PHOSPHORUS AND METAL SORPTION IN AGED BIORETENTION CELLS WITH FLY-ASH AMENDED FILTER MEDIA

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Submitted to the Faculty of the
Graduate College of the
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in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
July, 2016

PHOSPHORUS AND METAL SORPTION IN AGED BIORETENTION CELLS WITH FLY-ASH AMENDED FILTER MEDIA

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ACKNOWLEDGEMENTS

I wish to express sincere appreciation to my advisor, Dr. Glenn Brown, for his guidance, encouragement and support throughout my studies. His advice and encouragement have helped me grow both personally and professionally. I would also like to extend appreciation to my other committee members, Drs. Jason Vogel, Dan Storm, and Chad Penn for their valuable assistance. I extend my thanks to Joshua Bradely and Stuart Wilson for their guidance and help during the laboratory experiments.

I am also thankful to Alex, Riley, Mr. Walker, and Meghan for both the field and lab assistance. Thank you, Jinesh Niroula brother, for your support, encouragement and motivation during my tough time. Thank you Anup KC and Shiva Makaju for your assistance during data analysis. I am also thankful to Monesh Balla, and Rajiv for their encouragement and support during my PhD study.

Finally, I would like to thanks my parents and my family for their encouragement, love and patience during all these years and believing on me.

Name: SAROJ KANDEL

Date of Degree: JULY, 2016

Title of Study: PHOSPHORUS AND METAL SORPTION IN AGED BIORETENTION CELLS WITH FLY-ASH AMENDED FILTER MEDIA

Major Field: BIOSYSTEMS ENGINEERING

Abstract: Stormwater runoff from urban areas can transport a significant load of phosphorus (P) and heavy metals. Media samples from seven year old bioretention cells (BRC) were collected, to a depth of 0.6 m, to assess the accumulation of phosphorus and heavy metals. Analysis consisted of total soil digestion (T-P), Mehlich-3 (M3-P) and water soluble (WS-P) extraction for both metals and phosphorus. The mean T-P concentration increased over the seven years of operation, but the results were not statistically significant ($p > 0.05$). The average M3-P and WS-P concentrations in the media profiles showed higher P accumulation in the top 0.15 m of media. Significant ($p < 0.05$) P concentration reductions of 68% to 75% were achieved between the influent and drain effluent and P mass reductions of 76% to 93% were observed. Most of the metal accumulated in the top 0.15m of media. Metal concentration in the media significantly increased ($p < 0.05$) over the seven years compared to that of initial media samples. Significant zinc concentration reductions between influent and drain effluent of 56% to 60% were obtained, which corresponds to zinc mass reduction of 43% to 88%. The phosphorus and metals adsorption capacities were obtained from a series of batch and flow-through experiments. Both nonlinear forms of Langmuir and Freundlich isotherm models fitted the equilibrium data well ($r^2 > 0.9$). The batch sorption experiments showed phosphorus adsorption capacity of the fly-ash filter media after seven years of operation was (160 mg/g) around half the amount of the initial material (350 mg/g). Batch testing of the aged fly-ash amended filter media exhibited phosphorus removal of 61%, Zn Cu and Pb removal of 95%, 98%, and 99%. Desorption experiments showed the media released 24% of initially sorbed phosphorus and only 0.6% of initially sorbed Zn and Cu at initial phosphorus and metal concentration of 30 mg/L. Thus, phosphorus and heavy metal adsorption in sand/fly-ash filter media may be considered irreversible, and can provide long-term phosphorus and heavy metal retention.

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CHAPTER I

INTRODUCTION, CONCLUSIONS AND RECOMMENDATIONS

INTRODUCTION

Stormwater Overview

Urban stormwater runoff contains pollutants that degrade surface water quality, including streams and other water bodies and these pollutants has been identified as a critical non-point source pollution to receiving water bodies (USEPA 2002; Gorme et al. 2014). The increase in impervious land resulting from urban development, has adverse effects on the hydrologic cycle and corresponding water quality (Li and Davis 2009). As stormwater runoff flows across roofs, lawns and pavements, it accumulates and collects pollutants that impair water quality. Urban runoff contains a mixture of natural organic and inorganic material including suspended solids, organic carbon, oil and grease, nutrients such as nitrogen and phosphorus, heavy metals and pathogens (Davis et al. 2009). The reduction of phosphorus and heavy metals in stormwater runoff is important for both environmental quality and water reuse. Most importantly, excess phosphorus in water bodies can lead to eutrophication (Hunt et al. 2006). Urban phosphorus sources include lawn fertilizers, and domestic and wild animal waste. Heavy metals are of interest in urban stormwater due to their potential toxicity and non-degradable nature (Davis et al. 2001). Numerous sources of metals in urban runoff have been reported including vehicular brake emission and tire wear as sources for zinc and copper respectively (Muthanna et al. 2007).

Bioretention Cells

In past two decades, stormwater management has focused on the development of best management practices (BMP) to improve urban stormwater runoff quality to mitigate its adverse impacts to receiving water bodies. Among these BMP, bioretention cells (BRC), also known as biofilters or raingardens, are widely used in the United States and internationally (Davis et al. 2009). BRC have shown potential for both stormwater retention and pollutant removal. BRC typically consist of a filter material, a top mulch layer, a storage pool of between 0.15 and 0.30 m of deep, and plants designed for retention and treatment of the pollutants through processes including sedimentation, sorption, and plant uptake (Mangangka et al. 2015). BRC have been shown to reduce peak flows and runoff volume (Hunt et al. 2006; Christianson et al. 2012). Several field and laboratory studies have been conducted to determine pollutant removal efficiency of BRC (Davis 2007; Davis et al. 2001; Dietz and Clausen 2005; Hunt et al. 2006), but the major treatment mechanisms are not well understood (Daly et al. 2012).

High removal of pollutants including phosphorus, heavy metals, oil and grease and total suspended solids (TSS) have been observed in field and laboratory monitoring of BRC.

Ammonia and nitrate removal were low, and in some cases, production of nitrate was recorded (DiBlasi et al. 2008; Hsieh et al. 2007; Li and Davis 2008). However, phosphorus removal in bioretention systems has been highly variable and inconsistencies in phosphorus removal have been reported from various field monitoring of BRC. Davis et al. (2007) conducted a study in two BRC, where phosphorus concentrations were reduced by an average of 68% and 74%. Various bioretention field studies reported, phosphorus concentration removal of 50% to 94% and phosphorus mass reduction of 44% to 90% (Houdeshel et al. 2015; Erickson et al. 2012; Carpenter and Hallam 2010; Hurley and Forman 2011; Brown and Hunt 2012; Debusk and Wynn 2011). Whereas, in a number of studies significant phosphorus leaching from BRC was noted (Dietz and Clausen 2005; Hunt et al. 2006).

Metals are of concern due to their ecotoxicity accumulation potential (Jones and Davis 2012). It has been observed that the surface layer of bioretention systems performs a significant role in retaining metals (Li and Davis 2008). Laboratory scale studies conducted by Davis et al. (2006), Davis et al. (2003), and McIntyre et al. (2014) reported concentration reduction of more than 90% for zinc (Zn) and lead (Pb), while copper (Cu) concentration reduction was more than 70%. David et al. (2015) conducted a field study on metal removal efficiencies of BRC and reported concentration reductions of 93% for Zn, 83% for Cu and 51 % for Pb. Also, field studies conducted by Hunt (2003). and Muthanna et al. (2007) reported greater than 90% concentration reductions of Zn and Cu through monitored bioretention systems. All of these studies suggest that bioretention appears to be an efficient technology to remove heavy metals from urban runoff.

Bioretention Filter Media and Amendments

The type of media used in BRC is a key design factor. Selection of the media type should be based on the desired treatment performance, local site conditions and prescribed infiltration rates (Liu et al. 2014). Bioretention media typically consists of organic matter, sand (sandy loam or loamy sand) and a top mulch (LeFevre et al. 2015). Organic matter (compost and/or mulch) provides nutrients to plants, moisture retention, cation exchange capacity (CEC) and promotes microbial growth within the BRC systems (Kim et al. 2003; Lintern et al. 2011). P index is a measure of the potential for leaching of phosphorus from the media (Clark and Pitt 2012). For effective phosphorus removal, media with low P index and high CEC is recommended (Hunt et al. 2006). Phosphorus and metal sorption in media is associated with several soil properties, including the content of amorphous aluminum, iron oxides, manganese oxides, oxyhydroxides and organic matter, in addition to the soil water pH, and chemistry (Dubus and Becquer 2001; Guppy et al. 2005; Sims et al. 2005).

Amendment of the filter media to improve BRC performance is an active area of research. Several studies have been conducted on the use of various potential filter media that possess good hydraulic properties and are effective in removing nutrients and heavy metals found in stormwater. Amendments include sand augmented with activated carbon, water treatments residuals containing aluminum, iron slag, peat moss, compost, cedar bedding, and coconut fiber, coal fly ash, crab shells, biochar, and wood chips (Iqbal et al. 2015; Lee et al. 2015; Ulrich et al. 2015; Penn et al. 2011; Gironas et al. 2008; Samuel et al. 2012; Singhal et al. 2008). However, the cost of these materials may limit their use as a filter media in large BRC systems. Thus, researchers have been investigating more economical sorptive filter material that is readily available, has higher phosphorus and heavy metals sorption capacity, and is easily replaceable (Reddy 2013). However, sorption capacities of different filter media used in BRC are still poorly understood, and the transport and fate of various pollutants within the media is not well defined.

Fly ash is a fine residual obtained from burning of coal, wood and other organics. Previous research, from batch sorption studies has shown fly ash is an effective sorptive media for removing phosphorus and metals including Cu, Zn, and Pb from aqueous solutions (Ayala et al. 1998; Bayat 2002). Zhang et al. (2008 a, b) conducted laboratory experiments using expanded shale, limestone, fly ash and other materials as a potential bioretention media to improve phosphorus and heavy metal retention and removals. Based on his testing, class C fly ash was identified as a material with significant potential for phosphorus and metal sorption. Mixtures of sand with 5% by weight of fly ash exhibited higher phosphorus and heavy metal sorption than all the other materials tested. In addition desorption tests indicated negligible release of adsorbed phosphorus and heavy metals. While promising, no research has been carried out to demonstrate the long-term P and metal retention capacity of fly ash. Finally only limited research has been reported on the long-term performance of any BRC. Known, previous studies are limited to Komlos and Traver (2012), and Muerdter et al. (2015) who reported phosphorus accumulation in the top 0.06-0.1 m of bioretention media from their studies of seven and nine years old BRC.

Quantifying Contaminants in Filter Media

A major concern in this study was quantifying the concentration of phosphorus and heavy metals in the BRC filter media. Three different extractions methods were used, total soil digestion, water soluble extraction and Mehlich-3 extraction. Total phosphorus and metals in media samples were extracted by total soil digestion following EPA 3050 (EPA, 1996). This boiling strong-acid extraction measured the total phosphorus and metals including that held in the mineral structure of the sample.

Water soluble extraction gives a measure of soluble mineral salts and weakly sorbed ions in porous media. Water soluble phosphorus and metals were determined by 1:10 by weight solid to deionized water extractions. Two grams of sample 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.

Mehlich-3 extraction is a multi-nutrient extraction method developed to estimate plant availability of macro and micro-nutrients in soils (Mehlich 1984). The extracting solution combines acetic acid, ammonium nitrate, ammonium fluoride and ethylene diamine tetraactetic acid (EDTA). It has grown in popularity due to its ability to allow a single extraction for both phosphorus and heavy metals. It is also well suited to a wide range of soils, both acidic and basic in nature (Mehlich 1984). In this method, the acetic acid solution promotes the dissolution of calcium phosphate and the ammonium fluoride promotes ligand exchange. K, Ca, Mg and Na are extracted by ammonium nitrate and nitric acid, while heavy metals including Cu, Mn, Zn, Fe, and Pb are dissolved and complexed by ammonium nitrate and EDTA, which functions as a chelating agent (Topp et al. 1993; Pierzynski 2000). Chelation is the process by which metals bond to ligands or functional chelate groups (Evangelou 1998).

For all three extractions, phosphorus and metal concentrations were determined at the Soil, Water, and Forage Analytical Laboratory (SWFAL), Oklahoma State University, Stillwater, OK, using inductively coupled plasma atomic emission spectroscopy.

Grove Bioretention Cells

In 2007, several full-scale BRC were constructed in Grove, Oklahoma, using the sand with 5% by weight of fly-ash filter media designed by Zhang et al. (2008 a, b) (Chavez et al. 2015). Since 2007 they were subject to normal site hydrology and contaminant loading and have operated relatively unattended. These BRC provide an excellent opportunity to examine the long-term phosphorus and metal retention under field conditions.

OBJECTIVES

The objectives of this study were to quantify phosphorus and heavy metals accumulated in the fly-ash amended filter media used in the BRC constructed in Grove, Oklahoma, and evaluate the remaining potential to retain phosphorus and metals. More specifically the objectives were to;

- Evaluate phosphorus accumulation in filter media in the seven years since construction, and quantify current phosphorus reduction in BRC effluent,

- Evaluate heavy metal accumulation in filter media and quantify current metal reduction in the BRC effluent, and
- Compare the current phosphorus and metal adsorption and desorption capacity with that of the initial filter media tested by Zhang et al. (2008 a, b).

These three objectives are addressed in Chapters II, III, and IV. Chapter II and III evaluate the phosphorus and metal accumulated in filter media using three different laboratory extraction methods. Chapter IV evaluates the phosphorus and metal sorption and desorption capacity of filter media.

Throughout this dissertation, the term adsorption is used to describe any solute that is retained by the porous media. This includes, solutes bound by physical adsorption, precipitation, and within organic matter. Likewise, desorption is used to describe any solute that is released by porous media regardless of its original form and retention mechanism.

SUMMARY, RESULTS AND CONCLUSIONS

In Chapter II, the P accumulation in the Grove BRC between 2007 and 2014 was evaluated. Analysis consisted of T-P, M3-P, and WS-P. In addition to media sampling, stormwater influent and effluent samples were monitored for one year between 2014 and 2015. The filter media M3-P and WS-P profiles indicated significant phosphorus accumulation ($p < 0.05$) within the top 0.15 m of media on all four BRC analyzed. Below 0.15 m, average media M3-P and WS-P concentrations significantly increased ($p < 0.05$), which indicated fly-ash amended filter media effectively adsorbed P within the bioretention media during seven years of BRC operation. The variability in P concentrations below the top 0.15 m of the media profile may be due to the spatial variability in fly ash content and possible preferential flow. Substantial and statistically significant ($p < 0.05$) stormwater P concentration reductions of 64% to 75% and mass reduction of 76% to 93% from monitoring were observed.

In Chapter III, heavy metal accumulation in the media profile between 2007 and 2014 media core samples were evaluated along with influent and effluent monitoring on three of the BRC from 2014 to 2015. Zn and Pb accumulated within the top 0.15 m of the media. Zn and Pb concentrations in the media significantly increased ($p < 0.05$) over the seven years in 2014 compared to that of initial media samples from 2007, indicating fly-ash amended filter media adsorbed metals within the media. Significant ($p < 0.05$) Zn concentration and mass reduction from BRC influent to effluent were also observed.

In Chapter IV, current phosphorus and metals adsorption capacity of fly-ash amended filter media used in four BRC after seven years of operation were estimated from a series of batch experiments. Langmuir and Freundlich isotherms fitted the adsorption data satisfactorily ($r^2 > 0.9$). However, the Freundlich isotherm generated a better fit to the adsorption data. Even after seven years of operation, the fly-ash media exhibited P removal roughly two-thirds of the initial, while Zn and Cu were essentially unchanged. The amount of phosphorus sorbed by the filter media in BRC after seven years of operation was around half (160 mg/g) to the initial sorbed amount (350 mg/g) tested by Zhang et al. (2008). It was noted that with the phosphorus initial concentration of 1, 3, and 10 mg/L, the sand/fly-ash filter media after seven years of operation released an average of 10% to 16% of the sorbed phosphorus. This predicts the long term P retention capacity of fly-ash amended filter media with very low P desorption even after seven years of operation. The desorption of Zn and Cu at the initial concentration of 1, 3, and 10 mg/L was only 0.1% to 0.3% of the sorbed Zn and 0.2% to 0.4% of the sorbed Cu. The desorption of Zn and Cu from the fly-ash amended filter media after seven years was less than 0.5% of the adsorbed metals, almost negligible. Thus, the phosphorus and metal adsorption in sand/fly ash may be considered irreversible with a long term phosphorus and metal retention.

RECOMMENDATIONS

As presented in the following chapters, the objectives of this study have been accomplished. Future research in this topic should focus in the following areas:

- Any follow-up investigations on filter materials amendments for phosphorus and metal retention should focus on media infiltration rate. For BRC or other stormwater infiltration systems, the infiltration capacity of filter media is critical parameter. Depending on the allowable depth of ponding water, the hydraulic conductivity of a filter media should be adequate to drain the water in BRC within the desired time and design requirements. Different filter media amendments will impact the media infiltration capacity. Thus, research should be conducted regarding the infiltration capacity of amendments before selecting any material to be used in BRC media.
- This study quantified effluent water quality for over one year. Additional field monitoring of influent and effluent to evaluate the pollutant removal efficiency of these BRC is justified to strengthen the results and conclusions.

- The extraction procedure used to evaluate the phosphorus and metal sorbed to the media samples needs to be verified by frequent sampling of media and comparison to effluent concentrations. This is critical to define the accuracy and variability of the laboratory methods.
- Large variability in phosphorus and heavy metal concentrations within the media profiles were observed during this study, which may be due to variability in fly ash content within the filter media, consistent with the findings of Chavez et al. (2012). Thus, further research should be conducted on finding appropriate mixing methods for fly ash with sand to ensure an adequately mixed and uniform filter media.
- Column leaching tests should be conducted for determining phosphorus and heavy metal breakthrough at field influent concentrations to better predict long-term treatment capacity and the ultimate life of the filter media.
- Finally, studies on evaluating removal efficiencies of fly-ash amended media for other common urban stormwater pollutants such as hydrocarbons, oil and grease and emerging contaminants should be conducted.

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CHAPTER II

PHOSPHORUS RETENTION BY FLY-ASH AMENDED FILTER MEDIA IN AGED BIORETENTION CELLS

ABSTRACT

Bioretention cells (BRC) are urban stormwater best management practices (BMP) employed to collect, store, infiltrate and treat urban stormwater runoff, and thus reduce pollutant loads to lakes and streams. BRC have shown potential for stormwater quantity and quality control and are growing in popularity. However, the phosphorus (P) removal in BRC has been highly variable due to the diverse properties of soils used as a filter media. The goals of this research were to identify and evaluate P removal rates in four BRC constructed in Grove, OK in 2007. Each cell has a sand and fly-ash media designed to remove phosphorous. Filter media samples from the BRC were collected in 2014 across the cell surface and to a depth of 0.6 m to quantify the accumulation of P in the media. Analysis consisted of total P (T-P), Mehlich-3 P (M3-P), and water soluble P (WS-P). The mean T-P concentration increased over the seven years of operation, but the changes were not statistically significant ($p > 0.05$). The average M3-P and WS-P concentrations in the media profiles showed higher P accumulation in the top 0.15 m of media. The average M3-P and WS-P concentrations between 0.15 to 0.30 m, and 0.30 to 0.60 m were variable on all four BRC media. The media with 5% fly ash significantly retained ($p < 0.05$) M3-P and WS-P over the top 0.15 m of the media. In addition to media sampling, stormwater influent and effluent samples from three of the BRC were monitored over one year. Flow-weighted, composite water quality samples were collected and unfiltered samples analyzed for P. Significant ($p < 0.05$) P concentration reductions of 68% to 75% were achieved between the influent and effluent, and P mass reductions of 76% to 93% were observed.

