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Phosphorus Retention by Fly Ash Amended Filter Media in Aged Bioretention Cells

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Abstract: Bioretention cells (BRCs) have shown potential for storm water quantity and quality control. However, the phosphorus (P) removal in BRC has been variable due to differences of soil properties in filter media. The objectives of this research were to identify and evaluate P accumulation in filter media and to quantify effluent P reduction in BRC. Each cell has a sand and fly ash media designed to remove phosphorous. Filter media were collected in 2014 across the cell surface and to a depth of 0.6 m to quantify the P accumulation. The mean total P (T-P) concentration increased over the seven years of operation, but the changes were not statistically significant. The average Mehlich-3 P (M3-P) and water-soluble P (WS-P) concentrations in the media profiles showed higher P accumulation in the top 0.15 m. The average M3-P and WS-P concentrations between 0.15 m to 0.30 m, and 0.30 m to 0.60 m were variable on all four BRCs media. The media with 5% fly ash significantly retained M3-P and WS-P over the top 0.15 m. Stormwater influent and effluent samples from three of the BRCs monitored over one year showed reductions in both P concentration (68% to 75%) and P mass (76% to 93%).

Keywords: bioretention; filter media; fly ash; phosphorus; stormwater; water quality

1. Introduction

Urban storm water has been identified as a critical non-point source pollution to receiving water systems [1]. The transport of pollutants by stormwater from parking lots, roadways, car washes and fertilized lawns can carry a significant amount of contamination to surface waters [2]. In the past two decades, stormwater management has focused on the development of best management practices (BMP) to mitigate the adverse impact of stormwater runoff to water bodies. In 1997, the Department of Environment Resources in Prince George's County (PGC), Maryland, introduced Low Impact Development (LID), a comprehensive approach for stormwater management [3].

In recent years, the bioretention cell (BRC) has gained considerable attention due to its potential for stormwater retention and pollutant removal. Several field and laboratory studies have been conducted to determine pollutant removal efficiency of BRC. High removal for pollutants including phosphorus (P), heavy metals, and oil and grease have been observed in field and laboratory monitoring of BRC, while ammonia and nitrate removal were low, and in some cases, production of nitrate was recorded [4–8].

Davis [9] conducted a study in two BRCs where influent P concentrations were reduced by an average of 74% and 68%. However, a number of studies showed significant P leaching from BRC [10,11]. While P is an essential nutrient, excess P is usually considered to be pollutant to water bodies as it can lead to eutrophication. Phosphorus management plan has been widely accepted to protect water bodies from the consequences of eutrophication [12]. Filtration, biological uptake, precipitation in media such as high calcareous sand, and sorption in filter media are the primary mechanisms of P retention [7,13]. Particulate P can easily be removed by filtration, thus current BMP mostly address removal of particulate P. Orthophosphate, the major form of dissolved P, can be untaken by plants directly, and thus create a risk for eutrophication if leached to receiving waters [14]. Reducing dissolved P requires sorption in the filter media. Dissolved P sorption processes in soils include adsorption, ion exchange and precipitation [15].

BRC filter media typically consist of organic matter, sand, sandy loam, loamy sand or topsoils [16]. In a study conducted by [11], P exporting was noted with P leaching from the media itself. The P index, a measure of media P content, is the potential for leaching of P from the media [17]. Organic matter, including mulch and compost used in BRC, can increase P in the infiltrating water as the organic matter decomposes and releases both organic and inorganic P [18,19]. Thus, media should be selected with low P index and low organic content in order to prevent production of P from media itself [16]. For effective P removal, media with low P index and high cation exchange capacity (CEC) are recommended [11]. P sorption processes in BRC are largely affected by soil properties, including amorphous aluminum and iron oxyhydroxides content, organic matter, calcium carbonate, clay and soil water chemistry [15,20–23]. Dissolved P can bind with aluminum and ferric hydroxides, and also precipitate with calcium in BRC filter media [17,24].

Several studies have been conducted on the use of various potential filter materials, including sand augmented with activated carbon, peat moss, compost, cedar bedding, garden bark, glass bends, coconut fiber, and kitty litter, which possess good hydraulic properties and are effective in removing nutrients found in stormwater [25–29]. However, the cost of these materials may limit their large-scale use. Thus, many researchers have been investigating more economic sportive filter material that are both easily available and replaceable [30]. Other BRC media amendments, including fly ash, expanded shale, slag, red mud, iron fillings and cement have been reported to remove P effectively [31–37]. Erickson [37] conducted column studies using 5% iron fillings mixed with sand (also called "Minnesota filter") as a filter media for phosphate removal from stormwater runoff. Their results indicated that filter media with 5% iron fillings captured 88% phosphate for 200 m treated depth. Zhang [14] studied different soil amendments as potential bioretention media to improve P removal. Based on his testing, fly ash was identified with the greatest potential for P sorption. Mixtures of sand with 5% fly ash exhibited 85% removal of P due to adsorption. Also, desorption tests conducted on the same material produced negligible amounts of P leaching with clean influent, while non-amended sand samples desorbed 42% of adsorbed P.

