma, H.; Minami, C.; Winogradoff, D. (2003) Water Quality Improvement Through Bioretention: Lead, Copper, and Zinc. *Water Environ. Res.,* **75** (1), 73–82.

Heathwaite, A. L.; Dils, R. M. (2000) Characterising Phosphorus Loss in Surface and Subsurface Hydrological Pathways. *Sci. Total Environ.,* **251–252,** 523–538.

Hillel, D. (1998) *Environmental Soil Physics.* Academic Press: San Diego, California.

Hsieh, C.-h.; Davis, A. P. (2005) Evaluation and Optimization of Bioretention Media for Treatment of Urban Storm Water Runoff. *ASCE J. Environ. Eng.,* **131** (11), 1521–1531.

Kunze, G. W.; Dixon, J. B. (1989) *Pretreatment for Mineralogical Analysis, Methods of Soil Analysis, Part 1—Physical and Mineralogical Methods,* 2nd ed.; Agronomy Society of America and Soil Science of America: Madison, Wisconsin, 91.

Maguire, R. O.; Sims, J. T. (2002) Soil Testing to Predict Phosphorus Leaching. *J. Environ. Qual.,* **31,** 1601–1609.

McDowell, R.; Sharpley, A.; Brookes, P.; Poulton, P. (2001) Relationship Between Soil Test Phosphorus and Phosphorus Release to Solution. *Soil Sci.,* **166** (2), 137–149.

McGechan, M. B.; Lewis, D. R. (2002) Sorption of Phosphorus by Soil, Part 1: Principles, Equations and Models. *Biosystems Eng.,* **82** (1), 1–24.

Mehlich, A. (1984) Mehlich 3 Soil Test Extractant: A Modification of Mehlich 2 Extractant. *Commun. Soil Sci. Plant Anal.,* **15** (12), 1409–1416.

Murphy, J.; Riley, J. P. (1962) A Modified Single Solution Method for the Determination of Phosphate in Natural Waters. *Anal. Chim. Acta.,* **27,** 31–36.

Pitt, R.; Chen, S.-E.; Clark, S. (2002) Compacted Urban Soils Effects on Infiltration and Bioretention Stormwater Control Designs. *Proceedings of the 9th International Urban Drainage Conference, Global Solutions for Urban Drainage* [CD-ROM], Portland, Oregon, Sept. 8–13; American Society for Civil Engineers: Reston, Virginia; and International Water Association: London.

Rechcigl, J. E. (1995) *Soil Amendments and Environmental Quality.* CRC Press: Boca Raton, Florida.

Reddy, K. R.; Kadlec, R. H.; Flaig, E.; Gale, P. M. (1999) Phosphorus Retention in Streams and Wetlands: A Review. *Crit. Rev. Environ. Sci. Technol.,* **29** (1), 83–146.

Sansalone, J. J.; Buchberger, S. G. (1997) Partitioning and First Flush of Metals in Urban Roadway Storm Water. *ASCE J. Environ. Eng.,* **123** (2), 134–143.

Sawhney, B. L.; Hill, D. E. (1975) Phosphate Sorption Characteristics of Soils Treated with Domestic Waste Water. *J. Environ. Qual.,* **4** (3), 342–346.

Sharpley, A. N. (1985) The Selective Erosion of Plant Nutrients in Runoff. *Soil Sci. Soc. Am. J.,* **49** (6), 1527–1534.

Sims, J. T.; Heckendorn, S. E. (1991) *Methods of Analysis of the University of Delaware Soil Testing Laboratory,* Coop. Bull. 10; University of Delaware, Newark, Delaware.

Sims, J. T.; Leytem, A. B.; Gartley, K. L. (2001) *Interpreting Soil Phosphorus Tests,* Coop. Bull, NM-04; College of Agriculture and Natural Resources, University of Delaware, Newark, Delaware.

Sparks, D. (1995) *Environmental Soil Chemistry.* Academic Press: San Diego, California.

Stormont, J. C.; Anderson, C. E. (1999) Capillary Barrier Effect from Underlying Coarser Soil Layer. *ASCE J. Geotech. Geoenviron. Eng.,* **125** (8), 641–648.

U.S. Environmental Protection Agency (1996) *Managing Urban Runoff,* EPA-841/F-96-004G; U.S. Environmental Protection Agency: Washington, D.C.

U.S. Environmental Protection Agency (1999) *Preliminary Data Summary of Urban Storm Water Best Management Practices,* EPA-821/R-99-012; U.S. Environmental Protection Agency, Office of Water: Washington, D.C.

U.S. Environmental Protection Agency (1998) *The Quality of Our Nation's Waters—A Summary of the National Water Quality Inventory: 1998 Report to Congress,* EPA-841/S-00-001; U.S. Environmental Protection Agency: Washington, D.C., http://www.epa.gov/305b/98report/98brochure.pdf.

Van Cuyk, S.; Siegrist, R.; Logan, A.; Masson, S.; Fischer, E.; Figueroa, L. (2001) Hydraulic and Purification Behaviors and their Interactions during Wastewater Treatment in Soil Infiltration Systems. *Water Res.,* **35** (4), 953–964.

Vinten, A. J. A.; Mingelgrin, U.; Yaron, B. (1983) The Effect of Suspended Solids in Wastewater on Soil Hydraulic Conductivity: II. Vertical Distribution of Suspended Solids. *Soil Sci. Soc. Am. J.,* **47** (3), 408–412.