KEYWORDS: Bioretention, filter media, phosphorus, fly ash, stormwater, water quality

INTRODUCTION

Urban stormwater has been identified as a critical non-point source pollution to receiving water systems (Gorme et al. 2014). 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 (Reddy et al. 2014). 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 (Prince George's County 2002).

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 (Chi-hsu and Davis 2005; DiBlasi et al. 2008; Hsieh et al. 2007; Li and Davis 2009; Li and Davis 2008).

Field monitoring of BRC have found variable and inconsistent P removal. Davis (2007) conducted a study in two BRC where influent P concentrations were reduced by an average of 74% and 68%. However, in a number of studies, significant P leaching from BRC were noted (Dietz and Clausen 2005; Hunt et al. 2006).

While P is an essential nutrient, excess P is usually considered to be pollutant to water bodies as it can lead to eutrophication. It is now widely accepted that a P management plan is essential in order to protect water bodies from the consequences form eutrophication (Heathcote 1998). Filtration, biological uptake, and sorption in filter media are the primary mechanism of P retention (Davis et al., 2009). 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 (Zhang et al. 2008). Reducing dissolved P requires sorption in the filter media Dissolved P sorption processes in soils includes adsorption, ion exchange and precipitation (Sims et al. 2005).

BRC filter media typically consist of organic matter, sand, sandy loam, loamy sand or top soils (LeFevre et al. 2015). In a study conducted by Hunt et al. (2006), 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 (Clark and Pitt 2012). Organic matter, including mulch and compost used in BRC, can increase P in the infiltrating water as the organic matter decomposes and release both organic and inorganic P (Bratieres et al. 2008; Paus et al. 2014). Thus, media should be selected with low P index and low organic content in order to prevent production of P from media itself (LeFevre et al. 2015). For effective P removal, media with low P index and high cation exchange capacity (CEC) are recommended (Hunt et al. 2006). 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 (Dubus and Becquer 2001;

Guppy et al. 2005; Sims et al. 2005; Singh and Gilkes 1991; Villapando and Graetz 2001). Dissolved P can bind with aluminum and ferric hydroxides, and also precipitate with calcium in BRC filter media (Clark and Pitt 2012; Davis et al. 2001).

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 (Gironas et al. 2008; Kus et al. 2012; Samuel et al. 2012; Seelsaen et al. 2006; Singhal et al. 2008). 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 (Reddy 2013). Other BRC media amendments, including fly ash, expanded shale, slag, red mud, and cement have been reported to remove P effectively (Agyei et al. 2002; Akay et al. 1998; Cheung et al. 1994; Cheung and Venkitachalam 2000; Forbes et al. 2005; Johansson and Gustafsson 2000). Zhang et al. (2008) researched using 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 BRC were constructed in Grove, Oklahoma that used the mixture of sand with 5% by weight of fly-ash (Chavez et al. 2015). Since, that time they have operated relatively unattended, and were subject to the normal site hydrology and contaminant loading. The goal of this research was to analyze those aged BRC 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. Media core samples were collected from four BRC in 2014 and were analyzed with three extraction methods to evaluate the P accumulation in media. Finally water samples from influent and effluent at three BRC were collected for one year to quantify the current stormwater P reduction provided by the BRC.

Throughout this dissertation, 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. Likewise, desorption is used to describe any solute that is released by the porous media regardless of its original form and retention mechanism.

MATERIALS AND METHODS

Site Description

Four BRC constructed in Grove, Oklahoma, in 2007 (Chavez et al. 2015) were subjected to testing in this study. A typical BRC section is shown in Figure 2.1 and Table 2.1 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, impervious surfaces 95% 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 BRC, and all were designed with a pool storage depth of not more than 0.3 m. All the cells contain a top soil layer approximately 0.15 m deep. A mix of sand and 5% fly ash by weight was used (Chavez et al. 2015).

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 2.2. Previous studies conducted on operating BRC sampled three to six cores samples with sampling near inlet, outlet and along the centerline of the cell. Jones and Davis (2012) collected six core samples, Chen et al. (2013) collected five core samples, Muerdter et al. (2015) collected six core samples, Komlos et al. (2012) collected five core samples and Brown and Hunt (2009) 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, 0.15-0.30, 0.30-0.45 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 addition to the 2014 cores, 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.

Media Associated Phosphorus Analysis

Three different extractions methods were used to provide insight into the relative strength of the adsorption of the phosphorus to the filter media. Total phosphorus (T-P) in media samples was extracted using EPA Method 3050 (EPA 1996). This boiling strong-acid method measured essentially all phosphorus including that held tightly in the mineral structure. As such, its results include phosphorus that were incorporated into 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 0.45µm 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 (Mehlich 1984). The extracting solution combines acetic acid, ammonium nitrate, ammonium fluoride and ethylene diamine tetraactetic 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 deionize 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).

Water Sampling and Analysis

Three of the BRC (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 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, 950 mL, acid washed bottles. Samplers were programed to take 100 mL samples with each bottle holding up to nine samples. The flow-weighted volume that each sample represents was adjusted for each site based on the first 61 mm 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 such 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 º 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 (2007).

RESULTS AND DISCUSSION

Media pH

Based on the 24 cores and 96 soil samples collected from the four BRC 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) were 8.4 ± 0.9, 8.1 ± 0.7, 8.2 ± 03, and 10.2 ± 0.4 at ECP, GHS, GLA and SR, respectively (Chavez et al. 2012). The pH of the filter media samples after operating for seven years in field was still above 8 indicating the fly ash was still present.

Phosphorus Accumulation in Bioretention Media

Core sample P concentrations are presented in Table 2.2. An Analysis of Variance (two-way ANOVA) for P accumulation between 2007 and 2014 at $\alpha = 0.05$ was performed using SAS version 9.4 (SAS Institute 2014). The comparisons of mean P concentrations were done using the Tukey's HSD test, at α value of 0.05, and presented in Table 2.2.

P concentration profiles (T-P, WS-P, and M3-P) between 2007 and 2014, and by sites and media layer, are presented in Figures 2.3 to 2.5. An increase in T-P concentration in the top soil (0-0.15 m) and filter media (0.15-0.60 m) on all four BRC were observed between 2007 and 2014. However, the increase in average T-P concentration for both top soil 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, which may be due to spatial variability in the fly ash content resulting from the initial construction mixing (Chavez et al. 2012).

T-P

The increase in T-P in the top soil (0-0.15 m) was 83 mg/kg at ECP, 66 mg/kg at GHS, 14 mg/kg at GLA and 142 mg/kg at SR. The increase in T-P concentration at both ECP and GHS cells were consistent since both had drainage 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 at ECP, 40 mg/kg at GHS, 28 mg/kg at GLA and 17 mg/kg at SR cells. While lower than the top soil, the trend for ECP, GHS and GLA is similar to the top soil. 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.

WS-P

The increase in WS-P between 2007 and 2014 for the top soil (0-0.15 m) was 1.3 mg/kg at ECP, 1.5 mg/kg at GHS, 2.5 mg/kg at GLA and 5.7 mg/kg at SR. The increase in WS-P in the filter media (0.15-0.60 m) was 0.9 mg/kg, 0.4 mg/kg, 0.8 mg/kg and 0.8 mg/kg 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 top soil 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 then T-P. This indicates the P in media samples are tightly bond and not soluble.

M3-P

The increase in M3-P concentrations between 2007 and 2014 for the top soil (0-0.15 m) was 26 mg/kg at ECP, 27 mg/kg at GHS, 20 mg/kg at GLA and 35 mg/kg at SR. M3-P increases in the filter media (0.15-0.60 m) were 4.4 mg/kg at ECP, 14.1 mg/kg at GHS, 10 mg/kg at GLA and 9 mg/kg at SR. The increase in M3-P for both top soil 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 top soil for both ECP and GHS with more than 90% impervious surface were similar and SR was the highest. However, GLA had an intermediate value.

Discussion

Previous studies on M3-P depth profiles in BRC media also reported higher P accumulation (56.6 mg/kg) in the top layer (0.06-0.1 m) compared to below 0.1 m (14.3 mg/kg) (Komlos and Traver 2012; Muerdter et al. 2015). The increase in M3-P and WS-P between 2007 and 2014 media samples were statistically significant ($p < 0.05$) in both the top soil and filter media layers on all four BRC analyzed. This strongly indicates fly-ash amended filter media had effectively adsorbed P within the BRC media during the seven year 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 yet prove to be the better indicator for measuring adsorbed P

Phosphorus Depth Profiles in the Bioretention Media

Average P concentration (T-P, WS-P and M3-P) profiles in all four BRC in 2014 are shown in Figure 2.6, and listed in Table 2.3. The P concentrations between depths were compared a two-way ANOVA at α value of 0.05 using the PROC GLM command using SAS software (SAS Institute 2014). No significant ($p > 0.05$), T-P accumulation at the top surface (0-0.15 m) were 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 by (Komlos and Traver 21012; Muerdter et al. 2015) 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 (Chavez et al. 2012), who performed numerical simulations on the impact of the variability of fly ash content on BRC.

The correlation between T-P, M3-P and WS-P in 2014 samples were compared using a Pearson correlation coefficient test, with a significant level of $\alpha = 0.05$. A correlation of

T-P with WS-P (r = -0.01), and with M3-P (r = -0.28) was obtained. Similarly, a correlation between M3-P and WS-P (r = 0.49) was obtained. The relationship between T-P and M3-P is stronger, indicating M3-P tends to decrease as T-P increases.

Stormwater Monitoring Results

Stormwater samples were collected at ECP, GLA and GHS from 2014 to 2015. A summary of P inflow and outflow concentration and mass loading for the three BRC are summarized in Table 2.4. Those results were used to compare the P mass removal rates and concentration reduction from BRC effluent. Influent and effluent mean concentration of total suspended solid, turbidity, pH and electric conductivity are presented in Table 2.5. The P mass input and mass 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. The Wilcoxon Rank-Sum Test, a non-parametric analysis with a significance level of $\alpha = 0.05$ was performed using SAS version 9.4 to determine if BRC treatment made a significant reduction in effluent P concentration and mass output.

Elm Creek Plaza (ECP)

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 ($p < 0.05$).

Grove High School (GHS)

At GHS, fifteen 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 April 1 and May 20, 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 ($p < 0.05$).

Grand Lake Association (GLA)

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 of 64% relative to the influent was statistically significantly ($p < 0.05$). T-P effluent mass was 76% lower than of the influent mass with a significant T-P mass reduction ($p < 0.05$).

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 area of drainage area. Previous bioretention field studies found phosphorus concentration removal of 50% to 94% and phosphorus mass reduction of 44% to 90% (Houdeshel et al. 2015; Erickson et al. 2012; Carpenter and Hallam 2010; Brown and Hunt 2012; Li and Davis 2009). 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.

Phosphorous retained within the bioretention media

*Estimates from Core Sample*s: Phosphorus retained with the bioretention media during seven years of operation can be calculated by the simple mass balance.

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

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

A top soil 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 2.6. The T-P retained within the media depth (0-0.60 m) was 0.40 kg/year at ECP, 0.33 kg/year at GHS, 0.51 kg/year at GLA and 0.60 kg/year 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 and 0.05 mg/L, and retained similar T-P within the media. The T-P retained within the media at GHS and SR were higher of 0.51 kg/year and 0.60 kg/year. The mean T-P influent concentration collected at GHS was 0.21 mg/L, highest among the three monitored.

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 (Runkel et al. 2004) 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 BRC were 0.27 kg/year at ECP, 0.18 kg/year at GHS and 0.37 kg/year at GLA. These values are comparable to the mass of T-P increase calculated from core samples of 0.4 kg/year at ECP, 0.33 kg/year at GHS and 0.51 kg/year 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 the media. These values can be compared to the mass increase of M3-P of 0.08 kg/year at ECP, 0.21 kg/year at GHS and 0.23 kg/year at GLA, and the mass increase of WS-P of 0.008 kg/year at ECP, 0.008 kg/year at GHS and 0.022 kg/year 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.

CONCLUSIONS

Substantial reductions of stormwater phosphorus from seven year old BRC were quantified in this study. Stormwater P concentration reductions at three monitored BRC ranged from 64% to 75%. While P mass reduction ranged from 76% to 93%. Both phosphorus concentration and mass reduction were statistically significant ($p < 0.05$). Filter media M3-P and WS-P, depth profiles indicated significant phosphorus accumulation within the top 0.15 m of media on all four BRC, which consistent with .previous studies (Komlos and Traver 2012; Muerdter et al. 2015). Average M3-P and WS-P concentrations significantly increased ($p < 0.05$) between 2007 and 2014 which indicates fly-ash amended filter media has effectively adsorbed P during the seven years of operation. The increase in T-P concentrations between 2007 and 2014 were not statistically significant ($p > 0.05$), but similar in magnitude to the loading calculated by LOADEST. Average WS-P was only 1 to 2% of average the T-P indicating most P is strongly bound in the media. M3-P extraction may be considered as the better indicator for measuring P adsorbed within the BRC media since it was significant ($p < 0.05$). 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. The T-P retained within the media at GLA and SR was highest at 0.51 kg/year and 0.60 kg/year. The mean T-P influent concentration at GLA was 0.21 mg/L and the highest among the three monitored indicating that GLA was receiving high P loading from runoff. Variability in P concentrations below the top 0.15 m of the media profile was observed. This variability may be due to spatial variation of fly-ash content within the media and from possible preferential flow. Overall, the BRC filter media with fly-ash amendment was effectively retaining phosphorus from stormwater runoff.

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Table 2.1. Design Summary for bioretention cell at Grove, OK (Chavez et al. 2015)

Site	**Grand Lake Association (GLA)**	**Grove High School (GHS)**	**Elm Creek Plaza (ECP)**	**Spicer Residence (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
Land Cover (%) Impervious	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 (m)[a]	15.7	24.1	23.4	4.20

[a] Based on Zhang et al. 2008

Table 2.2. Phosphorus concentration (mean ± standard deviation) in top soil (0-0.15 m) and filter media (0.15-0.60 m) for 2007 and 2014 samples in bioretention cells at Grove, OK. (Two-way ANOVA followed by Tukey's HAD test at α = 0.05).

Site	Media Depth	Variable	Initial (2007) mg/kg n=8	Final (2014) mg/kg n=24	Significance level
ECP	Top Soil (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	Top Soil (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	Top Soil (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	Top Soil (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	*

*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*).

T-P = total phosphorus, WS-P = Water soluble phosphorus and M3-P = Mehlich 3 extracted phosphorus.

Table 2.3. Phosphorus concentration (mean ± standard deviation) on bioretention media depths in 2014 samples at Grove, OK. (Two-way ANOVA at $\alpha = 0.05$)

			Media Depth (m)			
Site	**N**	**Variable**	**0-0.15**	**0.15-0.30**	**0.30-0.45**	**0.45-0.60**
ECP	24	T-P	308 ± 88^{a}	$467 \pm 99^{a,b}$	489 ± 153^{b}	$426 \pm 196^{a,b}$
		WS-P	1.4 ± 0.2^{c}	0.97 ± 0.2^{d}	1.0 ± 0.3^{d}	$1.2 \pm 0.3^{c,d}$
		M3-P	27.5 ± 5^{e}	6.5 ± 0.8^{f}	6.0 ± 0.6^{f}	10 ± 7^{f}
GHS	24	T-P	331 ± 114^{g}	279 ± 50^{g}	282 ± 23^{g}	285 ± 9^{g}
		WS-P	1.5 ± 0.3^{h}	0.67 ± 0.1^{i}	0.93 ± 0.35^{i}	0.82 ± 0.42^{i}
		M3-P	35 ± 7^{j}	15 ± 3^{k}	16 ± 5^{k}	31 ± 6^{j}
GLA	24	T-P	290 ± 60^{l}	207 ± 33^{m}	$255 \pm 75^{l,m}$	205 ± 30^{m}
		WS-P	2.6 ± 1^{n}	0.70 ± 0.12^{o}	1.4 ± 1^{o}	1.4 ± 0.62^{o}
		M3-P	29 ± 5^{p}	15 ± 2^{q}	26 ± 8^{p}	25 ± 9^{p}
SR	24	T-P	312 ± 170^{r}	414 ± 267^{r}	387 ± 238^{r}	315 ± 230^{r}
		WS-P	5.7 ± 1^{s}	1.0 ± 0.5^{t}	1.0 ± 0.63^{t}	1.2 ± 0.9^{t}
		M3-P	40 ± 18^{u}	$9.6 \pm 3.5^{v,w}$	7.5 ± 1^{w}	20 ± 10^{v}

Concentrations with same letters are not significantly different among media depths at the 0.05 probability level ($p > 0.05$).

Concentrations with different letters are significantly different among media depths ($p < 0.05$).

T-P = Total phosphorus, WS-P = Water soluble phosphorus and M3-P = Mehlich 3 extracted phosphorus.

Table 2.4. Inlet and underdrain T-P mean concentration for three bioretention cells monitored at Grove, OK from 2014 to 2015.

		Mean T-P Concentration (mg/L)				T-P Loading (g)			
BRC	Strom events (n)	Inflow (mg/L)	Underdrain (mg/L)	% reduction	Significance	Inflow (g)	Underdrain (g)	% reduction	Significance
ECP	20	0.12	0.03	75%	$p < 0.05$	3.25	0.22	93%	$p < 0.05$
GHS	10	0.15	0.05	67%	$p < 0.05$	5.13	0.83	84%	$p < 0.05$
GLA	11	0.21	0.08	64%	$p < 0.05$	13.8	3.22	76%	$p < 0.05$

The Wilcoxon Rank-Sum Test, a non-parametric analysis at α value of 0.05 was performed using SAS version 9.4 to determine if the BRC treatment made a significant improvement on media P reduction.

$p < 0.05$ indicates significant reduction in effluent T-P concentrations.

Table 2.5. Mean influent and effluent water quality parameters monitored at three bioretention cells at Grove, Oklahoma from 2014 to 2015.

BRC	Pollutant	Storm events (n)	Inflow	Underdrain	% reduction or (increase)	Significance
ECP	TSS (mg/L)	20	106	41	61%	$p < 0.05$
	Turbidity (NTU)	20	66	7.0	89%	$p < 0.05$
	pH	20	6.71	7.72	-15%	$p > 0.05$
	EC(µmhos/cm)	20	75	208	-179%	$p < 0.05$
GHS	TSS (mg/L)	7	110	45	59%	$p < 0.05$
	Turbidity (NTU)	7	19	2.8	86%	$p < 0.05$
	pH	8	6.36	7.51	-18%	$p > 0.05$
	EC(µmhos/cm)	8	147	174	-19%	$p > 0.05$
GLA	TSS (mg/L)	11	95	29	70%	$p < 0.05$
	Turbidity (NTU)	11	9	3.8	60%	$p < 0.05$
	pH	11	7.11	7.96	-12%	$p > 0.05$
	EC(µmhos/cm)	11	86	348	-301%	$p < 0.05$
ECP	TSS (g)	12	2460	275	89%	$p < 0.05$
GHS	TSS (g)	7	5702	950	83%	$p < 0.05$
GLA	TSS (g)	11	1840	1681	9%	$p > 0.05$

The Wilcoxon Rank-Sum Test, a non-parametric analysis at α value of 0.05 was performed using SAS version 9.4 to determine if the BRC treatment made a significant increase or reduction in concentration and mass of monitored water quality parameters.