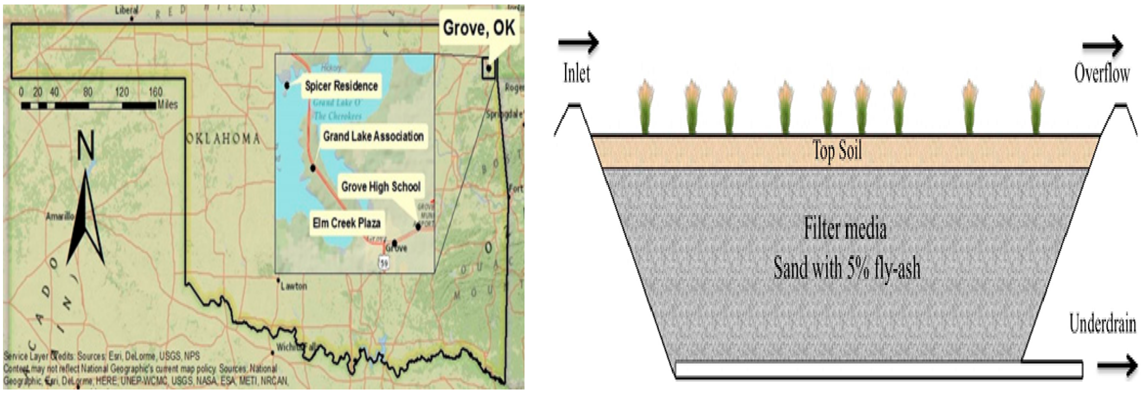
In 2007, several full-scale BRCs were constructed in Grove, Oklahoma that used the mixture of sand with 5% by weight of fly ash [38]. These units continued operating relatively unattended, and were subject to the normal site hydrology and contaminant loading. The objectives in this study were to analyze those aged BRCs to identify and evaluate P accumulation in the filter media over the seven years since construction, and to quantify current P reduction in the BRC effluent.

2. Materials and Methods

2.1. Site Description

Four BRCs constructed in Grove, OK, USA in 2007 [38] were subjected to testing in this study. A typical BRC section and locations are shown in Figure 1a,b and Table 1 presents the design summary of each BRC. The impervious area within each drainage area of each BRC was calculated using Google Earth Pro. The Grand Lake Association (GLA) cell treats runoff from a tourist information center with 36% of the total drainage area impervious. The Grove High School (GHS) cell treats runoff from a faculty parking lot with 95% impervious surface of total drainage area. The Elm Creek Plaza (ECP) cell treats runoff from a busy commercial strip mall parking lot with 100% impervious area. The Spicer Residence (SR) cell is located on the shore of Grand Lake and treats runoff from a residential lot with

13% impervious surface. The surface area to drainage ratio ranged from 2.2% to 6.7% for these BRCs, and all were designed with a pool storage depth of not more than 0.3 m. All the cells contain a topsoil layer approximately 0.15 m deep. A mix of sand and 5% fly ash by weight was used [38].



(**a**) (**b**)

Figure 1. (**a**) Bioretention cell locations at Grove, Oklahoma; (**b**) Typical section of bioretention cell at Grove, Oklahoma.

Table 1. Design summary for four bioretention cells [Grand Lake Association (GLA), Grove High School (GHS), Elm Creek Plaza (ECP), Spicer Residence (SR)] used in the field study at Grove, Oklahoma, USA [38].

Site	GLA	GHS	ECP	SR
Location	36°36′39″ N, 94°48′14″ W	36°37′19″ N, 94°44′50″ W	36°34′47″ N, 94°46′08″ W	36°38′59″ N, 94°46′08″ W
Property Type	Public	Public	Commercial	Residential
Impervious Land Cover (%)	36	90	100	13
Drainage area (ha)	0.76	0.26	0.25	0.15
Cell area (m^2)	172	149	63	101
Surface/drainage area ratio (%)	2.2	5.7	2.5	6.7
Sampled media depth (m)	0.6	0.6	0.6	0.6
Mean annual loading depth [a] (m)	15.7	24.1	23.4	4.20

Note: [a] Based on [14].

2.2. Filter Media Collection and Analysis

A 15-SCS/Model Giddings core machine with a 50.8 mm outer diameter and 38.1 mm inner diameter plastic liner was used for sampling the BRC filter media. Six soil core samples were collected from each BRC in June 2014 as diagramed in Figure 2. Previous studies conducted on operating BRC sampled three to six core samples with sampling near inlet, outlet and along the centerline of the cell. Jones [39] collected six core samples, Chen [40] collected five core samples, Muerdter [41] collected six core samples, Komlos [42] collected five core samples and Brown [43] collected three core samples from the BRC for their studies.

Soil cores with media depth of 0.6 m were sectioned into four distinctive sub-samples (0–0.15 m, 0.15–0.30 m, 0.30–0.45 m, and 0.45–0.60 m). Each segment was separated with a pre-cleaned saw, and stored in a clean soil bag. This produced a total of 96 subsamples in 2014. In addition, 32 samples of the filter media collected by hand during the 2007 construction and stored in the lab until this study were subject to the same analysis.

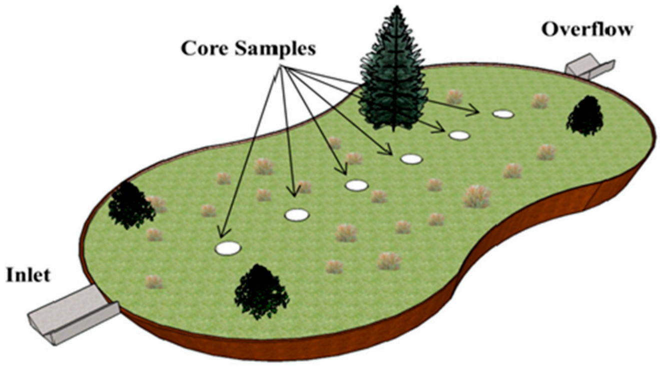


Figure 2. Soil core sampling layout at bioretention cells with approximate core locations.

2.3. Media Associated Phosphorus Analysis

Three different extraction methods were used to provide insight into the relative strength of the adsorption of the phosphorus to the filter media. Throughout this paper, the term adsorption is used to describe any solute that is retained by porous media. This would include, solutes bound by physical adsorption, precipitation, and within organic matter. Total phosphorus (T-P) in media samples was extracted using EPA Method 3050 [44]. This boiling strong-acid method measured essentially all phosphorus including the tightly held phosphorus in the mineral structure. Its results include phosphorus that was incorporated into the original mineral crystals, and not necessarily adsorbed during the field trial, or for that matter, available for transport under any field conditions. However, total soil digestion will quantify very strongly bonded phosphorus not measured by the other methods.

Water-soluble phosphorus (WS-P) was extracted using a 1:10 by weight, solid to deionized water extraction. Two-gram samples were placed in a 50-mL centrifuge tube with 20 mL of deionized water, shaken for one hour on an end-to-end shaker at low setting, and then centrifuged for 5 min. The clear supernatant was then vacuum filtered using a 0.45 μm membrane and analyzed for phosphorus. Water-soluble extraction gives a measure of soluble mineral salts and weakly adsorbed ions in the porous media.

Mehlich-3 phosphorus (M3-P) extraction is a multi-nutrient extraction method that estimates plant availability of most macro- and micro-nutrients in soils [45]. The extracting solution combines acetic acid, ammonium nitrate, ammonium fluoride and ethylene diamine tetraacetic acid (EDTA). It has grown in popularity due to its ability to allow a single extraction for both phosphorus and heavy metals, and is well suited to a wide range of soils, both acidic and alkaline in nature (Mehlich 1984). In this method, the acetic acid solution promotes the dissolution of calcium phosphate and the ammonium fluoride promotes ligand exchange.

Filter media pH was measured at a soil to deionized water ratio of 1:3. Phosphorus concentrations on all extractions were determined at the Soil, Water and Forage Analytical Laboratory (SWFAL), Oklahoma State University, Stillwater, OK, using inductively coupled plasma atomic emission spectroscopy (ICP-AEC).

2.4. Water Sampling and Analysis

Three of the BRCs (GLA, GHS and ECP) were monitored for influent and effluent water quantity and quality. H flumes were installed at the influent inlets, underdrains were outfitted with Palmer–Bowlus flumes, and rectangular steel, sharp-edge weirs were placed at the overflow outlets. ISCO 6712R refrigerated autosamplers (C.C. Lynch & Associates, Inc., Beachwood, OH, USA) were assigned to the influent, effluent and overflow at each cell for water sampling. Each autosampler was also equipped with an ISCO 720 flow meter. Finally, each influent sampler was equipped with a factory calibrated ISCO 674 tipping bucket rain gauge. Stormwater monitoring began in May 2014 and concluded in October 2015.

Flow-weighted sampling was employed for influent, underdrain and overflow at each cell. Each sampler contained 14 acid washed bottles. Each bottle had 950 mL volume capacity. Samplers were programed to take 100 mL samples with each bottle holding up to nine samples. The flow-weighted volume that each sample represented was adjusted for each site based on the first 61 mm of runoff on all three sites. The goal was to represent the higher sample volume resolution for small (first 13 mm) storm events. A two-part program for the inlets and overflows was implemented so that the first two bottles represented the first 13 mm of runoff and the remaining twelve bottles collected the additional runoff. Autosampler storage temperature was set to <4 °C and samples were retrieved within one day of sampling. After collection, unfiltered samples were sent to SWFAL for analysis. Since the water samples were unfiltered, the results reflect both soluble and particulate P. Total suspended solids were analyzed following ASTM D 3997-97 [46].