$p < 0.05$ indicates significant increase or reduction in effluent concentrations

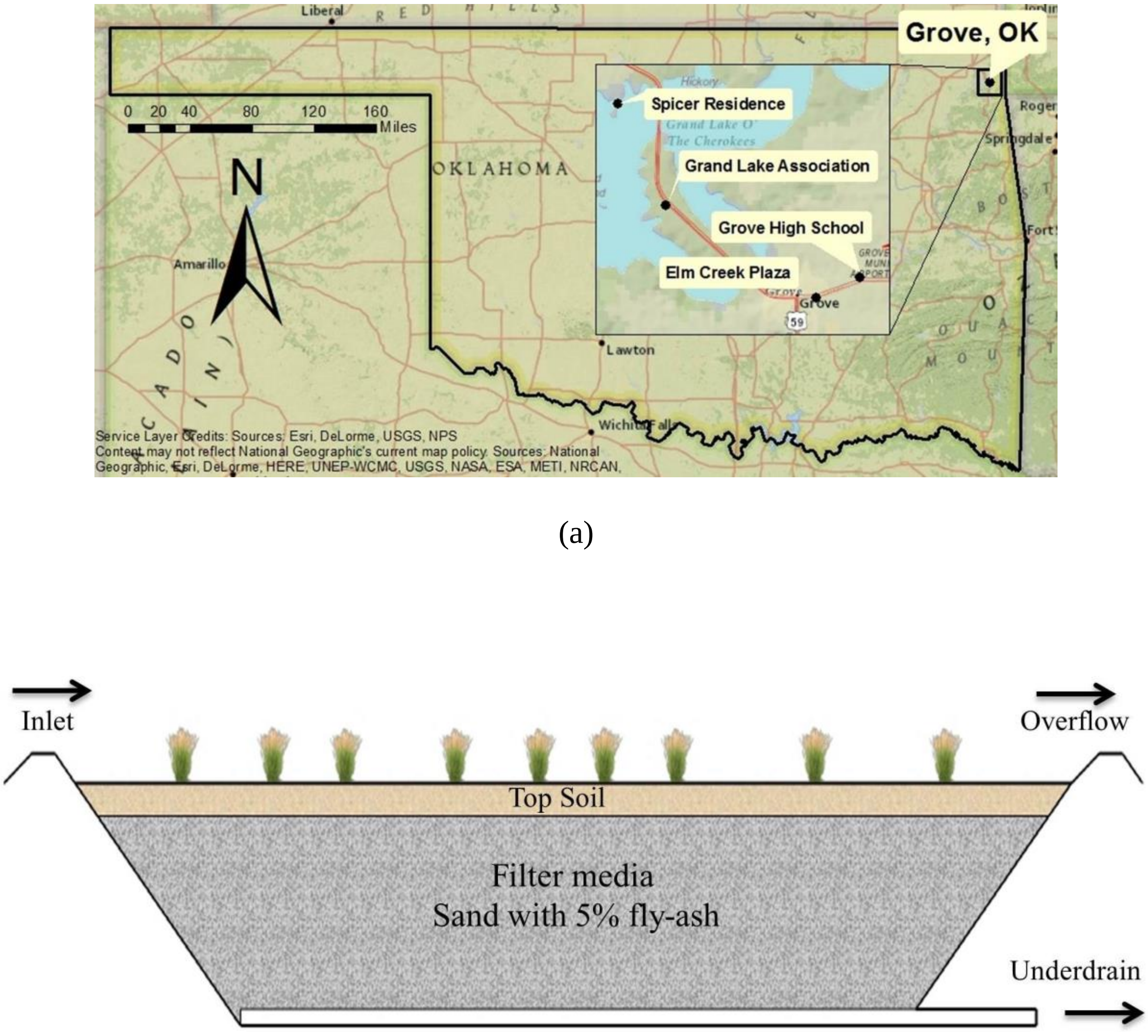
$p > 0.05$ indicates no significant increase or reduction in effluent concentrations

Table 2.6. 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/yr)	M3-P retained (kg/yr)	WS-P retained (kg/yr)	LOADEST Inlet T-P (kg/yr)
ECP	Top Soil	0-0.15	0.16	0.05	0.002	0.27
	Filter media	0.15-0.45	0.24	0.03	0.006	
	Total	0.45-0.60	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	0.45-0.60	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	0.45-0.60	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	0.45-0.60	0.60	0.33	0.042	

T-P = Total phosphorus, WS-P = Water soluble phosphorus and M3-P = Mehlich 3 extracted phosphorus.

N/A = No samples.



(b)

Figure 2.1. (a) Bioretention cell locations at Grove, OK. (b) Typical section of bioretention cell at Grove, OK.

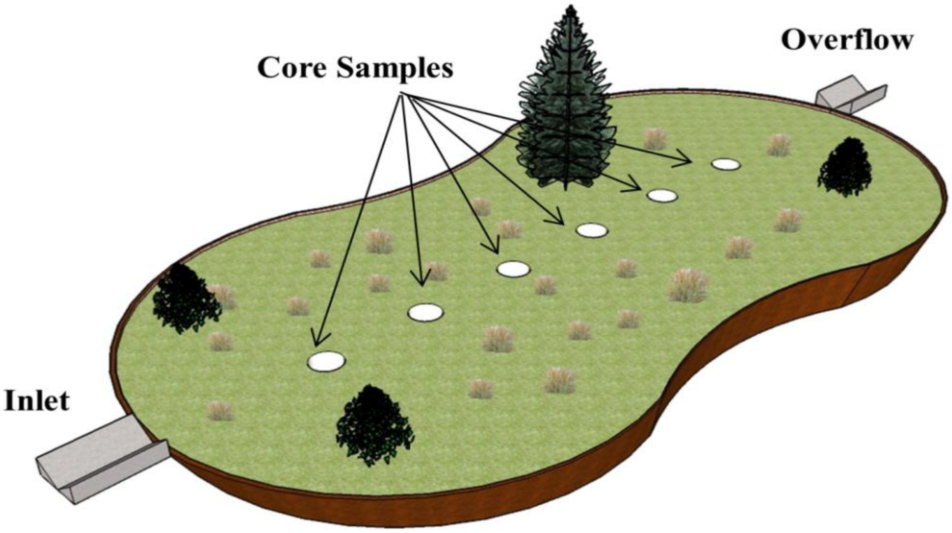


Figure 2.2. Soil core sampling layout at bioretention cells with approximate core locations

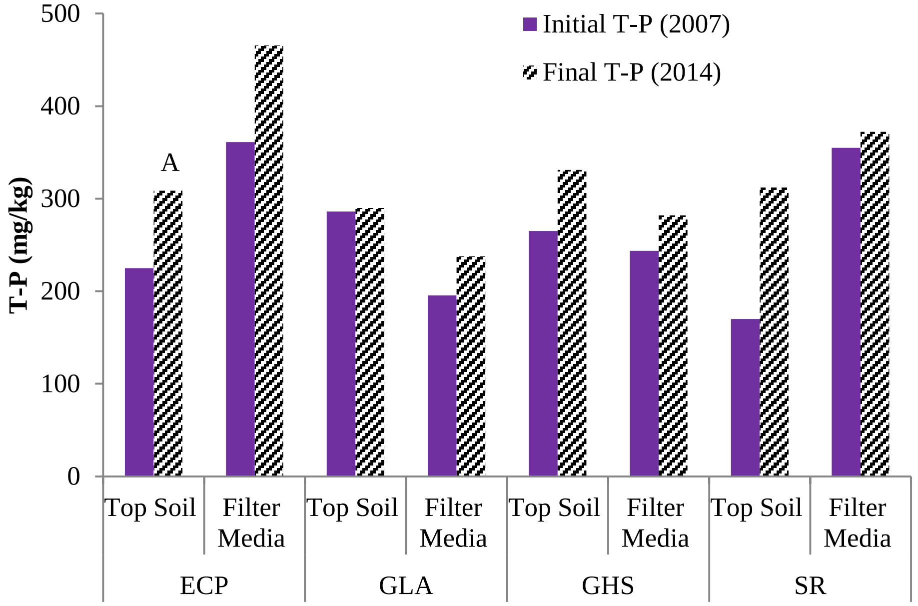


Figure 2.3. Mean total phosphorus (T-P) concentration profiles in 2007 (n = 8) and 2014 (n = 24) media samples collected from four bioretention cells at Grove, OK.

There was no significant difference (*p* > 0.05) in mean T-P concentration between the period, and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test at α = 0.05.

Top soil depth = 0-0.15 m and Filter media depth= 0.15-0.60 m.

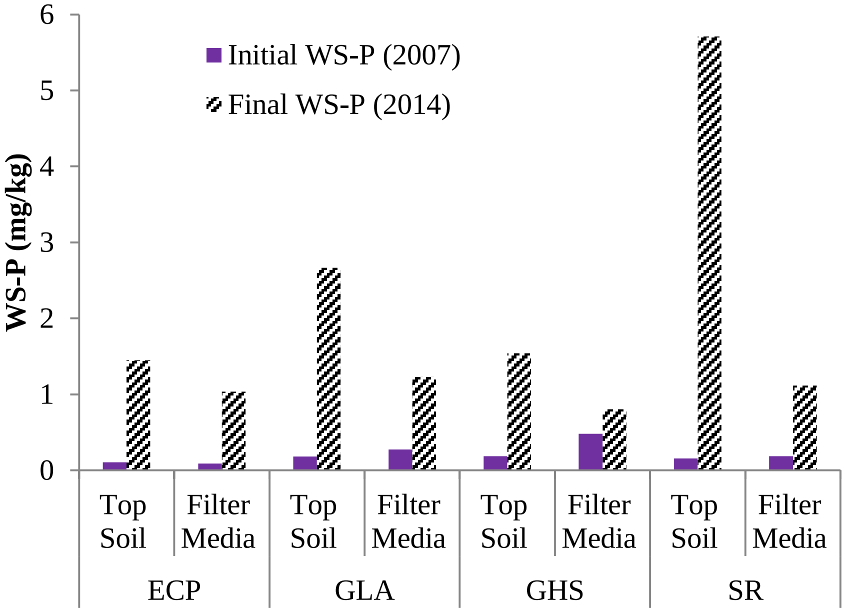


Figure.2.4. Mean water soluble phosphorus (WS-P) concentration profiles in 2007 (n = 8) and 2014 (n = 24) media samples collected from four bioretention cells at Grove, OK.

There was a significant difference in WS-P concentration between period and media layer at each site based on a two-way ANOVA, followed by Tukey's HSD test at α = 0.05.

Top soil depth = 0-0.15 m and filter media depth= 0.15-0.60 m.

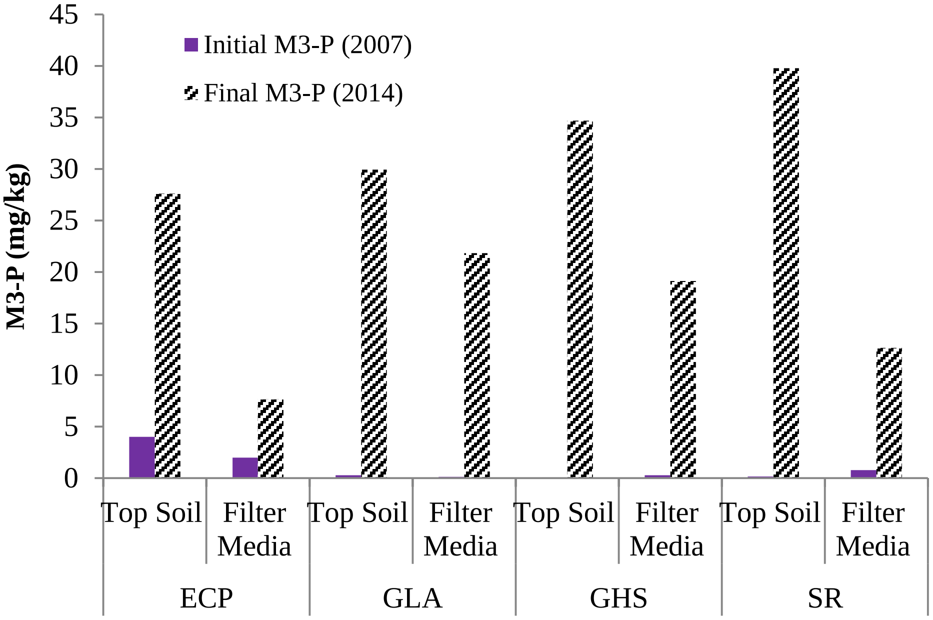


Figure 2.5. Mean Mehlich 3 phosphorus (M3-P) concentration profiles in 2007 (n = 8) and 2014 (n = 24) media samples collected from four bioretention cells at Grove, OK.

There was a significant difference in M3-P concentration between period, and media layer at each site based on two-way ANOVA followed by Tukey's HSD test at α = 0.05.

Top soil depth = 0-0.15 m and Filter media depth= 0.15-0.60 m.

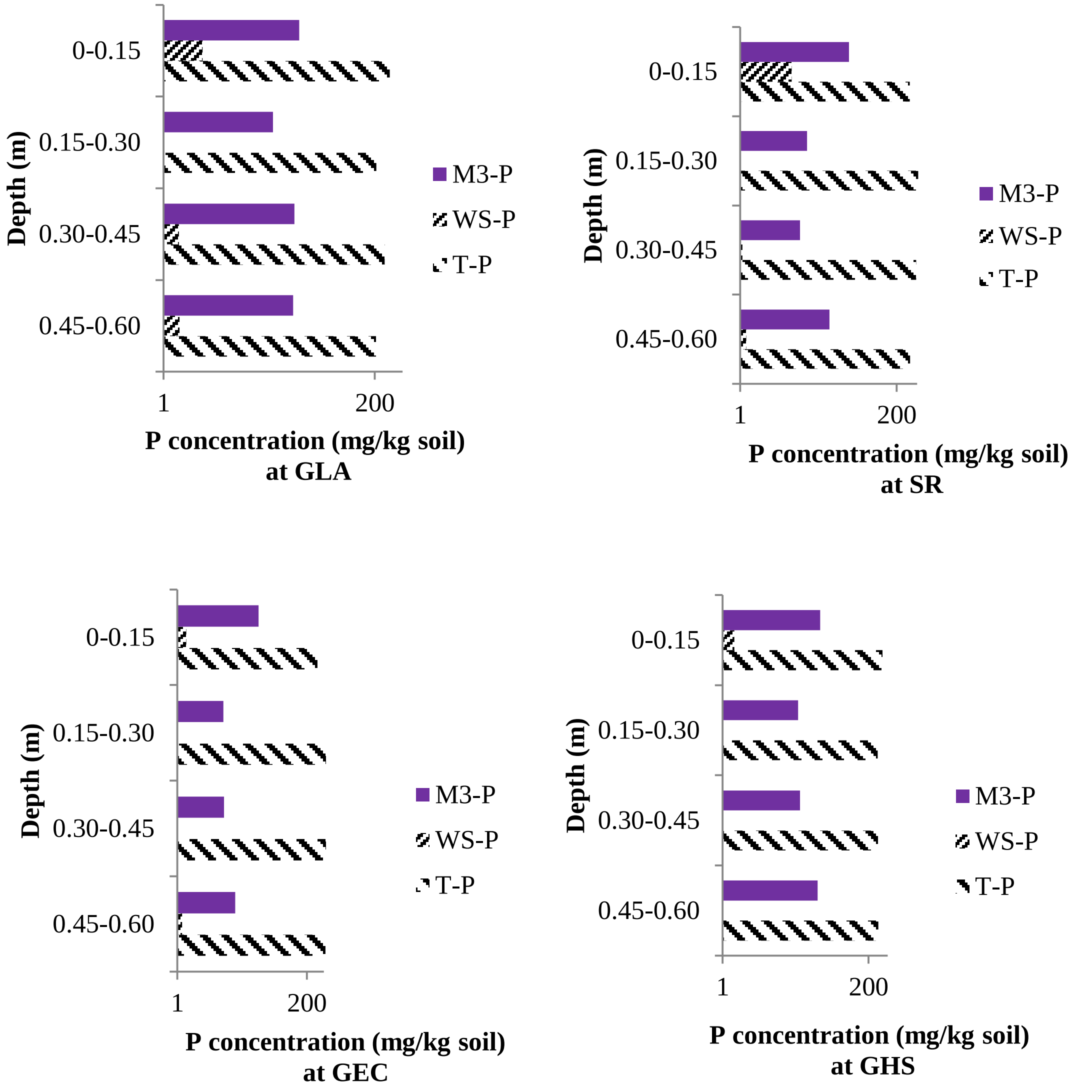


Figure 2-6. Mean phosphorus concentration profiles in 2014 samples (n = 96) in four bioretention cells at Grove, OK.

M3-P = Mehlich 3 phopshorus, WS-P = Water soulble phosphorus, and T-P = Total phopshorus

CHAPTER III

HEAVY METAL ACCUMULATION BY FLY-ASH AMENDED FILTER MEDIA IN AGED BIORETENTION CELLS

ABSTRACT

Heavy metals are of interest in urban stormwater runoff due to their potential toxicity, and their non-degradable nature. Stormwater runoff from urban areas can transport a significant load of heavy metals. Bioretention cells (BRC) have been proposed and constructed to remove metals from stormwater. However, the metal accumulations within the BRC filter media and the long-term capacity filter media to retain heavy metals have not been well assessed. Media samples from a seven year old BRC were collected across the cell surface and to a depth of 0.6 m to assess the accumulation of zinc lead and copper in the media profile. Analysis consisted of total metal from total soil digestion, Mehlich-3 metal from Mehlich-3 extraction and water soluble metal from water soluble extractions. Most of the metal accumulated in the top 0.15m of media. Metal concentrations in the media significantly increased ($p < 0.05$) over the seven years in 2014 compared to that of initial media samples from 2007. In addition to soil samples, influent and effluent samples samples from three of the BRC were monitored for over one year from 2014 to 2015. Influent and effluent concentration of copper and lead were below the detection limit of 0.01mg/L for three BRC monitored. Significant zinc concentration reductions of 56% to 60% were obtained which corresponds to zinc mass reduction of 43% to 88%.

KEYWORDS: Bioretention, filter media, zinc, copper, lead, fly ash, stormwater

INTRODUCTION

Non-point source pollution resulting from urban stormwater runoff has been increasing gradually over time due to urbanization and industrialization (Trenouth and Gharabaghi 2015; Ngabe et al. 2000). Urban stormwater runoff is the second largest source of water pollution for lakes and estuaries, and the third most common source for rivers in the United States (USEPA 2002). Due to urban development in recent decades, impervious surface areas have significantly increased causing increases in stormwater volume and peak flow, and downstream pollution (Dietz 2007; Lucke and Beecham 2011). Heavy metals are of interest in urban stormwater runoff due to their potential toxicity and their non-degradable nature. Numerous sources of metals in urban runoff have been reported including, vehicular brake emission and tire wear as a source for zinc and copper respectively, and various building materials and atmospheric deposition as sources of copper, zinc, lead, and cadmium (Davis et al. 2001).

A number of studies have found significant levels of heavy metals in urban and highway runoff (Smolders et al. 2001; Zhang et al. 2003; Zobrist et al. 2000). A number of studies have found lead (Pb), copper (Cu), zinc (Zn), and cadmium (Cd) concentrations were directly correlated to traffic intensity on highways, streets, and parking lots (Boller and Steiner 2002; Prestes et al. 2006). Concentration of heavy metals in urban runoff by (Walker et al. 1999) reported metal concentration ranges for Cu (0.00006 to 1.41 mg/L), Pb (0.00057 to 26.0 mg/L) and Zn (0.0007 to 22.0 mg/L). In an study conducted in Queensland, Australia, the heavy metals concentration in the runoff from 21 road sites had Zn of160 to 1850 µg/L, Cu of 30 to 305 µg/L, and Pb of 50 to 575 µg/L (Drapper et al. 2000).