2.5. Statistical Analyses

The PROC GLM procedure in SAS version 9.4 [47] was used for the statistical analyses. The ANOVA (two-way) for T-P, WS-P and M3-P accumulation in bioretention media (between 2007 and 2014) and among media depth profiles (in 2014) was performed and the mean concentrations were compared using the Tukey's HSD test at α value of 0.05. The Wilcoxon Rank-Sum test, a non-parametric analysis at α value of 0.05 was used to compare inlet and underdrain T-P concentrations ($mg \cdot L^{-1}$), mass loading (g), and basic water quality parameters.

3. Results and Discussion

3.1. Media pH

Based on the 24 cores and 96 soil samples collected from the four BRCs in 2014, the soil surface layer (0–0.15 m) at GEC, GLA, GHS and SR had an average pH of 7.7 ± 0.3, 7.6 ± 0.3, 7.2 ± 0.2, and 8.0 ± 0.6, respectively, while the filter media (0.15–0.60 m) had an average pH of 8.6 ± 0.07, 8.1 ± 0.5, 8.0 ± 0.4 and 8.3 ± 0.9, respectively. The filter media pH was higher than the surface layer due to its fly ash content. The initial filter media (0.15–0.60 m) pH from 2007 samples (n = 24) was 8.4 ± 0.9, 8.1 ± 0.7, 8.2 ± 03, and 10.2 ± 0.4 at ECP, GHS, GLA and SR, respectively [48]. The pH of the filter media samples after operating for seven years in the field was still above 8 indicating the fly ash was still present.

3.2. Phosphorus Accumulation in Bioretention Media

Core sample P concentrations and mean comparisons are presented in Table 2. An increase in T-P concentration in the topsoil (0–0.15 m) and filter media (0.15–0.60 m) on all four BRCs were observed between 2007 and 2014. However, the increase in average T-P concentration for both topsoil and filter media were not statistically significant (p > 0.05) based on the two-way ANOVA, Tukey's multiple comparison test. This may be due to the high variability in the sample results, possibly due to spatial variability in the fly ash content resulting from the initial construction mixing [48].

Table 2. Phosphorus concentration (mean ± SD) in topsoil (0–0.15 m) and filter media (0.15–0.60 m) for 2007 and 2014 samples in bioretention cells at Grove, Oklahoma.

Site	Media Depth	Variable	Initial (2007) mg·kg^{-1} n = 8	Final (2014) mg·kg^{-1} n = 24	Significance Level
ECP	Topsoil (0–0.15 m)	T-P	225 ± 14	308 ± 87	ns †
		WS-P	0.11 ± 0.10	1.4 ± 0.2	***
		M3-P	1.7 ± 0.1	27.6 ± 4.6	***
	Filter Media (0.15–0.60 m)	T-P	361 ± 110	400 ± 140	ns †
		WS-P	0.10 ± 0.06	1.0 ± 0.3	***
		M3-P	3.2 ± 0.2	7.6 ± 3.7	*
GHS	Topsoil (0–0.15 m)	T-P	265 ± 3.5	331 ± 114	ns †
		WS-P	0.20 ± 0.01	1.5 ± 0.3	**
		M3-P	8.0 ± 0.1	34 ± 8	**
	Filter Media (0.15–0.60 m)	T-P	243 ± 3	281 ± 33.0	ns †
		WS-P	0.40 ± 0.05	0.80 ± 0.30	*
		M3-P	5.1 ± 1.4	19 ± 8	**
GLA	Topsoil (0–0.15 m)	T-P	276 ± 19	290 ± 60	ns †
		WS-P	0.20 ± 0.01	2.7 ± 1.2	*
		M3-P	10 ± 0.1	30 ± 5	**
	Filter Media (0.15–0.60 m)	T-P	195 ± 28	223 ± 53	ns †
		WS-P	0.30 ± 0.18	1.1 ± 0.8	*
		M3-P	13 ± 3	23 ± 9	*
SR	Topsoil (0–0.15 m)	T-P	170 ± 18	312 ± 70	ns †
		WS-P	0.10 ± 0.01	5.7 ± 1.2	***
		M3-P	5 0± 0.1	40 ± 18	*
	Filter Media (0.15–0.60 m)	T-P	355 ± 129	372 ± 35	ns †
		WS-P	0.20 ± 0.04	1.0 ± 0.7	*
		M3-P	4.0 ± 0.3	13 ± 8	*

Notes: Two-way ANOVA followed by Tukey's honest significant difference (HSD) test at α = 0.05; T-P = total phosphorus; WS-P = Water soluble phosphorus; and M3-P = Mehlich 3 extracted phosphorus. * Significant at the 0.05 probability level; ** Significant at the 0.01 probability level; ** Significant at the 0.001 probability level; † ns, not significant ($p > 0.05$).

3.3. Discussion on T-P, WS-P, and M3-P

The increase in T-P in the topsoil (0–0.15 m) was 83 mg·kg^{-1} at ECP, 66 mg·kg^{-1} at GHS, 14 mg·kg^{-1} at GLA and 142 mg·kg^{-1} at SR. The increase in T-P concentration at both ECP and GHS cells were consistent since both had drainage areas with more than 90% impervious area. The increase in T-P at GLA with drainage of 36% impervious area was lower compared to both ECP and GHS. However, the SR cell at a residential property with the lowest impervious surface of 13% had the highest increase in T-P. This may be due to higher P loading from fertilizer use in the residential garden and the geese that frequent this BRC near the shoreline. The increase in T-P between 2007 and 2014 for the filter media (0.15–0.60 m) was 39 mg·kg^{-1} at ECP, 40 mg·kg^{-1} at GHS, 28 mg·kg^{-1} at GLA and 17 mg·kg^{-1} at SR cells. While lower than the topsoil, the trend for ECP, GHS and GLA is similar to the topsoil. However, the SR concentrations are reversed. This may indicate that more of the P loading at SR was particulate P, which would be filtered near the surface. Therefore, the P loading into BRC depends on land cover with high impervious surfaces contributing higher runoff into BRC. Also, the use of fertilizers produce higher P load into the BRC. The P loading from runoff with more than 90% impervious surface at ECP and GHS were similar, whereas in SR with only 13% impervious surface of the drainage area had higher P loading into the cell contributing due to excess use of fertilizer.

The increase in WS-P between 2007 and 2014 for the topsoil (0–0.15 m) was 1.3 mg·kg^{-1} at ECP, 1.5 mg·kg^{-1} at GHS, 2.5 mg·kg^{-1} at GLA and 5.7 mg·kg^{-1} at SR. The increase in WS-P in the filter media (0.15–0.60 m) was 0.9 mg·kg^{-1}, 0.4 mg·kg^{-1}, 0.8 mg·kg^{-1} and 0.8 mg·kg^{-1} at ECP, GHS, GLA and SR cells, respectively. These increases, while more than an order of magnitude smaller than T-P, were statistically significant ($p > 0.05$) based on a two-way ANOVA, Tukey's HSD test. Again, the paved sites with more than 90% impervious surface were similar and SR was the highest. However, the GLA with only 36% impervious surface area had a higher WS-P than both ECP and GHS. WS-P in the filter media was lower than that of topsoil at all sites. Likewise, the increase in average WS-P concentrations in the filter media between 2007 and 2014 were more than an order of magnitude smaller than T-P. This indicates the P in media samples are tightly bond and not soluble.

The increase in M3-P concentrations between 2007 and 2014 for the topsoil (0–0.15 m) was 26 mg·kg^{-1} at ECP, 27 mg·kg^{-1} at GHS, 20 mg·kg^{-1} at GLA, and 35 mg·kg^{-1} at SR. M3-P increases in the filter media (0.15–0.60 m) were 4.4 mg·kg^{-1} at ECP, 14.1 mg·kg^{-1} at GHS, 10 mg·kg^{-1} at GLA, and 9 mg·kg^{-1} at SR. The increase in M3-P for both topsoil and filter media were statistically significant ($p < 0.05$) based on a two-way ANOVA, Tukey's HSD test. The M3-P increases were about 25% of the T-P increase. The increases in the topsoil for both ECP and GHS with more than 90% impervious surface were similar and SR was the highest. However, GLA had an intermediate value.

Previous studies on M3-P depth profiles in BRC media reported higher P accumulation (56.6 mg·kg^{-1}) in the top layer (0.06–0.1 m) compared to below 0.1 m (14.3 mg·kg^{-1}) [41,42]. The increase in M3-P and WS-P between 2007 and 2014 media samples was statistically significant ($p < 0.05$) in both the topsoil and filter media layers on all four BRCs analyzed. This strongly indicates fly ash amended filter media had effectively adsorbed P within the BRC media during the seven years of operation. Average WS-P was about 1% to 2% of T-P while average M3-P was 7% to 13% of the T-P in 2014. Conversely in 2007, the average WS-P was less than 1% and M3-P was 2% to 5% of the average T-P. This indicates that while P adsorbed within the BRC during the seven years are strongly bonded, there is a small and growing proportion of weakly bound P within the media.

Based on the three extraction methods, T-P concentrations were not statistically significant, while the average concentration of WS-P only being 1% to 2% of average the T-P concentration. Thus, while it is capturing less of the P increase, M3-P extraction may be considered the better indicator for P adsorbed within the BRC media as it provided a statistically significant measure. However, with higher P loading over longer times, average T-P in the media may increase in magnitude such that a statistically significant increase can be shown compared to the initial samples of 2007. Thus, in the long run, T-P extraction may be the better indicator for measuring adsorbed P.

3.4. Phosphorus Depth Profiles in the Bioretention Media

Average P concentration (T-P, WS-P and M3-P) in all four BRCs in 2014 is listed in Table 3. No significant difference in T-P accumulation ($p > 0.05$) at the top surface (0–0.15 m) was observed at ECP, GHS and SR. The highest WS-P and M3-P accumulation occurred in the top 0.15 m on all four BRC. Previous studies [41,42] also reported M3-P accumulation in the top 0.06–0.1 m of bioretention media. The variability in P below 0.15 m may be due to spatial variation in the fly ash content and preferential flow. This is in an agreement with results reported by [48], who performed numerical simulations on the impact of the variability of fly ash content on BRC.