The reduction of heavy metals in stormwater runoff is important for both environmental quality and water reuse. Best management practices (BMP) such as bioretention cells (BRC), infiltration ponds, vegetated filter strips, and green roofs have been developed to remove heavy metals from stormwater runoff (Sonstrom et al. 2002; Davis 2005). Among various BMP, BRC have been widely used in urban areas to manage stormwater by reducing peak flow and pollutant loads (Hunt et al. 2008). BRC consist of a filter media, a mulch layer, and plants designed for retention and treatment of urban stormwater through filtration, sedimentation, sorption and plant uptakes (Hatt et al. 2009). Water enters the cell, seeps down through the filter media, and is collected by underdrains at the base for discharge to downstream receiving bodies with pollutant reduction (Lucke and Nichols 2015).

A study conducted by Davis et al. (2006) on two field sites, using one simulated storm event at each site, reported large reduction of heavy metal concentrations (> 95% removal of Zn, Cu, and Pb) for one site and moderate reduction of concentrations at the other site (43% to 70% and 64% removal for Cu, Pb, and Zn). In another study conducted by Hunt (2003), three storm events were monitored with heavy metal removal rates of 98% for Cu and Zn. All these studies reported a significant removal of heavy metals in BRC with a underdrain, however results of these studies are based on a small numbers of storm events, of which some were simulated. David et al. (2015) conducted a field study on metal removal efficiencies of BRC and reported a reductions greater than

90% for Zn, 83% for Cu and 51% for Pb. Studies have found that the performance of BRC for pollutant removal are related to rainfall characteristics at the site and the BRC inflow and outflow limits (Davis 2008; Hunt et al. 2008; Mangangka et al. 2015). In spite of this significant research on the performance of BRC, the major treatment processes for pollutant removal within the systems are yet not clearly understood. Also, only limited research has been carried out to demonstrate the long term capacity of bioretention systems to retain heavy metals.

Sandy soils as a filter media may have low heavy metal retention (Liu et al. 2005; Zhang et al. 2003) Studies have been conducted on adsorption of metals to amended filter media using low cost sorbents including carbonaceous material, weathered soils, waste by-products, activated carbon, iron-oxide, sand, zeolites, rice bran and hulls, saw dust, and fly-ash amended with sand (Brown et al. 2000a; Brown et al. 2000b; Färm 2002; Ho et al. 2002; Naidu et al. 1998; Ricordel et al. 2001; Zhang et al. 2008a; Trenouth and Gharabaghi 2015; Iqbal et al. 2015; Lee at al. 2015; Ulrich et al. 2015). Finally, a number of studies carried at both laboratory and field scale have demonstrated that BRC with fine media filters are effective at removing heavy metals from stormwater runoff (Davis 2007; Dietz and Clausen 2006; Hatt et al. 2008). Therefore, determining sorption capacity of filter media for heavy metal retention in stormwater infiltration systems should be given a major attention.

Retention of heavy metals in soils is associated with the content of Fe, Al, and Mn oxides and hydroxides, and pH (Barbosa and Hvitved-Jacobsen 1999; Farrah and Pickering 1977; Gadde and Laitinen 1974; Gong and Donahoe 1997). Sedimentation and filtration processes in bioretention system removes the particulate forms of heavy metals (Davis 2008). Removal of particulate-bound heavy metals is expected to continue until the end of filter media useful life, which is assumed to occur when the bioretention system is clogged. However, a considerable amount of heavy metals from urban runoff is presented in dissolved form, which is only removed through chemical sorption (Davis et al. 2009; Dean et al. 2005). Also, studies conducted by Hatt et al. (2009) and Le Coustumer et al. (2012) reported heavy metal accumulation on dependent on the clogging of filter media in BRC. The accumulation of heavy metals in stormwater infiltration systems such as BRC raises a potential short and long-term management concern as metals cannot be broken down (Li and Davis 2008). In a study conducted by Li and Davis (2008) the management of heavy metals accumulated and environmental fate of captured heavy metals were addressed. They sampled two media cores from established BRC to determine the strengths of lead, copper and zinc affiliation with the filter media and metal accumulation with respect to media depth. The finding indicated high accumulation of zinc and lead in the top 10-20 cm surface and low mobility of captured metals. Similar metal profiles have been reported in laboratory-scale bioretention studies (Blecken et al. 2009; Hatt et al. 2008).

Many studies have been carried out to find more effective filter media for heavy metals removal from bioretention systems (Liu et al. 2005; Samuel et al. 2012; Lee et al. 2015). However, a cost effective filter media is needed to reduce the construction cost of BMP. Issues related to long term accumulation of heavy metals and pollutant capture mechanisms in BRC media have not adequately been identified and quantified. Zhang et al. (2008b) researched using different soil amendments as a potential BRC media to improve metal removal. Based on his testing, fly ash was identified as having the greatest potential for metal retention. A mixture of sand with 5% fly ash by weight was identified as having adequate hydraulic conductivity with good metal sorption. That mixture exhibited greater than 95% removal of Zn and Cu in batch experiments.

In 2007, several full-scale BRC were constructed in Grove, Oklahoma that used the mixture of sand with 5% by weight of fly-ash filter media (Chavez et al. 2015). Since, that time, they have operated relatively unattended and were subject to the normal site hydrology and contaminant loading. The goal of this research was to analyze those aged BRC to quantify heavy metal accumulation in the filter media over the seven years since construction and to define current metal reduction in the BRC effluent. Media core samples were collected from four BRC in 2014 and analyzed by three extraction methods to evaluate the metal accumulation in the media. Finally, water samples from influent and effluent at three BRC were collected for over one year, from 2014 to 2015, to quantify the current metal reduction provided by the BRC.

Throughout this dissertation, the term adsorption is used to describe any solute that is retained by the porous media. This would include, solutes bound by physical adsorption, precipitation, and within organic matter. Likewise, desorption is used to describe any solute that is released by the porous media regardless of its original form and retention mechanism.

MATERIALS AND METHODS

Four BRC constructed in Grove, Oklahoma, in 2007 (Chavez et al. 2015) were subjected to testing in this study. Each had a filter media consisting of sand and 5% fly ash. A typical BRC section is shown in Figure 2.1 and Table 2.1 presents the design summary of each BRC. The impervious area within each drainage area of each BRC was calculated using Google Earth Pro. Grand Lake Association, (GLA), treats runoff from a tourist information center having a 36% of the total area impervious. Grove High School, (GHS), treats runoff from a faculty parking lot, with 95% impervious drainage area. Elm Creek Plaza, (ECP), treats runoff from a busy commercial strip mall parking lot with 100% impervious area. Spicer Residence, (SR), 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 BRC, and all were designed with a pool storage of not more than 0.3 m. All the cells contain a top soil layer approximately 0.15 m deep.

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 2.2. Previous studies conducted on operating BRC sampled three to six cores samples with sampling near inlet, outlet and along the centerline of the cell. Jones and Davis (2012) collected six core samples, Chen et al. (2013) collected five core samples, Muerdter et al.

(2015) collected six core samples, Komlos et al. (2012) collected five core samples and Brown and Hunt (2009) 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, 0.15-0.30, 0.30-0.45 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 addition to the 2014 cores, 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.

Media Associated Metal Analysis

Three different extraction methods were used to provide insight into the relative strength of the adsorption of the metals to the filter media. Total zinc (T-Zn), total copper (T-Cu), and total lead (T-Pb) in media samples were extracted by total soil digestion using the EPA Method 3050 (EPA 1996). This boiling strong-acid method measured essentially all metals including that held tightly in the mineral structure. As such, its results include metals that were incorporated into 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 strong bonded adsorbed metals not measured by the other methods.

Water soluble zinc (WS- Zn), water soluble copper (WS- Cu), and water soluble lead (WS- Pb) were measured using a 1:10 by weight, solid to deionized water extraction. The sample was 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 than vacuum filtered using 0.45µm membrane and was analyzed for metals. Water soluble extraction gives a measure of soluble mineral salts and weakly adsorbed ions to the porous media.

Mehlich-3 metal extraction (M3-Zn, M3-Cu, and M3- Pb), is a multi-nutrient method that estimates plant availability of most macro- and micro nutrients in soils (Mehlich 1984). 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 basic in nature (Mehlich 1984). The extracting solution combines acetic acid, ammonium nitrate, ammonium fluoride and ethylene diamine tetraacetic acid (EDTA).

Filter media pH was measured at a soil to deionize water ratio of 1:3. Metal 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).

Water Sampling and Analysis

Three of the BRC (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 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, 950 mL, acid washed bottles. Samplers were programed to take 100 mL samples with each bottle holding up to 9 samples. The flow-weighted volume that each sample represents was adjusted for each site based on the first 61 mm 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 such that the first two bottles represented the first 13 mm of runoff and the remaining twelve bottles collected the additional runoff. Autosamplers storage temperature was set to < 4 º C and samples were retrieved within one day of sampling. Finally, filtered samples were sent to SWFAL for analysis. Total suspended solids were analyzed following ASTM D 3997-97 (2007).

RESULTS AND DISCUSSION

Media pH

Based on the 24 cores and 96 soil samples collected from the four BRC in 2014, the top soil (0-0.15 m) at ECP, 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 fly ash content. The initial filter media (0.15-0.60 m) pH from 2007 samples (n = 24) were 8.4 ± 0.9, 8.1 ± 0.7, 8.2 ± 0.3, and 10.2 ± 0.4 at

ECP, GHS, GLA and SR (Chavez et al. 2012). The pH of the filter media samples after operating for seven years in field was still above 8 indicating the fly ash was still present in media.

Metal Accumulation in Bioretention Media

Core sample metal concentrations are presented in Table 3.2. An Analysis of Variance (two-way ANOVA) for metal accumulation between 2007 and 2014 at $\alpha = 0.05$ was performed using SAS version 9.4 (SAS Institute 2014). The comparisons of mean concentrations were done using the Tukey's HSD test, at α value of 0.05, and are presented in Table 3.2.

A comparison of metal between 2007 and 2014 and by each site is presented in Figures 3.3 to 3.11. A statistically significant ($p < 0.05$) increase in T-Zn, and T-Pb in the top soil (0-0.15 m) and filter media (0.15-0.60 m) on all four BRC were observed. However, the increase in average T-Cu in the top soil at ECP, GHS, and SR and the filter media at GHS, GLA, and SR were not statistically significant ($p > 0.05$) based on the two-way ANOVA, Tukey's HSD test.

T-Zn, T-Cu and T-Pb

The increase in T-Zn concentration in the top soil (0-0.15 m) was 86 mg/kg at ECP, 96 mg/kg at GHS, 17 mg/kg at GLA and 20 mg/kg at SR. The increase in T-Cu concentration in the top soil was 3 mg/kg at ECP, 1 mg/kg at GHS, and 5 mg/kg at GLA and SR. The increase in T-Pb concentration in the top soil was 9 mg/kg at ECP, 13 mg/kg at GHS, and 12 mg/kg at both GLA and SR. The increase in T-Zn and T-Pb concentrations at both ECP and GHS cells were consistent as both had drainage with more than 90% impervious area. The increased T-Zn and T-Pb at GLA and SR with the drainage of 36% and 13 % impervious surface were lower compared to both ECP and GHS. The increase in T-Cu concentration at ECP and GHS were not consistent, but the increase in T-Cu concentration at GLA and SR with an impervious surface of 36% and 13 % were similar. The increase in T-Zn concentration between 2007 and 2014 for the filter media (0.15-0.60 m) was 8 mg/kg at ECP, 14 mg/kg at GHS, 9 mg/kg at GLA and 8 mg/kg at SR. Similarly the increase in T-Pb concentration in the filter media was 3 mg/kg at ECP, 12 mg/kg at GHS, 4 mg/kg at GLA and 5 mg/kg at SR. The filter media T-Zn and T-Pb is similar to the top soil at all four sites. The increase in T-Zn and T-Pb concentration in the both top soil and filter media between 2007 and 2014 were statistically significant ($p < 0.05$) based on the two-way ANOVA, Tukey's HSD test indicating the BRC media with fly ash had effectively accumulated metals in the media surface during the seven years of operation. Metal loading into the BRC with high impervious surface was higher, which may be due to the higher runoff from the parking lots to the BRC.

WS-Zn, WS-Cu and WS-Pb

The increase in WS-Zn, between 2007 and 2014 for the top soil (0-0.15 m) was 0.37 mg/kg at ECP and GHS, 0.3 mg/kg at GLA and 1.9 mg/kg at SR. The increase in WS-Zn in the filter media (0.15-0.60 m) was 0.15 mg/kg, 0.12 mg/kg, 0.17 mg/kg and 0.15 mg/kg at ECP, GHS, GLA and SR respectively. The increase in WS-Zn, WS-Cu and WS-Pb were similar for for the two BRC with more than 90% impervious area, ECP and

GHS. The increase in WS-Zn, WS-Cu and WS-Pb at GLA with 36% impervious surface was consistent with the ECP and GHS. However, the increase in WS-Zn, WS-Cu and WS-Pb in the top soil at SR was the greatest. These increases in both top soil and filter media, while more than an order of magnitude smaller than T-Zn, T-Cu and T-Pb. were statistically significant ($p < 0.05$) based on the two-way ANOVA, Tukey's HSD test. This indicates, the metals in media samples are tightly bond and not soluble.

M3-Zn, M3-Cu and M3-Pb

The increase in M3-Zn concentration between 2007 and 2014 in the top soil (0-0.15 m) was 33 mg/kg at ECP, 67 mg/kg at GHS, 10 mg/kg at GLA and 7 mg/kg at SR. M3-Zn increases in filter media (0.15-0.60 m) were 2 mg/kg at ECP, 5 mg/kg at GHS, 2 mg/kg at GLA and 2 mg/kg at SR. The increase in M3-Zn concertation for the ECP and GHS with more than 90% impervious area was higher than GLA and SR with 36% and 13% of impervious area. The increase in M3-Zn concentration at both top soil and filter media were statistically significant ($p < 0.05$) based on the two-way ANOVA, Tukey's HSD test. The increase in M3-Cu concentration between 2007 and 2014 in the top soil at four BRC were between 1.5 to 2 mg/kg and these increases were similar among the four BRC with no major effects for land cover. The increase in M3-Cu concentration in the top soil and filter media between 2007 and 2014 were statistically significant ($p < 0.05$) at ECP, GHS and GLA. The increase in M3-Pb concentration in the top soil was 2 mg/kg at both ECP and GHS, 5 mg/kg at GLA and 2 mg/kg at SR. The increases in M3-Pb at ECP and GHS with more than 90% impervious surface were similar with GLA the highest. The increase in M3-Pb concentration in the top soil and filter media were statistically significant ($p < 0.05$) based on the two-way ANOVA, Tukey's test. The M3-Zn and M3-Cu increases were about 50% of the T-Zn and T-Cu increase and the magnitudes of M3-Pb increase was about 33% of the T-Pb increase. The increase in T-Zn, WS-Zn and M3-Zn concentrations between 2007 and 2014 in the top soil at four BRC were similar. The increase in T-Zn, WS-Zn, and M3-Zn, at ECP and GHS with more than 90% impervious surface were similar and had the highest concentrations among four BRC.

Discussion

Previous studies on metal profiles in BRC media reported a higher metal (Zn, Cu and Pb) accumulation in the top 0.05- 0.2 m of BRC media (Li and Davis 2008; Jones and Davis 2013; Lim et al. 2015). The increase in T-Zn and T-Pb, WS-Zn, WS-Cu and WS-Pb and M3-Zn and M3-Pb between 2007 and 2014 media samples were statistically significant ($p < 0.05$) in both the top soil and filter media layers on all four BRC. This strongly indicates fly-ash amended filter media had effectively adsorbed metals within the BRC media during the seven year of operation. However, the increase in T-Cu in both the top soil and filter media at GHS and SR and M3-Pb concentration increase in SR were not statistically significant ($p > 0.05$). Average WS-Zn, WS-Cu and WS-Pb were about 1 to 4% of the total metal concentration, while average M3-Zn, M3-Cu and M3-Pb were 33 to 40% of the total averages. This indicates that while metals adsorbed within the BRC during the seven years are strongly bonded, there is a small and growing proportion of weakly bound metal within the media.

Based on the three extraction methods, all three total water soluble and Mehlich 3 extracted metal concentration increases were statistically significant, for top soil and filter media between 2007 and 2014, except for T-Cu and M3-Cu. Average concentration of WS-Zn, WS-Cu and WS-Pb were only 1 to 4% of average T-Zn, T-Cu and T-Pb. both total digestion and Mehlich 3 extraction are considered adequate indicator for measuring metal adsorbed within the BRC media.

Metal Depth Profiles in the Bioretention Media

Average metal depth profiles for each metal by each extraction method in all four BRC in 2014 are shown in Figure 3.12 to 3.15, and listed in Table 3.3. The metal concentrations between depths were compared with a two-way ANOVA at α value of 0.05 using PROC GLM command using SAS software (SAS Institute 2014). The average T-Zn, T-Pb, WS-Zn and M3-Zn, M3-Pb concentrations were highest in the top 0.15 m and significant accumulation ($p < 0.05$) at media top surface (0-0.15 m) was observed in all four BRC.

Total, Water soluble and Mehlich-3 Zn and Pb accumulation in the top 0.15 m of bioretention media for all four BRC were observed in this study. However, the T-Cu concentration had a somewhat different trend, with high concentrations deeper in the profile. Previous studies on metal concentration profiles on BRC media depth also reported a higher metal (Zn, Cu and Pb) accumulation in the top 0.05- 0.2 m of BRC media (Nightingale 1987; Dechesne et al. 2005; Li and Davis 2008; Jones and Davis 2012; Lim et al. 2015). Turer et al. (2001) also found that zinc and lead concentration in soils along the urban highways was concentrated in the top 0.15 m. Variability in metal concentrations below 0.15 m were observed and may be due to spatial variation in in the fly ash content within the media and some preferential flow. This is an agreement with results reported by (Chavez et al. 2012), who performed numerical simulations on the impact of the variability of fly ash content on BRC.

Stormwater Monitoring Results

Influent and effluent stormwater samples were collected from ECP, GLA and GHS from 2014 to 2015. More than 80% of the influent and effluent concentrations for Cu and Pb at the three BRC were below detection limit (D L= 0.01 mg/L for both). So, statistical analysis was not applicable. A summary of Zn inflow and outflow concentration and mass loading for three BRC are summarized in Table 3.4. Influent and effluent mean concentration of total suspended solid, turbidity, pH and electric conductivity are presented in Table 3.5. Those results were used to compare the Zn mass removal rates and concentration reduction. The metal mass input and mass output for each cell were calculated as a product of the metal event mean concentration and the total runoff volume measured during a runoff event. The Wilcoxon Rank-Sum Test, a non-parametric analysis with a significance level of $\alpha = 0.05$ was performed using SAS version 9.4 to determine if the BRC treatment made a significant reduction in the effluent metal concentration and mass output.

Elm Creek Plaza (ECP)

At ECP 20 storm events occurred 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 achieved. Zn effluent concentration was

60% lower than the influent, and Zn effluent mass was 88% lower than the influent. Both reductions were statistically significant ($p < 0.05$). More than 80% (n=17) of the influent and effluent concentration of the total sample collected (n=20) for Cu and Pb were below detection limit (D L= 0.01 mg/L). Thus, statistical analysis was not applicable.