Table 3. Phosphorus concentration (mean ± SD) on bioretention media depths in 2014 samples Grove, Oklahoma.

			Media Depth (m)			
Site	**N**	**Variable (mg·kg^{-1})**	**0–0.15**	**0.15–0.30**	**0.30–0.45**	**0.45–0.60**
ECP	24	T-P	308 ± 88a	467 ± 99a,b	489 ± 153b	426 ± 196a,b
		WS-P	1.4 ± 0.2c	0.97 ± 0.2d	1.0 ± 0.3d	1.2 ± 0.3c,d
		M3-P	27.5 ± 5e	6.5 ± 0.8f	6.0 ± 0.6f	10 ± 7f
GHS	24	T-P	331 ± 114g	279 ± 50g	282 ± 23g	285 ± 9g
		WS-P	1.5 ± 0.3h	0.67 ± 0.1i	0.93 ± 0.35i	0.82 ± 0.42i
		M3-P	35 ± 7j	15 ± 3k	16 ± 5k	31 ± 6j

Table 3. *Cont.*

Site	N	Variable (mg·kg^{-1})	Media Depth (m) 0–0.15	0.15–0.30	0.30–0.45	0.45–0.60
GLA	24	T-P	290 ± 60l	207 ± 33m	255 ± 75l,m	205 ± 30m
		WS-P	2.6 ± 1n	0.70 ± 0.12o	1.4 ± 1o	1.4 ± 0.62o
		M3-P	29 ± 5p	15 ± 2q	26 ± 8p	25 ± 9p
SR	24	T-P	312 ± 170r	414 ± 267r	387 ± 238r	315 ± 230r
		WS-P	5.7 ± 1s	1.0 ± 0.5t	1.0 ± 0.63t	1.2 ± 0.9t
		M3-P	40 ± 18u	9.6 ± 3.5v,w	7.5 ± 1w	20 ± 10v

Notes: Two-way ANOVA at $\alpha = 0.05$; concentrations with the same letters are not significantly different among media depths; concentrations with different letters are significantly different among media depths; T-P = Total phosphorus; WS-P = Water soluble phosphorus; and M3-P = Mehlich 3 extracted phosphorus.

3.5. Stormwater Monitoring

A summary of P inflow and outflow concentration and mass loading for the three BRCs collected from 2014 to 2015 is presented in Table 4. The results were used to compare the P mass removal rates and concentration reduction from BRC effluent. The influent and effluent pH, electric conductivity, turbidity, and total suspended solids are presented in Table 5. The P mass input and output for each cell were calculated as a product of the pollutant event mean concentration and the total runoff volume measured during a runoff event.

At ECP, 20 storm events were sampled from May 2014 to October 2015. Event sizes ranged from 6 mm to 97 mm, the mean storm size was 26 mm, and the median storm size was 17 mm. No overflow occurred during any event. A mean flow volume reduction of 73% with a standard deviation of 12% ($n = 20$) was observed. T-P effluent concentration was 75% lower than the influent and T-P effluent mass was 93% lower than of the influent mass. Both reductions were statistically significant ($p < 0.05$).

At GHS, 15 storm events occurred from September 2014 to September 2015, of which ten events were sampled and analyzed. Event ranged from 8 mm to 80 mm, and the mean storm size was 30 mm. An overall mean flow volume reduction of 13%, with a standard deviation of 88% was achieved. Between 1 April and 20 May, this cell exhibited groundwater inflow seepage and had 30% more volume coming from the underdrain compared to the cell inlet on four storms. For the remaining six storms, the cell showed a volume reduction of 71% from the inlet to underdrain. T-P effluent concentration was 67% lower than the influent, and T-P effluent mass was 84% lower than of the influent mass. Both reductions were statistically significant ($p < 0.05$).

At GLA, eleven storm events occurred from June 2014 to September 2015 and were sampled and analyzed. Events ranged from 11 mm to 92 mm, the mean storm size was 38 mm, and the median storm size was 36 mm. Flow in the GLA underdrain was higher than the inlet for most of the storms monitored, because of groundwater seepage into the cell from upslope. Flow from the underdrain was noticed at times with no precipitation or influent. Overall, underdrain flow was 200% greater than influent during the monitoring period. For four storm events, out of the eleven, the flow volume in the underdrain was lower than the inlet flow volume, and an average flow reduction of 60%. For the remaining seven storms, this cell exhibited ground water inflow seepage and had 300% more volume coming from the underdrain compared to the cell inlet. The groundwater inflow seepage through the underdrain impacted the quantification of the BRC performance including flow volume and P mass reductions. Thus, control of groundwater seepage, if possible, must be taken into consideration in future monitoring on performances of BRC. However, even with the groundwater seepage, the T-P effluent concentration reduction was 64% relative to the influent ($p < 0.05$). T-P effluent mass was 76% lower than of the influent mass ($p < 0.05$).