Grove High School (GHS)

At GHS 15 storm events occurred from September 2014 to September 2015, of which 10 events were sampled and analyzed. Events ranged from 8 mm to 80 mm, and the mean storm size was 30 mm. The overall mean flow volume reduction was 13%, with a standard deviation of 88%. Between April 1 and May 20, 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. The Zn effluent concentration was 57% lower than of the influent and Zn effluent mass was 77% lower than of the influent. Both the reductions were statistically significant ($p < 0.05$). More than 80% (n=8) of the influent and effluent concentration of the total data collected (n=9) for Cu and Pb were below detection limit (D.L= 0.01 mg/L). Thus, statistical analysis was not applicable.

Grand Lake Association (GLA)

At the GLA, eleven storm events occurred from June 2014 to September 2015 and were sampled and analyzed. Event ranged from 11 mm to 92 mm, mean storm size was 38 mm, and the median storm size was 36 mm. One overflow event occurred during the event. 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 when there was no influent. Overall, underdrain flow was 200% greater than influent during the monitoring period. For four storm events out of eleven, the flow volume in the underdrain was lower than the inlet flow volume, and had a flow reduction of 60%. For remaining seven storms this cell exhibited groundwater seepage and had 300% more volume coming from the underdrain compared to the cell inlet. The groundwater seepage through the underdrain impacted the quantification of the BRC performance including flow volume reduction and Zn mass reduction. 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, Zn effluent concentration was significantly reduced ($p < 0.05$) by 56%. Zn effluent mass was 43% lower than of the influent mass but not statistically significant ($p > 0.05$). More than 80% (n=10) of the influent and effluent concentration of the total data collected (n=11) for Cu and Pb were below detection limit (DL= 0.01 mg/L) and statistical analysis was not applicable.

Zn concentration reduction of 56% to 60% and Zn mass reduction of 43% to 88% were achieved at the three BRC. Influent Zn concentration at ECP and GHS with the drainage area having greater than 90% impervious parking lot with high vehicular traffic were higher than Zn influent concentration at GLA a public property with only 36% impervious area and fewer cars. Laboratory scale studies conducted by (Davis et al. 2006; Davis et al. 2003; McIntyre et al. 2014) reported Zn concentration reduction of 90%. David et al. (2015) conducted a field study on metal removal efficiencies of BRC and reported a concentration reduction of 93% for Zn, 83% for Cu and 51% for Pb. Also, field studies conducted by (Hunt 2003; Muthanna et al. 2007) reported a Zn concentration reduction of 90% through monitored bioretention systems. However, these results were mostly obtained from new cell and probably do not reflect the long term performance. The BRC with fly-ash amended filter media, after seven years of construction displayed significant Zn concentration and mass reduction.

Metal retained within the bioretention media

Estimates from Core Samples: Metals retained within the bioretention media during seven years of operation can be calculated by the simple mass balance.

$$Metal_{trapped} = (Metal_{final} - Metal_{initial}) * V * \rho_b \qquad (1)$$

Where, $Metal_{final}$ is the metal concentration (mg/kg) in 2014 $Metal_{initial}$ is the initial metal concentration (mg/kg) in 2007, ρ_b is the bulk density (kg/m^3) of the media and *V* (m3) is the cell media volume.

A top soil dry bulk density of 1.4 g/cm^3 and a filter media dry bulk density of 1.5 g/cm^3 were used. Metal retained within the media are presented in Table 3.6. The T-Zn and M3-Zn retained within the media depth (0-60 m) at GHS was highest of 0.63 kg/yr and 037 kg/yr. while at ECP and GLA were similar and lowest at SR. The WS- Zn, Cu and Pb retained in media at four BRC were less than 0.01 kg/yr.

Estimates from Flow Monitoring: As an estimation of T-Zn loading during the seven years of BRC operation, a regression equation of flow versus precipitation was generated using the rainfall and BRC inflow 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 total inflow, rainfall, and measured Zn from the stormwater monitoring, the Load Estimator model (LOADEST) was used to predict the Zn load per year at the three BRC. LOADEST, Runkel et al. (2004) 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 estimates of Zn load using LOADEST to the BRC were 0.06 kg/year at ECP, 0.13 kg/year at GHS and 0.09 kg/year at GLA. These values can be compared to the increase of T-Zn of 0.21 kg/year at ECP, 0.63 kg/year at GHS, and 0.23 kg/year at GLA and WS-Zn of 0.002 kg/year at ECP, 0.003 kg/year at GHS, and 0.005 kg/year at GLA. Thus, the estimate of Zn retained by the media measured by the Mehlich-3 extraction may be a better estimator of Zn load.

CONCLUSIONS

Significant reductions of Zn from seven year old BRC were obtained during this study. Effluent Zn concentration removal at three BRC raged from 56% to 60% with a significant concentration reduction ($p < 0.05$), while Zn mass reduction ranged from 43% to 88%. The influent and effluent concentration for Cu and Pb were below the detection limits (D.L = 0.01 mg/L) on all three BRC monitored. The T-Zn, T-Pb, WS-Zn, T-Pb and M3-Zn, and M3-Pb depth profiles indicated significant Zn and Pb accumulation within the top 0.15 m of media on all four BRC, which is consistent with previous studies (Nightingale 1987; Dechesne et al. 2005; Li and Davis 2008; Jones and Davis 2012; Lim et al. 2015). Average T-Zn, T-Pb, WS-Zn, Ws-Cu, Ws-Pb and M3-Zn, and M3-Pb significantly increased ($p < 0.05$) between 2007 and 2014 in both the top soil (0-0.15 m) and filter media (0.15-0.60 m) on all four BRC analyzed. The depth profiles of metal accumulation on all four BRC, shows the top 0.15 m contributing the most the metal accumulation over the period. ECP and GHS had the highest T-Zn M3-Zn and WS-Zn accumulated in the top 0.15 m, indicating these sites with more than 90% impervious surface received higher Zn loading through runoff from parking lot and vehicular activities than those of GLA and SR with 36% and 13 % of impervious area. The mean influent Zn concentration was also higher at ECP and GHS than that of GLA. Since, most of the heavy metals captured, accumulated within top 0.15 cm of the filter media surface, results from this study can strongly be recommended for a shallow media design of 0.6 m with focus on heavy metal capture. This indicates that overall the BRC filter media with fly-ash amendment was effectively retaining substantial heavy metals from urban runoff.

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Table 3.1 Design Summary of bioretention cells at Grove (Chavez et al. 2015)

Site	**Grand Lake Association (GLA)**	**Grove High School (GHS)**	**Elm Creek Plaza (ECP)**	**Spicer Residence (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
Land Cover (%) Impervious	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 (m)[a]	15.7	24.1	23.4	4.20

[a] Based on Zhang et al. (2008 a).

Table 3.2. Metal concentration (mean ± standard deviation) in top soil (0-0.15 m) and filter media (0.15-0.60 m) for 2007 and 2014 core samples in four bioretention cells at Grove, OK. (Two-way ANOVA followed by Tukey's HSD test at α= 0.05)

Site	Media Depth (m)	Variable	Initial (2007) mg/kg n=8	Final (2014) mg/kg n =24	Significance level
ECP	Top Soil (0-0.15 m)	T-Zn	22 ± 2	108 ± 46	*
		T-Cu	9.0 ± 1	11 ± 2	ns†
		T-Pb	3.0 ± 0.7	11 ± 3	*
		WS-Zn	0.03 ± 0.03	0.4 ± 0.2	*
		WS-Cu	0.01 ± 0.01	0.08 ± 0.03	*
		WS-Pb	0.01 ± 0.01	0.4 ± 0.07	***
		M3-Zn	2.0 ± 0.04	35 ± 21	*
		M3-Cu	2.0 ± 0.35	4 0 ± 0.4	***
		M3-Pb	0.01 ± 0.01	2.0 ± 1.5	*
	Filter Media (0.15-0.60 m)	T-Zn	23 ± 3	31 ± 4	**
		T-Cu	13 ± 2	22 ± 5	**
		T-Pb	4.0± 0.4	7.0 ± 0.8	***
		WS-Zn	0.05 ± 0.03	0.2 ± 0.1	*
		WS-Cu	0.01 ± 0.01	0.06 ± 0.02	***
		WS-Pb	0.01 ± 0.01	0.2 ± 0.07	***
		M3h-Zn	2.0 ± 0.2	4.0 ± 0.5	***
		M3-Cu	1.0 ± 0.1	3.0 ± 0.8	***
		M3-Pb	0.01 ± 0.01	0.2 ± 0.1	*
GHS	Top Soil (0-0.15 m)	T-Zn	23 ± 1	119 ± 45	*
		T-Cu	3.0 ± 0.1	4.0 ± 2	ns†
		T-Pb	3.0 ± 0.2	16 ± 8	*
		WS-Zn	0.1 ± 0.01	0.4 ± 0.1	**
		WS-Cu	0.01 ± 0.01	0.05 ± 0.01	***
		WS-Pb	0.01 ± 0.01	0.05 ± 0.01	***
		M3-Zn	1.0 ± 0.07	68 ± 51	***
		M3-Cu	1.0 ± 0.07	3.0 ± 0.5	***
		M3-Pb	0.01 ± 0.01	3.0 ± 2	*
	Filter Media (0.15-0.60 m)	T-Zn	19 ± 1	33 ± 19	*
		T-Cu	4.0 ± 0.3	5.0 ± 1	ns†
		T-Pb	3.0 ± 1	15 ± 0.8	*
		WS-Zn	0.08 ± 0.03	0.2 ± 0.08	*
		WS-Cu	0.01 ± 0.01	0.05 ± 0.01	***
		WS-Pb	0.01 ± 0.01	0.05 ± 0.01	***
		M3-Zn	1.0 ± 0.08	6.0 ± 5	***
		M3-Cu	1.0 ± 0.1	2.0 ± 0.4	**
		M3-Pb	0.01 ± 0.01	0.1 ± 0.2	ns†

Table 3.2. Continuation

Site	Media Depth (m)	Variable	Initial (2007) mg/kg n=8	Final (2014) mg/kg n =24	Significance level
GLA	Top Soil (0-0.15 m)	T-Zn	29 ± 1	46 ± 6	*
		T-Cu	3.0 ± 0.1	8.0 ± 2	*
		T-Pb	6.0 ± 2	18 ± 1	***
		WS-Zn	0.2 ± 0.04	0.5 ± 0.09	*
		WS-Cu	0.01 ± 0.01	0.06 ± 0.02	*
		WS-Pb	0.01 ± 0.01	0.05 ± 0.01	***
		M3-Zn	2.0 ± 0.08	12 ± 3	**
		M3-Cu	1.0 ± 0.070	3.0 ± 1	*
		M3-Pb	0.01 ± 0.01	5 ± 0.8	***
	Filter Media (0.15-0.60 m)	T-Zn	21 ± 3	30 ± 6	**
		T-Cu	7.0 ± 1	9.0 ± 2	ns†
		T-Pb	4.0 ± 3	8.0 ± 2	*
		WS-Zn	0.03 ± 0.03	0.2 ± 0.1	**
		WS-Cu	0.01 ± 0.01	0.06 ± 0.02	***
		WS-Pb	0.01 ± 0.01	0.05 ± 0.01	***
		M3-Zn	2.0 ± 0.03	4.0 ± 0.8	***
		M3-Cu	1.0 ± 0.1	1.9 ± 0.6	ns†
		M3-Pb	0.01 ± 0.01	0.8 ± 0.9	*
SR	Top Soil (0-0.15 m)	T-Zn	26 ± 6	46 ± 7	*
		T-Cu	4.0 ± 0.1	9.0 ± 6	ns†
		T-Pb	4.0 ± 0.2	16 ± 2	***
		WS-Zn	0.1 ± 0.01	2 ± 0.2	***
		WS-Cu	0.01 ± 0.01	0.3 ± 0.6	ns†
		WS-Pb	0.01 ± 0.01	0.6 ± 0.7	*
		M3-Zn	2.0 ± 0.04	14 ± 3	**
		M3-Cu	2.0 ± 0.01	3.5 ± 2	ns†
		M3-Pb	0.01 ± 0.01	2 ± 1	*
	Filter Media (0.15-0.60 m)	T-Zn	12± 3	20 ± 8	*
		T-Cu	10 ± 1	14± 8	ns†
		T-Pb	2.0 ± 1	7.0± 4	*
		WS-Zn	0.05 ± 0.03	0.2 ± 0.1	*
		WS-Cu	0.01 ± 0.01	0.06 ± 0.03	*
		WS-Pb	0.01 ± 0.01	0.05 ± 0.01	*
		M3-Zn	0.9 ± 0.03	3 ± 0.7	**
		M3-Cu	1.6 ± 0.4	3 ± 1	ns†
		M3-Pb	0.05 ± 0.01	0.2 ± 0.5	*

***** Significant at the 0.05 probability level. ******Significant at the 0.01 probability level.

******* Significant at the 0.001 probability level. † ns, not significant ($p > 0.05$).

T-Zn, Cu, Pb = Total zinc, copper and lead, WS-Zn, Cu, Pb = Water soluble zinc, copper and lead, M3-Zn, Cu, Pb = Mehlich 3 extracted zinc, copper and lead.

Table 3.3. Metal concentrations (mean ± standard deviation) in bioretention media depths in 2014 samples at four bioretention cell at Grove, Oklahoma. (Two-way ANOVA at $\alpha = 0.05$).

			Media Depth (m)			
Site	**N**	**Variable**	**0-0.15**	**0.15-0.30**	**0.30-0.45**	**0.45-0.60**
ECP	24	T-Zn	108 ± 46^{a}	30 ± 2^{b}	33 ± 4^{b}	28 ± 4^{b}
		T-Cu	11 ± 2^{c}	20 ± 4^{d}	21 ± 6^{d}	25 ± 2^{d}
		T-Pb	11 ± 3^{e}	7.69 ± 0.6^{f}	7.0 ± 1^{f}	7.0 ± 0.9^{f}
		WS-Zn	0.4 ± 0.2^{g}	0.2 ± 0.1^{h}	0.2 ± 0.1^{h}	0.2 ± 0.1^{h}
		WS-Cu	0.1 ± 0.02^{i}	0.06 ± 0.02^{i}	0.06 ± 0.02^{i}	0.06 ± 0.02^{i}
		WS-Pb	0.4 ± 0.06^{j}	0.1 ± 0.06^{k}	0.3 ± 0.06^{l}	0.2 ± 0.06^{k,l}
		M3-Zn	35 ± 21^{m}	4.0 ± 0.4^{n}	4.0 ± 0.5^{n}	4.0 ± 0.5^{n}
		M3-Cu	4.0 ± 0.4^{o}	3.0 ± 0.4^{p}	4.0 ± 0.7^{p}	4.0 ± 1.4^{o,p}
		M3-Pb	2.0 ± 1.4^{q}	0.06 ± 0.02^{r}	0.20 ± 0.1^{r}	0.07 ± 0.02^{r}
GHS	24	T-Zn	119 ± 45^{s}	41 ± 28^{t}	25 ± 4^{t}	25 ± 2^{t}
		T-Cu	4.0 ± 2^{u}	4.0 ± 1^{u}	5.0 ± 2^{u}	6.0 ± 1^{u,v}
		T-Pb	16 ± 7^{w}	17 ± 7^{w}	6.0 ± 1^{x}	7.0 ± 0.5^{x}
		WS-Zn	0.4 ± 0.1^{A}	0.2 ± 0.06^{B}	0.09 ± 0.04^{C}	0.1 ± 0.05^{BC}
		WS-Cu	0.05 ± 0.01^{D}	0.05 ± 0.01^{D}	0.05 ± 0.01^{D}	0.05 ± 0.01^{D}
		WS-Pb	0.05 ± 0.01^{E}	0.05 ± 0.01^{E}	0.05 ± 0.01^{E}	0.05 ± 0.01^{E}
		M3-Zn	68 ± 51^{F}	10 ± 8^{G}	4.0 ± 0.7^{G}	4.0 ± 0.7^{G}
		M3-Cu	2.0 ± 0.4^{H}	2.0 ± 0.3^{H}	2.0 ± 0.5^{H}	2.0 ± 0.1^{H}
		M3-Pb	3.0 ± 2.3^{I}	0.20 ± 0.3^{J}	0.05 ± 0.01^{J}	0.05 ± 0.01^{J}
GLA	24	T-Zn	46 ± 6^{K}	35 ± 4^{L}	28 ± 6^{M}	27 ± 5^{M}
		T-Cu	7.0 ± 2^{N}	8.0 ± 1^{N}	9.0 ± 2^{N}	9.0 ± 2 ^{N}
		T-Pb	18 ± 1^{O}	10 ± 0.6^{P}	7.0 ± 3^{Q}	6.0 ± 0.2^{Q}
		WS-Zn	0.5 ± 0.09^{R}	0.2 ± 0.05^{S}	0.3 ± 0.1^{S}	0.2 ± 0.1^{S}
		WS-Cu	0.05 ± 0.01^{T}	0.05 ± 0.01^{T}	0.06 ± 0.01^{T}	0.05 ± 0.01^{T}
		WS-Pb	0.05 ± 0.01^{U}	0.05 ± 0.01^{U}	0.06 ± 0.01^{U}	0.05 ± 0.01^{U}
		M3-Zn	12 ± 2^{V}	5.0 ± 0.3^{W}	4.0 ± 0.7^{W}	3.0 ± 0.5^{W}
		M3-Cu	3.0 ± 1^{X}	1.6 ± 0.3^{Y}	2.0 ± 0.5^{Y}	2.0 ± 0.8^{X,Y}
		M3-Pb	5.0 ± 0.7^{a1}	1.6 ± 0.3^{b1}	1.0 ± 0.5^{c1}	0.05 ± 0.01^{c1}

Table 3.3. Continuation

			Media Depth (m)			
Site	**N**	**Variable**	**0-0.15**	**0.15-0.30**	**0.30-0.45**	**0.45-0.60**
SR	24	T-Zn	46 ± 7^{d1}	18 ± 9^{e1}	22 ± 7^{e1}	19 ± 7^{e1}
		T-Cu	9.0 ± 5^{f1}	13 ± 9^{f1}	13 ± 9^{f1}	16 ± 7^{f1}
		T-Pb	16 ± 2^{g1}	6.0 ± 1^{h1}	9.0 ± 7^{h1}	5.0 ± 2^{h1}
		WS-Zn	2 ± 0.2^{i1}	0.2 ± 0.1^{j1}	0.1 ± 0.09^{j1}	0.1 ± 0.08^{j1}
		WS-Cu	0.3 ± 0.6^{k1}	0.07 ± 0.04^{k1}	0.05 ± 0.01^{k1}	0.05 ± 0.01^{k1}
		WS-Pb	1 ± 0.7^{l1}	0.05 ± 0.01^{m1}	0.05 ± 0.01^{m1}	0.05 ± 0.01^{m1}
		M3-Zn	14 ± 3.2^{n1}	3.0 ± 0.6^{o1}	3.0 ± 0.9^{o1}	2.0 ± 0.7^{o1}
		M3-Cu	$3.0 \pm 2.^{p1}$	$2.0 \pm 1.^{p1}$	2.0 ± 1^{p1}	2.0 ± 1^{p1}
		M3-Pb	$2.0 \pm 1.^{q'}$	0.40 ± 0.8^{r1}	0.30 ± 0.6^{r1}	0.05 ± 0.01^{r1}

*Concentrations with same lower and upper case letters are not significantly different among media depth at the 0.05 probability level ($p > 0.05$).

*Concentrations with different upper and lower case letters are significantly different among media depth ($p < 0.05$), Alphabets with letter a, a^1 and A are different notations.

T-Zn, T-Cu, and T-Pb = Total zinc, copper and lead, WS-Zn, WS-Cu, and WS-Pb = Water soluble zinc, copper and lead, and M3-Zn, M3-Cu, and M3-Pb = Mehlich-3 extracted zinh, copper and lead.

Table 3.4. Inlet and underdrain Zn mean concentration for three bioretention cells monitored at Grove, Oklahoma, from 2014 to 2015.

		Mean Zn Concentration (mg/L)				Zn Loading (g)			
BRC	Storm events (n)	Inflow (mg/L)	Underdrain (mg/L)	% reduction	Significance	Inflow (g)	Underdrain (g)	% reduction	Significance
ECP	20	0.05	0.02	60%	p <0.05	1.1	0.13	88%	p <0.05
GHS	10	0.07	0.03	57%	p <0.05	3.1	0.72	77%	p <0.05
GLA	11	0.04	0.02	50%	p <0.05	2.46	1.40	43%	p >0.05

The Wilcoxon Rank-Sum test, a non-parametric analysis at α value of 0.05 was performed using SAS version 9.4 to determine if the BRC treatment made a significant improvement on media Zn reduction. $p < 0.05$ indicates significant reduction in effluent Zn reduction.

Table 3.5. Mean influent and effluent water quality parameters monitored at three bioretention cells at Grove, Oklahoma, from 2014 to 2015.

BRC	Pollutant	Storm events (n)	Inflow	Underdrain	% reduction or (increase)	Significance
ECP	TSS (mg/L)	20	106	41	61%	*p* < 0.05
	Turbidity (NTU)	20	66	7	89%	*p* < 0.05
	pH	20	6.7	7.7	-15%	*p* > 0.05
	EC(µmhos/cm)	20	75	208	-179%	*p* < 0.05
GHS	TSS (mg/L)	7	110	45	59%	*p* < 0.05
	Turbidity (NTU)	7	19	2.8	86%	*p* < 0.05
	pH	8	6.3	7.5	-18%	*p* > 0.05
	EC(µmhos/cm)	8	147	174	-19%	*p* > 0.05
GLA	TSS (mg/L)	11	95	29	70%	*p* < 0.05
	Turbidity (NTU)	11	9	3.8	60%	*p* < 0.05
	pH	11	7.1	7.9	-12%	*p* > 0.05
	EC(µmhos/cm)	11	86	348	-301%	*p* < 0.05
ECP	TSS (g)	12	2460	275	89%	*p* < 0.05
GHS	TSS (g)	7	5702	950	83%	*p* < 0.05
GLA	TSS (g)	11	1840	1681	9%	*p* > 0.05

The Wilcoxon Rank-Sum Test, a non-parametric analysis at α value of 0.05 was performed using SAS version 9.4 to determine if the BRC treatment made a significant increase or reduction in concentration and mass of monitored water quality parameters.

p < 0.05 indicates significant increase or reduction in effluent concentrations.

p > 0.05 indicates no significant increase or reduction in effluent concentrations.

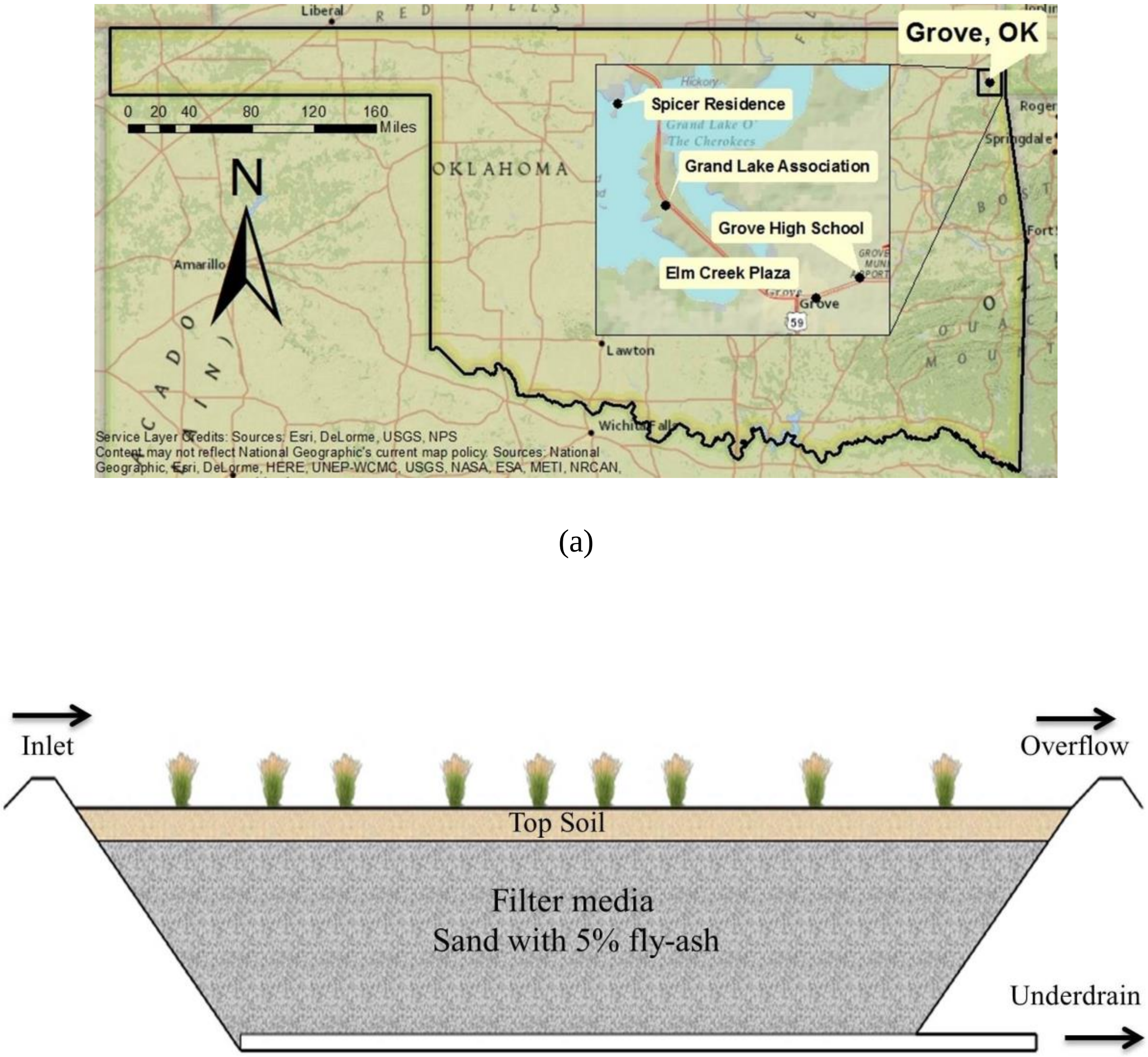
TSS = Total suspended solids.

Table 3.6. Metal retained within the bioretention media analyzed from three different extraction methods and inlet Zn load in three bioretention cells monitored estimated using LOADEST software.

Site	Media	Media depth (m)	Total-metal retained (kg/yr)			WS-metal retained (kg/yr)			M3-metal retained (kg/yr)			LOADEST Inlet Zn (kg/yr)
			Zn	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	
ECP	Top soil	0-0.15	0.16	0.004	0.015	0.001	0.0001	0.001	0.062	0.004	0.004	0.06
	Filter Media	0.15-0.45	0.05	0.055	0.018	0.001	0.0003	0.001	0.012	0.012	0.001	
	Total	0.60	0.21	0.059	0.033	0.002	0.0004	0.002	0.074	0.016	0.005	
GHS	Top soil	0-0.15	0.43	0.004	0.058	0.001	0.0002	0.0002	0.30	0.009	0.013	0.13
	Filter Media	0.15-0.45	0.20	0.014	0.172	0.002	0.001	0.001	0.07	0.014	0.001	
	Total	0.60	0.63	0.018	0.23	0.003	0.0012	0.0012	0.37	0.023	0.014	
GLA	Top soil	0-0.15	0.09	0.026	0.062	0.002	0.0003	0.0002	0.052	0.010	0.026	0.09
	Filter Media	0.15-0.45	0.15	0.033	0.066	0.003	0.001	0.001	0.033	0.015	0.013	
	Total	0.60	0.24	0.059	0.128	0.005	0.0013	0.0012	0.085	0.025	0.039	
SR	Top soil	0-0.15	0.06	0.015	0.036	0.006	0.001	0.002	0.036	0.005	0.006	N/A
	Filter Media	0.15-0.45	0.08	0.039	0.049	0.001	0.0005	0.0004	0.02	0.014	0.001	
	Total	0.60	0.14	0.054	0.085	0.007	0.0015	0.0024	0.056	0.019	0.007	

Total metal = Total zinc, copper and lead (T-Zn, T-Cu, and T-Pb), WS-metal = Water soluble zinc, copper and lead (WS-Zn, WS-Cu, and WS-Pb), M3-metal = Mehlich 3 extracted zinc, copper, and lead (M3-Zn, M3-Cu, and M3-Pb).

N/A = No samples.



(a)

(b)

Figure 3.1. (a) Bioretention cell locations at Grove, OK. (b) Typical section of bioretention cell at Grove, OK.

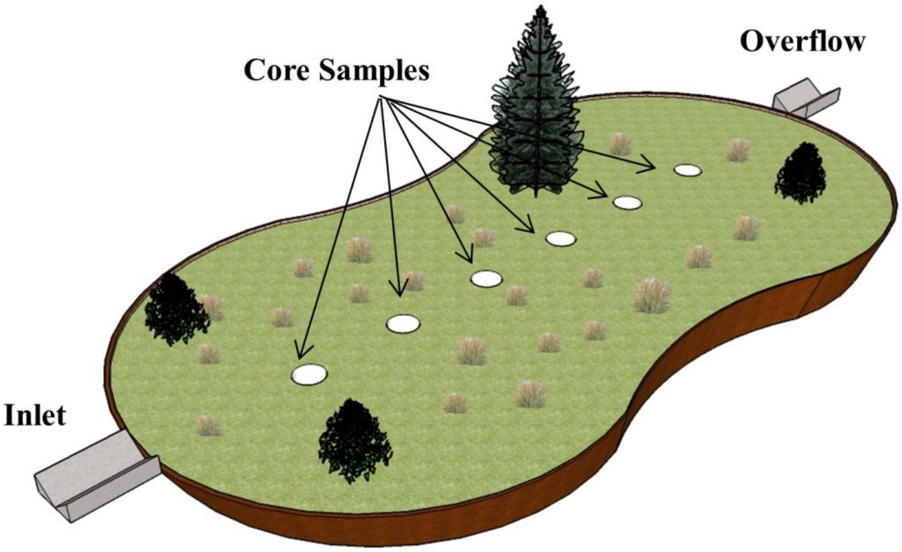


Figure 3.2. Soil core sampling layout at bioretention cells with approximate core locations.

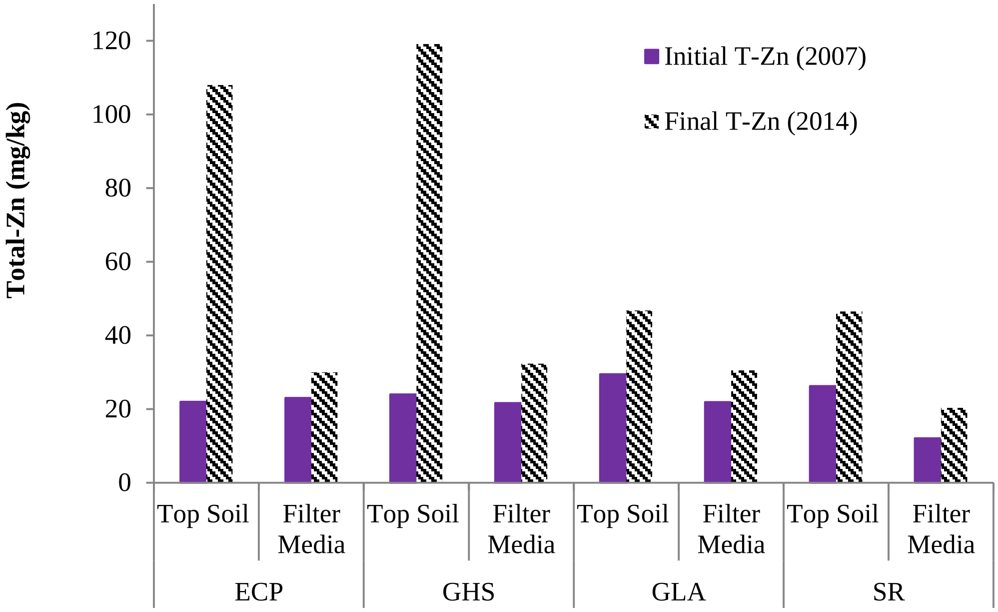


Figure 3.3. Mean total zinc (T-Zn) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

There was a significant difference in mean T-Zn concentration between the period and media layer at each site based on a two-way ANOVA, followed by Tukey's HSD test at α = 0.05.

Top soil depth = 0.15 m and Filter media depth = 0.60 m.

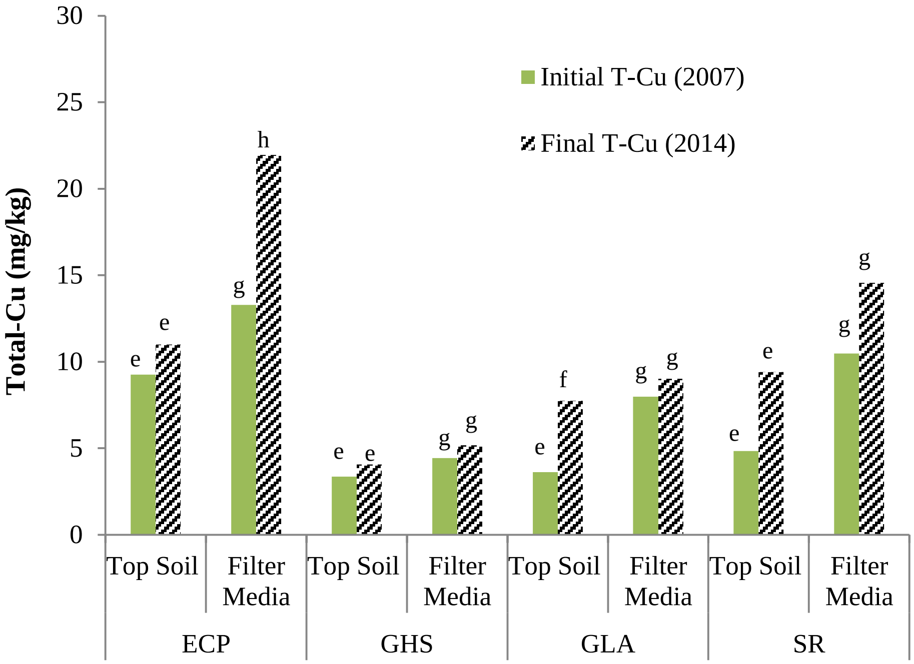


Figure 3.4. Mean total copper (T-Cu) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

Different lower-case letter indicate significant difference in mean T-Cu concentrations between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test ($p < 0.05$). Same lower-case letter indicate no significant difference in mean T-Cu concentrations between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test ($p > 0.05$).

Top soil depth = 0.15 m and Filter media depth = 0.60 m.

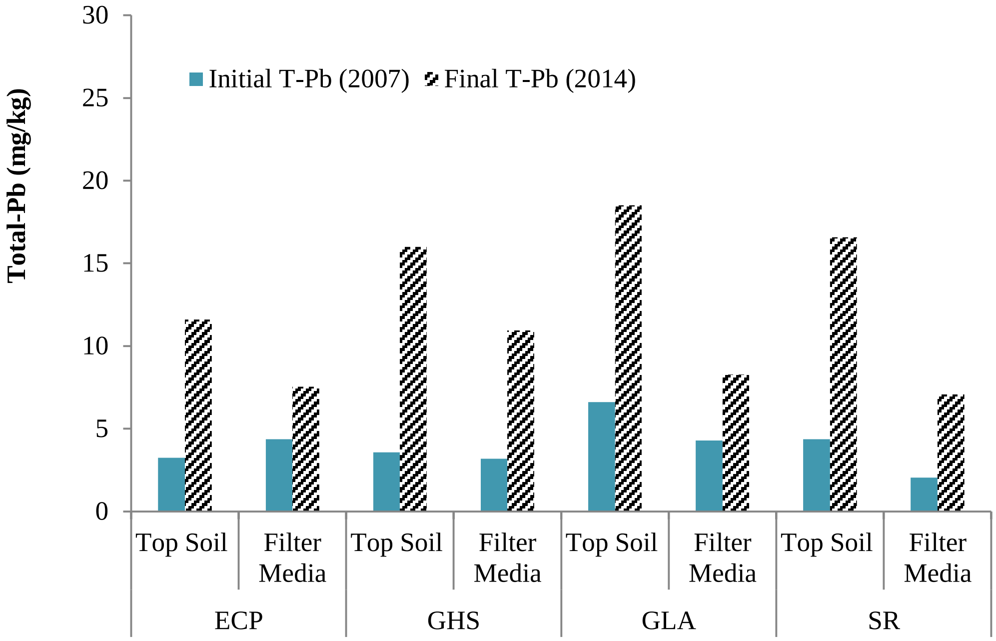


Figure 3.5. Mean total lead (T-Pb) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

There was a significant difference in mean T-Pb concentration between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test at $\alpha = 0.05$.

Top soil depth = 0.15 m and Filter media depth = 0.60 m.

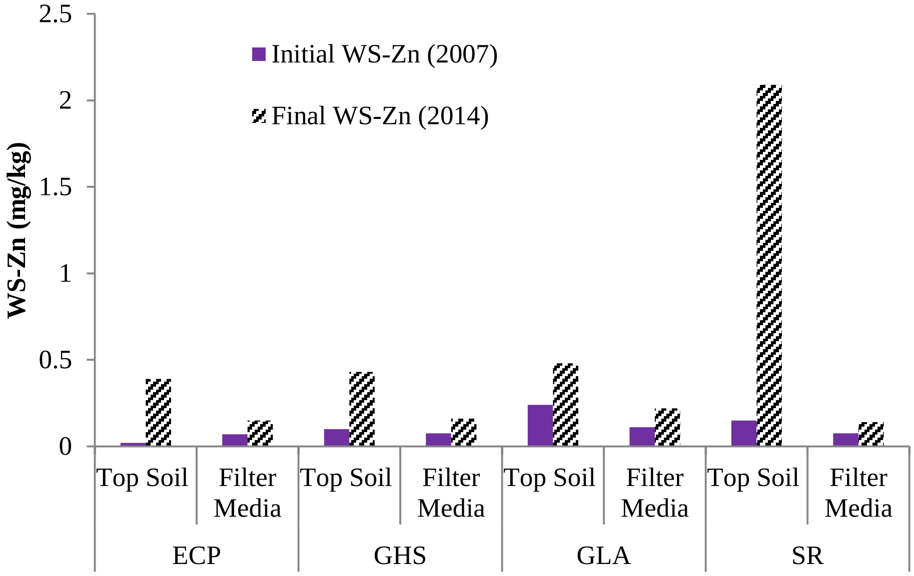


Figure 3.6. Mean water soluble zinc (WS-Zn) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

There was a significant difference in mean WS-Zn concentration between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test at $\alpha = 0.05$.