Table 4. Inlet and underdrain T-P mean concentration (mg·L^{-1}) and loading (g) for three bioretention cells (BRC) monitored at Grove, OK from 2014 to 2015.

BRC	Storm Events (n)	Inflow (mg·L^{-1})	Underdrain (mg·L^{-1})	% Reduction	Significance	Inflow (g)	Underdrain (g)	% Reduction	Significance
ECP	20	0.12 ± 0.11	0.03 ± 0.02	75%	$p < 0.05$	3.25 ± 5.12	0.22 ± 0.2	93%	$p < 0.05$
GHS	10	0.15 ± 0.13	0.05 ± 0.07	67%	$p < 0.05$	5.13 ± 5.44	0.83 ± 0.95	84%	$p < 0.05$
GLA	11	0.21 ± 0.13	0.08 ± 0.10	64%	$p < 0.05$	13.8 ± 14.92	3.22 ± 2.83	76%	$p < 0.05$

Notes: The Wilcoxon Rank-Sum Test, a non-parametric analysis at α value of 0.05; $p < 0.05$ indicates significant reduction in effluent T-P concentration and loading.

Table 5. Mean influent and effluent water quality parameters monitored at three bioretention cells (BRC) at Grove, OK from 2014 to 2015.

BRC	Pollutant	Storm Events (n)	Inflow	Underdrain	% Reduction (+) or Increase (−)	Significance
ECP	TSS (mg·L^{-1})	20	106 ± 70	41 ± 32	61	$p < 0.05$
	Turbidity (NTU)	20	66 ± 48	7.0 ± 4.0	89	$p < 0.05$
	pH	20	6.71 ± 0.77	7.72 ± 0.23	−15	$p > 0.05$
	EC(μmhos/cm)	20	75 ± 25	208 ± 38	−179	$p < 0.05$
GHS	TSS (mg·L^{-1})	7	110 ± 64	45 ± 28	59	$p < 0.05$
	Turbidity (NTU)	7	19 ± 44	2.8 ± 1.5	86	$p < 0.05$
	pH	8	6.36 ± 0.71	7.51 ± 0.17	−18	$p > 0.05$
	EC(μmhos/cm)	8	147 ± 238	174 ± 28	−19	$p > 0.05$
GLA	TSS (mg·L^{-1})	11	95 ± 11	29 ± 30	70	$p < 0.05$
	Turbidity (NTU)	11	9 ± 4	3.8 ± 2.6	60	$p < 0.05$
	pH	11	7.11 ± 0.35	7.96 ± 0.25	−12	$p > 0.05$
	EC(μmhos/cm)	11	86 ± 21	348 ± 90	−301	$p < 0.05$
ECP	TSS (g)	12	2460 ± 2423	275 ± 480	89	$p < 0.05$
GHS	TSS (g)	7	5702 ± 4038	950 ± 570	83	$p < 0.05$
GLA	TSS (g)	11	1840 ± 1763	1681 ± 1260	9	$p > 0.05$

Notes: The Wilcoxon Rank-Sum Test, a non-parametric analysis at α value of 0.05; $p < 0.05$ indicates significant reduction or increase in effluent water quality parameters through the BRC system.

T-P concentration reductions of 64% to 75% and T-P mass reduction of 76% to 93% were achieved at the three BRC. Influent T-P concentrations at GHS and ECP with drainage area having greater than 90% impervious surface were lower than the influent T-P concentration at GLA with 36% impervious surface of drainage area. Previous bioretention field studies found phosphorus concentration removal of 50% to 94% and phosphorus mass reduction of 44% to 90% [7,37,49–51]. However, these results were obtained from new cells and probably do not reflect long-term performance. The BRC with fly ash amended filter media after seven years of construction displayed significant P concentration and mass reduction.

3.6. Phosphorous Retained within the Bioretention Media

3.6.1. Estimates from Core Samples

Phosphorus retained within the bioretention media during seven years of operation can be calculated by the simple mass balance.

$$P_{trapped} = \left(P_{final} - P_{initial}\right) \times V \times \rho_b \tag{1}$$

where, P_{final} is the T-P concentration (mg·kg^{-1}) in 2014 $P_{initial}$ is the initial T-P concentration (mg·kg^{-1}) in 2007, ρ_b (kg/m^3) is the bulk density of the media and V is the cell media volume (m^3).

A topsoil dry bulk density of 1.4 g/cm^3 and a filter media dry bulk density of 1.5 g/cm^3 were used. Phosphorus retained within the media is presented in Table 6. The T-P retained within the media depth (0–0.60 m) was 0.40 kg·year^{-1} at ECP, 0.33 kg·year^{-1} at GHS, 0.51 kg/year at GLA and 0.60 kg·year^{-1} at SR. Both ECP and GHS with similar site characteristics of greater than 90% impervious drainage area had consistent mean T-P influent concentration of 0.03 mg·L^{-1} and 0.05 mg·L^{-1}, and retained similar T-P within the media. The T-P retained within the media at GHS and SR was higher of 0.51 kg·year^{-1} and 0.60 kg·year^{-1}. The mean T-P influent concentration collected at GHS was 0.21 mg·L^{-1}, highest among the three monitored.

Table 6. Phosphorus retained within the bioretention media analyzed from three different extraction methods and inlet T-P load in three bioretention cells monitored estimated using LOADEST software.

Site	Media	Media Depth (m)	T-P Retained (kg·Year^{-1})	M3-P Retained (kg·Year^{-1})	WS-P Retained (kg·Year^{-1})	LOADEST from Inlet T-P (kg·Year^{-1})
ECP	Topsoil	0–0.15	0.16	0.05	0.002	0.27 †
	Filter media	0.15–0.45	0.24	0.03	0.006	
	Total	0–0.60	0.40	0.08	0.008	
GHS	Top	0–0.15	0.29	0.08	0.004	0.18 †
	Filter media	0.15–0.45	0.04	0.13	0.004	
	Total	0–0.60	0.33	0.21	0.008	
GLA	Top	0–0.15	0.07	0.09	0.012	0.37 †
	Filter media	0.15–0.45	0.44	0.14	0.01	
	Total	0–0.60	0.51	0.23	0.022	
SR	Top	0–0.15	0.43	0.18	0.029	N/A
	Filter media	0.15–0.45	0.17	0.15	0.013	
	Total	0–0.60	0.60	0.33	0.042	

Notes: T-P = Total phosphorus; WS-P = Water soluble phosphorus and M3-P = Mehlich 3 extracted phosphorus; N/A = No Samples. † The values are estimated for overall media depth.

3.6.2. Estimates from Flow Monitoring

As an estimation of total P loading during the seven years of BRC operation, a regression equation of flow versus precipitation was generated using the rainfall and BRC influent volume measured in 2014 and 2015. For missing storm events not measured by the on-site rain gauge rainfall at the Jay, OK, Mesonet (https://www.mesonet.org/) station was used. With the generated regression equation for influent, rainfall, and measured P, the Load Estimator model (LOADEST) was used to predict the P load per year at the three-monitored BRC. LOADEST [52] is a USGS program that estimates annual loads of water-borne constituents, based on the concentration of samples collected at the desired location. The program creates a linear regression model to predict the instantaneous load based on one or more input variables including discharge and concentration in collected samples. LOADEST automatically creates several multiple regression models and selects the best model from those based on the lowest Akaike Information Criteria statistic. The LOADEST estimates of P loading to the three BRCs were 0.27 kg·year^{-1} at ECP, 0.18 kg·year^{-1} at GHS, and 0.37 kg·year^{-1} at GLA. These values are comparable to the mass of T-P increase calculated from core samples of 0.4 kg·year^{-1} at ECP, 0.33 kg·year^{-1} at GHS, and 0.51 kg·year^{-1} at GLA. The estimated T-P load into the cells from LOADEST and total P retained in the BRC media using soil digestion method (EPA, 3050) provided a rough estimation of the T-P that was retained by filter media. These values can be compared to the mass increase of M3-P of 0.08 kg·year^{-1} at ECP, 0.21 kg·year^{-1} at GHS, and 0.23 kg·year^{-1} at GLA, and the mass increase of WS-P of 0.008 kg·year^{-1} at ECP, 0.008 kg·year^{-1} at GHS, and 0.022 kg·year^{-1} at GLA. Thus, the estimate of T-P retained in media measured by the total soil digestion method is a better estimator of T-P load.

4. Conclusions

Substantial reductions of stormwater phosphorus from seven-year-old BRCs were quantified. Stormwater P concentration reductions at three-monitored BRC ranged from 64% to 75%, while P mass reduction ranged from 76% to 93%. The M3-P and WS-P concentrations in media profile indicated significant phosphorus accumulation within the top 0.15 m in all four BRC consistent with previous studies. M3-P and WS-P concentrations significantly increased between 2007 and 2014 indicating fly ash amended filter media had effectively adsorbed P during the seven years of operation. However, the study showed no significant increase in T-P concentrations between 2007 and 2014. Average WS-P was only 1% to 2% of average T-P indicating most P is strongly bound in the media. M3-P extraction may be a better indicator for measuring P adsorbed within the BRC media. Based on observation at GHS and ECP, an influent T-P concentration was lower with drainage area having higher impervious surface. The mean T-P influent concentration at GLA was the highest among the three monitored BRCs indicating that GLA was receiving high P loading from runoff. The study showed variability in P concentrations below the top 0.15 m of the media profile which may be due to spatial variation of fly ash content within the media and from possible preferential flow. Further research is needed to find appropriate mixing methods for fly ash with sand to ensure an adequately mixed and uniform filter media for BRC. Overall, the BRC filter media with fly ash amendment was effectively retaining phosphorus from stormwater runoff.

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