Top soil depth = 0.15 m and Filter media depth = 0.60 m

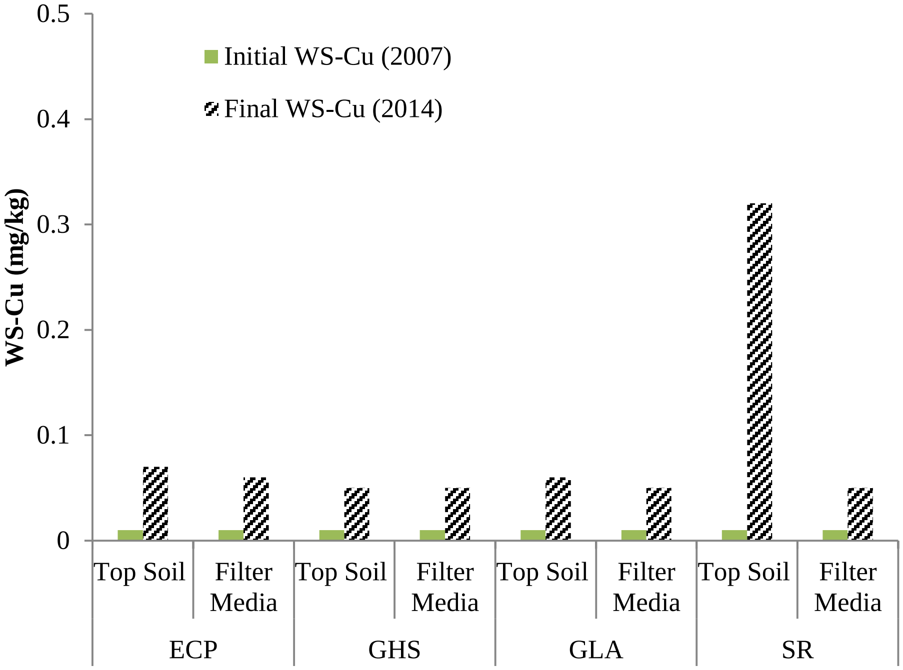


Figure 3.7. Mean water soluble copper (WS-Cu) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

There was a significant difference in mean WS-Cu concentration between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test at α = 0.05.

Top soil depth = 0.15 m and Filter media depth = 0.60 m

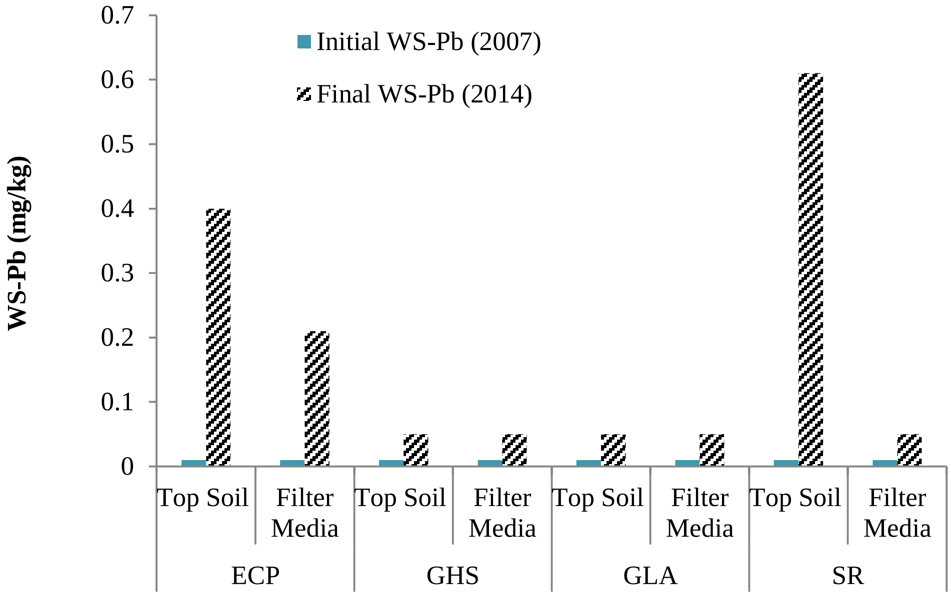


Figure 3.8. Mean water soluble lead (WS-Pb) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

There was a significant difference in mean WS-Pb concentration between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test at $\alpha = 0.05$.

Top soil depth = 0.15 m and Filter media depth = 0.60 m

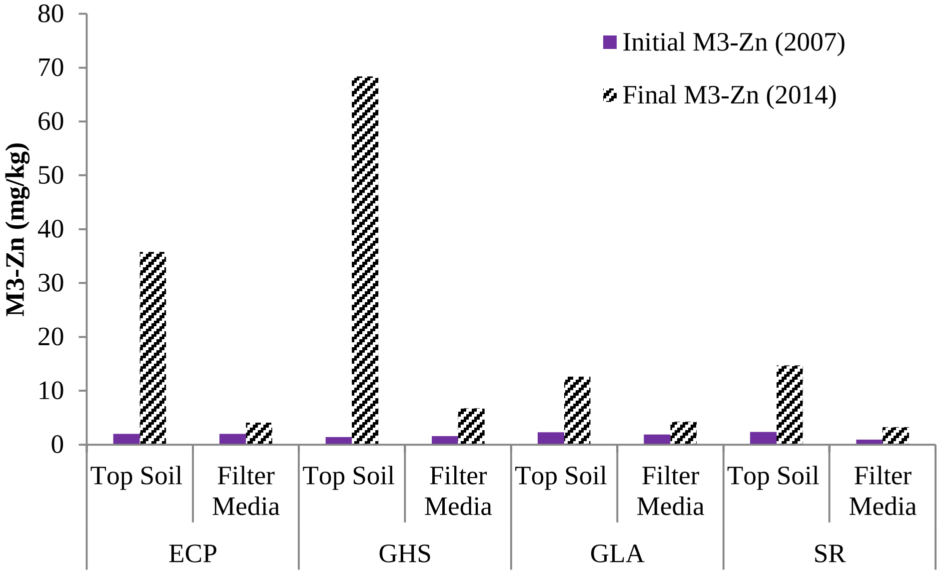


Figure 3.9. Mean Mehlich 3 zinc (M3-Zn) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

There was a significant difference in mean M3-Zn concentration between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test at $\alpha = 0.05$.

Top soil depth = 0.15 m and Filter media depth = 0.60 m

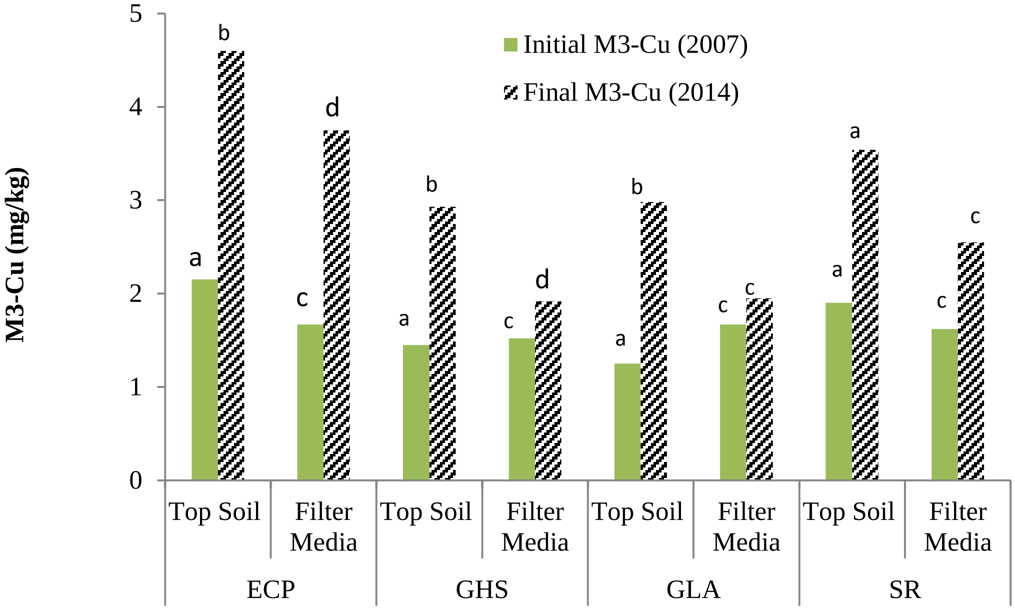


Figure 3.10. Mean Mehlich 3 copper (M3-Cu) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

Different lower-case letter indicate significant difference in mean M3-Cu concentrations between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test ($p < 0.05$). Same lower-case letter indicate no significant difference in mean M3-Cu concentrations between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test ($p > 0.05$).

Top soil depth = 0.15 m and Filter media depth = 0.60 m

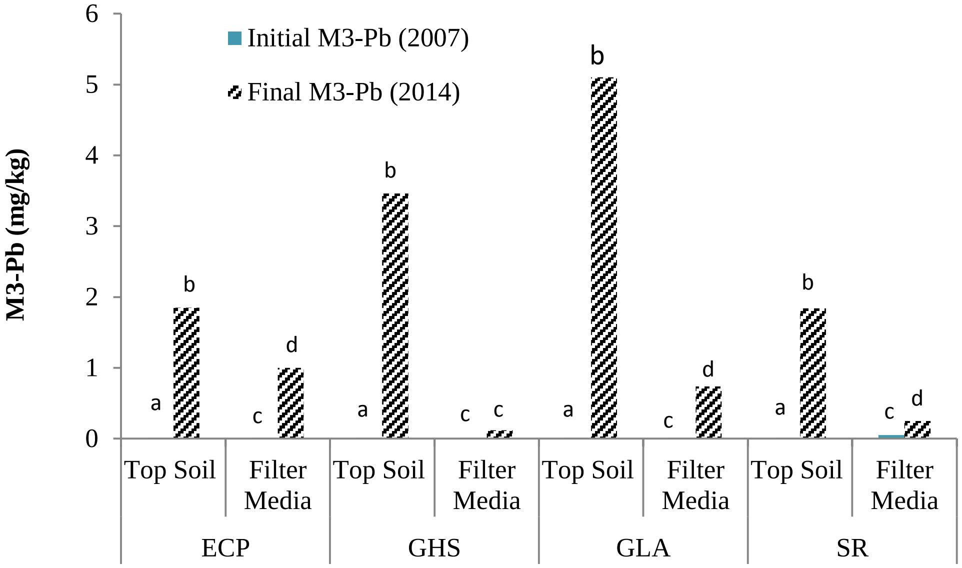


Figure 3.11. Mean Mehlich 3 lead (M3-Pb) concentration in 2007 (n = 8) and 2014 (n = 24) from four bioretention cells at Grove, OK.

Different lower-case letter indicate significant difference in mean M3-Pb concentrations between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test ($p < 0.05$). Same lower-case letter indicate no significant difference in mean M3-Pb concentrations between the period and media layer at each site, based on a two-way ANOVA, followed by Tukey's HSD test ($p > 0.05$).

Top soil depth = 0.15 m and Filter media depth = 0.60 m

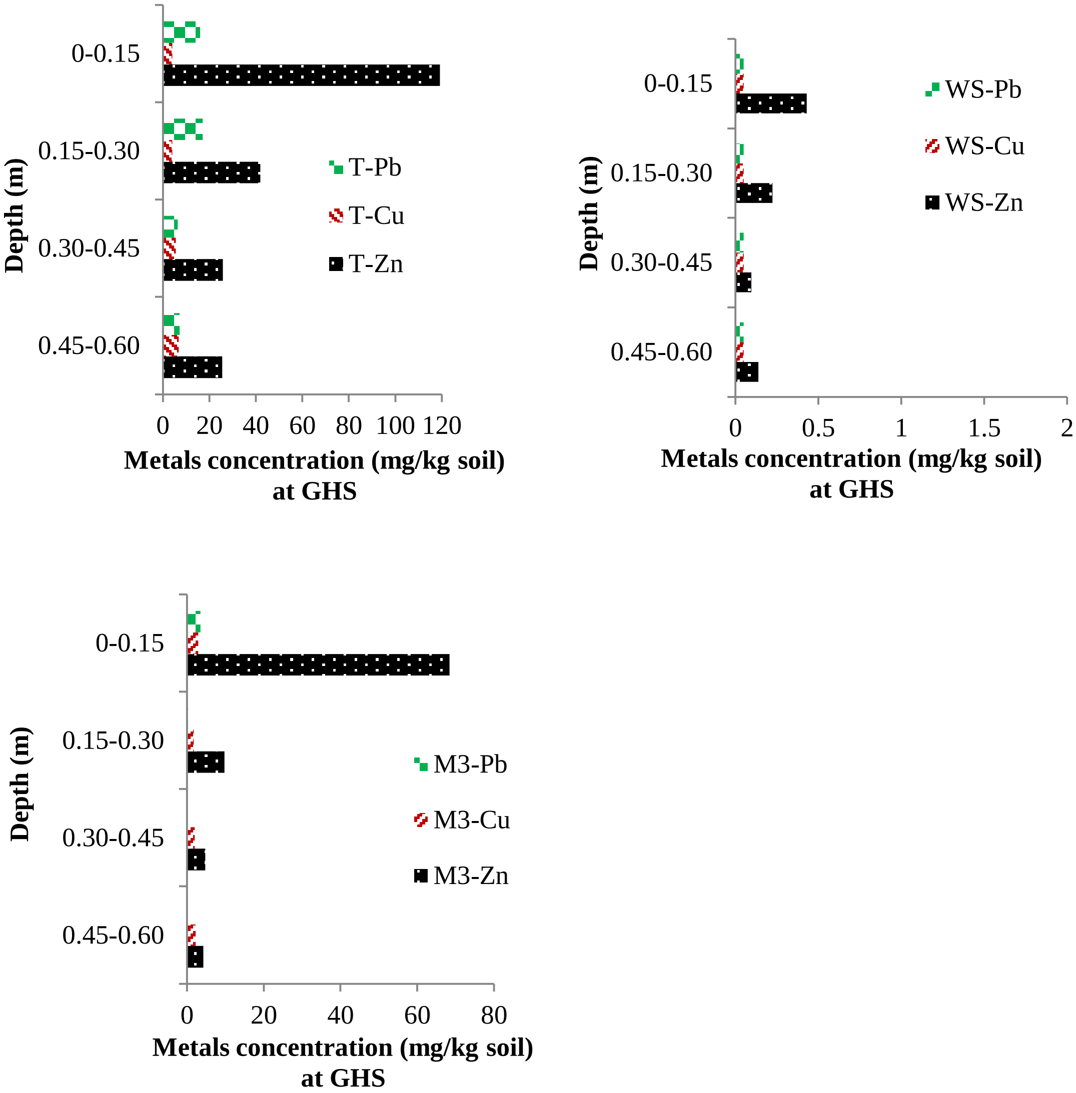


Figure 3.12. Mean total, water soluble and Mehlich-3 metal concentration profiles in 2014 (n = 96) in GHS cell at Grove, OK.

T-Zn, T-Cu, and T-Pb = Total metal concentration.

WS-Zn, WS-Cu, and WS-Pb = Water soluble metal concentration.

M3-Zn, M3-Cu, and M3-Pb = Mehlich 3 extracted metal concentration.

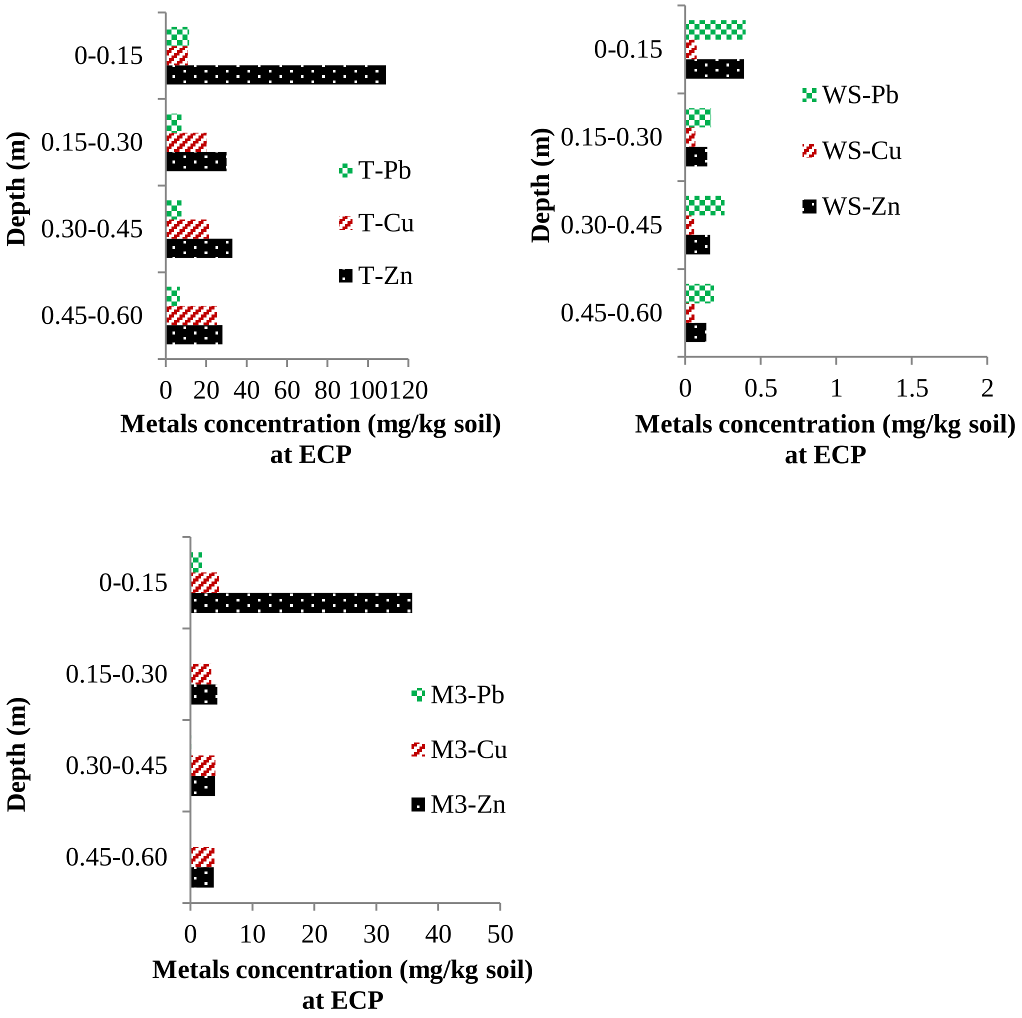


Figure 3.13. Mean total, water soluble and Mehlich-3 metal concentration profiles in 2014 (n = 96) in ECP cell at Grove, OK.

T-Zn, T-Cu, and T-Pb = Total metal concentration.

WS-Zn, T-Cu, and T-Pb = Water soluble metal concentration.

M3-Zn, M3-Cu, and M3-Pb = Mehlich 3 extracted metal concentration.

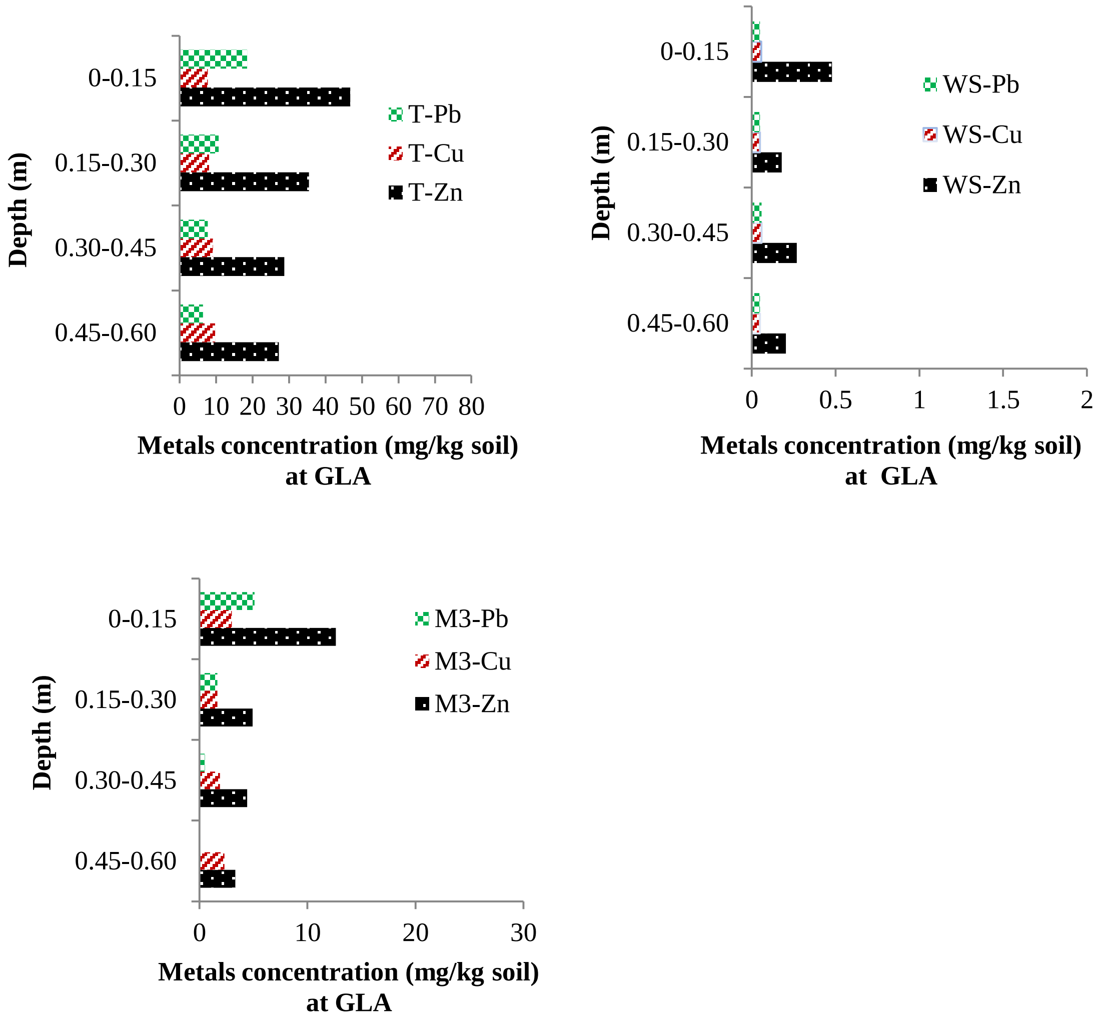


Figure 3.14. Mean total, water soluble and Mehlich-3 metal concentration profiles in 2014 (n = 96) in GLA cell at Grove, OK.

T-Zn, T-Cu, and T-Pb = Total metal concentration.

WS-Zn, WS-Cu, and Ws-Pb = Water soluble metal concentration.

M3-Zn, M3-Cu, and M3-Pb = Mehlich 3 extracted metal concentration.

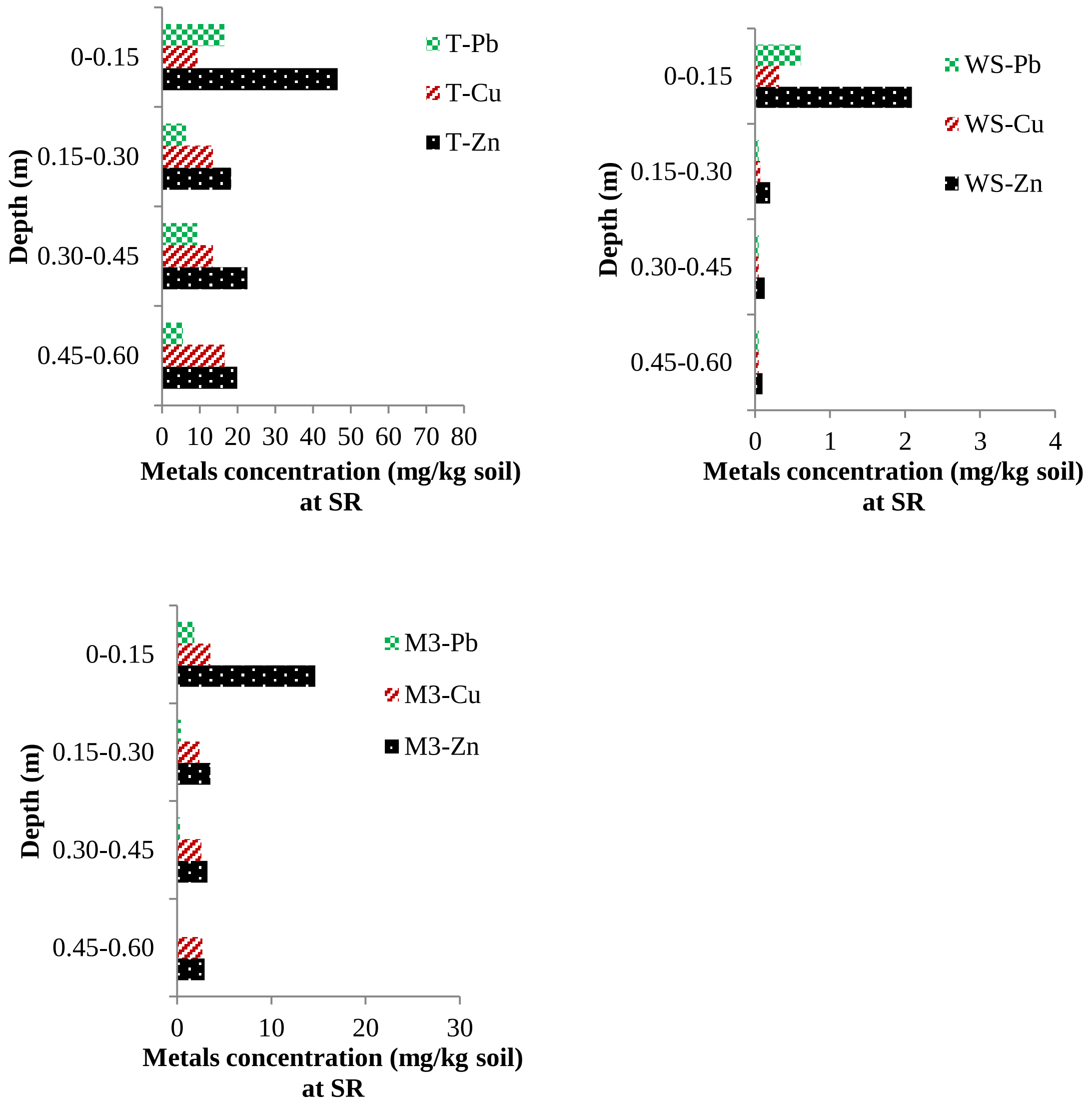


Figure 3.15. Mean total, water soluble and Mehlich-3 metal concentration profiles in 2014 in SR cell at Grove, OK.

T-Zn, T-Cu, and T-Pb = Total metal concentration.

WS-Zn, WS-Cu, and WS-Pb = Water soluble metal concentration. M3-Zn, M3-Cu, and M3-Pb = Mehlich 3 extracted metal concentration.

CHAPTER IV

PHOSPHORUS AND METAL ADSORPTION ON AGED FLY-ASH AMENDED FILTER MEDIA IN BIORETENTION CELLS

ABSTRACT

Adsorption and desorption of phosphorus (P) and heavy metals (Zn, Pb and Cu) on a fly-ash amended filter media used in four different bioretention cells (BRC) after seven years of operation were studied. The phosphorus and metals adsorption capacities were obtained from a series of batch and flow-through experiments. Both nonlinear forms of Langmuir and Freundlich isotherm models fitted the equilibrium data well ($r^2 > 0.9$). The batch sorption experiments showed phosphorus adsorption capacity of the fly-ash filter media after seven years of operation was (160 mg/g) around half the amount of the initial material (350 mg/g). Batch testing of the aged fly-ash amended filter media exhibited phosphorus removal of 61%, Zn, Cu and Pb removal of 95%, 98%, and 99%. Desorption experiments showed the media released 24% of initially sorbed phosphorus and only 0.6% of initially sorbed Zn and Cu at initial phosphorus and metal concentration of 30 mg/L. Thus, Phosphorus and heavy metal adsorption in sand/fly-ash filter media may be considered irreversible, and can provide long-term phosphorus and heavy metal retention.

Keywords: adsorption; desorption; isotherm, batch experiments

INTRODUCTION

Over the past several years, many best management practices (BMP) have been developed and implemented to reduce the adverse environmental effects and improve the quality of urban stormwater runoff prior to discharge in receiving water bodies (Davis et al. 2009). Among these BMP, bioretention cells (BRC), also known as biofilters or raingardens, are widely used in the United States (Davis et al. 2009), and also are used in other countries (Fujita 1997; Wong 2006; Woods-Ballard et al. 2007).

The removal of solutes including phosphorus (P) and heavy metals depends on the BRC filter media. Bioretention media typically consists of sand (sandy loam or loamy sand) and mulch (LeFevre et al. 2014). However, the sorption capacity of filter media used in BRC is poorly defined and the transport and fate of various pollutants within the media is not well understood. Several studies have been conducted on the use of various filter materials, including sand augmented with activated carbon, peat moss, compost and cedar bedding, which were effective in removing nutrients from stormwater (Gironas et al. 2008; Seelsaen et al. 2006). However, the costs of these materials may limit their use as filter media in large scale application.

Thus, many researchers have been investigating more economic sportive filter media that are easily available, have high P and metal sorption capacity, and also, are easily replaceable (Reddy 2013; Allred 2012). Previous research, from batch sorption studies have shown fly ash as an effective sportive media for removing P and metals including Cu, Cd, Zn, Cr and Pb from aqueous solutions (Ayala et al. 1998; Bayat et al. 2002). Zhang et al. (2008 a, b) researched using different materials as potential BRC media to improve P and heavy metal removal. Based on his testing, fly ash was identified as a material with significant adsorption potential for P and heavy metals. Batch sorption experiments with sand amended with 5% fly ash by weight increased the P and Zn adsorption distribution by a factor of 40 and 200 respectively over the pure sand.

Phosphorous and heavy metals retention by soils are commonly studied by adsorption isotherm experiments (Siddique and Robinson 2003). The performance of an adsorbent can be characterized from adsorption isotherm data, which is obtained from batch sorption experiments in laboratory (Thompson et al. 2001). Modeling with adsorption isotherm data is a widely accepted method for predicting and comparing the adsorption performance of absorbents, which is crucial for reliable prediction of adsorbent behavior and effective design of the adsorption systems (Hossain et al. 2013; Bilgili 2006). Several adsorption isotherm equations have been used in the modeling of adsorption data. The most commonly used isotherm models include Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models (Langmuir 1916; Freundlich 1906; Dubinin et al. 1947). According to recent studies, the use of nonlinear isotherm represents a potential viable and better estimation tool for adsorption parameters than the linear isotherm analysis (Chowdhury et al. 2011; Ho 2006).

In 2007, several full scale prototypes BRC were constructed in Grove, Oklahoma that used sand with 5% by weight of fly-ash filter media (Chavez et al. 2015). Since, then they have operated relatively unattended, and subjected to normal site hydrology and contaminant loading. These BRC offer an excellent opportunity to quantify the actual performance of fly-ash media over several years. The objectives of this study were to; 1) estimate the P and heavy metal sorption capacity of fly-ash amended filter media from the four aged BRC by batch sorption and flow through experiments. and 2) compare the current P and metal adsorption and desorption capacity with that of the initial filter media material tested by Zhang et al. (2008a, b).

Throughout this dissertation, the term adsorption is used to describe any solute that is retained by the porous media. This would include solutes bound by physical adsorption, precipitation, and within organic matter. Likewise, desorption is used to describe any solute that is released by the porous media regardless of its original form and retention mechanism.

MATERIALS AND METHODS

Site Description

Four BRC constructed in Grove, Oklahoma, in 2007 (Chavez et al. 2015) were subjected to testing in this study. A mix of sand and 5% fly ash by weight was used as a filter media in these four BRC. The sample collected from four BRC were Elm Creek Plaza (ECP), Grand Lake Association (GLA), Grove High School (GHS) and the Spicer Residence (SR). Design summaries of each BRC are presented in Table 4.1.

Filter Media Collection

A 15 SCS/Model Gidding core machine with a 5.08 mm outer diameter and 38.1 mm inner diameter plastic liner was used for sampling the BRC filter media. One soil core was collected near the inlet of each BRC in June 2014. The 0.6 m in depth cores were sectioned into two distinctive sub-samples (0-15 m and 0.15-0.60 m). The sections were separated in the laboratory with a pre-cleaned saw, and stored in a clean soil bag. Only the 0.15 to 0.60 m sample, which represents the fly-ash amended filter media, was used in this study.

Batch Sorption Experiments

Phosphorus and metal sorption isotherms were measured for the filter media samples by batch sorption experiments following ASTM D 4646- 03 (2004) consistent with Zhang et al. (2008 a, b). Duplicate two grams samples were sieved through a 2-mm sieve size and placed in 50 ml centrifuge tubes. Previous studies on batch experiments by Dutta and Singh (2011); Behnamfard and Salarirad (2009) and Ho (2006) were also conducted in duplicates. For phosphorus adsorption, 40 ml of 0.01 mol/L KCl solution (20:1 water to solid ratio) with five initial concentrations (1, 3, 10, 20, and 30 mg/L P) of sodium phosphate ($Na_3PO_4.12H_2O$) were used. Similarly, for the metals batch adsorption, 20:1 solutions of 0.01 mol/L KCl with single metals at initial concentrations of 1, 3, 10, 20, and 30 mg/L of (Zn, Cu and Pb) were used. Tubes were shaken at 30 rpm at room temperature (21 ± 2 ºC) on a rotary agitator for 24 hours. Then the suspensions were centrifuged for 15 minutes at 50 RPM, filtered through 0.45µm membranes, acidified, and analyzed. Phosphate and metals concentration were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in the Soil, Water and Forage Analytical Laboratory (SWFAL), Oklahoma State University.

The amount of phosphate and metals adsorbed at equilibrium (q_e, mg/g) was calculated by,

$$q_e = \left(\frac{(C_O - C_e)V}{M_s} \right) \tag{1}$$

where, C_o and C_e were the initial and equilibrium phosphate and metals concentrations (mg/L), respectively, V (mL) was the volume of the solution used, and M_s was the mass of sample (g), Phosphorus and metal removal efficiency was calculated as (ASTM, 2004),

$$\% \text{ Removal} = \left(\frac{C_O - C_e}{C_O} \right) * 100 \tag{2}$$

Phosphorus and metal desorption experiments were carried out consistent with Zhang et al (2008 a). After removing the initial adsorption solution from the tubes, 20 ml of 0.01 mol/L KCl solutions was added for the desorption measurement. Then the same procedure of separation and analysis used in the adsorption experiments were conducted.

Batch experimental data were fitted to both nonlinear and linear forms of the isotherms models to determine the P and metals adsorption capacity of the filter media samples. Langmuir and Freundlich isotherm models have been commonly used to evaluate the phosphorus and metals sorption capacity of materials (Forbes et al. 2004; Vallapando and Graetz, 2001).

Nonlinear Isotherm Models

The Langmuir isotherm, an empirical model describing a monolayer adsorption of adsorbate onto a homogenous adsorbent surface (Bilgili 2006), is given (Langmuir 1916) as,

$$q_e = q_m K_L \frac{C_e}{1 + K_L C_e} \tag{3}$$

where, q_m is the maximum adsorption capacity (mg/g) and K_L (L/mg) is the constant related to the free energy of adsorption, respectively. The empirical Freundlich isotherm model considers heterogeneous adsorptive energies on the adsorbent surface and was expressed as (Freundlich 1906),

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F and n are Freundlich constants related to the adsorption capacity and intensity of adsorption, respectively. The Langmuir has an advantage over the Freundlich for estimating the maximum phosphorus sorption capacity. The Langmuir is based on the assumptions that the forces of interaction between sorbed molecules are negligible and once the molecule occupies an adsorption surfaces no further sorption takes place (Janos et al. 2003).

All isotherm parameters were evaluated by non-linear regressions method using Minitab 17 software and Microsoft Excel 2015. The coefficient of determination (r^2) was used to test the best- fitting isotherm to the experimental data by:

$$r^2 = \frac{\sum (q_m - \bar{q}_e)^2}{\sum (q_m - \bar{q}_e)^2 + \sum (q_m - \bar{q}_e)^2} \tag{5}$$

where q_m and q_e were the equilibrium capacity obtained from the isotherm model and experimental data, respectively and $\overline{q_e}$ was the average of q_e.

Flow-through Experiments

The current P and Zn sorption capacity of the aged fly-ash filter media was evaluated by laboratory flow-through experiments (Penn and McGrath 2011). Influent P and Zn concentrations of 1.0 mg/L were used. Two gram of filter media samples (0.15-0.60 m depth) from the four BRC consistent with batch experiment was used. This produced a total of eight media samples including duplicates for each BRC media sample. Those two grams of samples were mixed with up to three grams of acid-washed, lab-grade sand (pure Si sand, 14808-60-7, Acros Organics, Morris Plains, NJ). The result was packed into flow-through cells with pore volume of 1.68 cm^3. Flows through cells were constructed with high density polyethylene as described by DeSutter et al. (2006). The proportion of media sample to sand was varied depending upon how much P and Zn was adsorbed. A suitable amount of silica sand mix that would not result in 100% or 0% P and Zn removal for the duration of the entire experiment was determined by trial and error. A 0.45µm filter was placed beneath the materials, and the bottom of the cell was connected to a single channel peristaltic pump. Retention time in minutes (*RT*) was expressed as,

$$RT = \left(\frac{P.V}{Q} \right) \tag{6}$$

where, $P.V$ was the pore volume (cm^3) and Q was the flow rate (min^{-1}). An 8 minute retention time was achieved by adjusting the pump to 0.21ml/min. A constant head Mariotte bottle was used to maintain a constant volume of P and Zn solution on the sample materials. Sample materials were subjected to flow for five hours, during which the effluent from the cells were sampled at 30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 min. As before, solutions were analyzed for P and Zn by ICP-AES in SWFAL. All flow-through P and Zn concentration were duplicated for each material. Discrete P and Zn sorption onto materials were calculated at each sampling time as a percentage decrease in outflow relative to inflow P and Zn concentrations.

RESULTS AND DISCUSSION

Phosphorus and Metal Removal from Batch Test

The phosphorus and metals adsorbed at equilibrium at different initial concentrations are presented at Table 4.2. Phosphorus and metal removal efficiency results from the batch test are provided in Table 4.3. Average phosphorus removal was 61% and 57% at initial concentrations of 1 and 3 mg/L, respectively. Zhang et al. (2008 a) in his batch study obtained average P removal of 87% and 91% with an initial concentration of 1 and 3 mg P/L. Average Zn removal of 98% to 99% at an initial concentration of 1 mg/L, and 99% removal at initial concentration of 3 mg/L were observed. Similarly, average Cu removal of 97% to 99% at an initial concentration of 1 mg/L and 99% removal at an initial concentration of 3 mg/L were observed. Zhang et al. (2008 a), obtained average Zn removal of 97% and average Cu removal of 92% with an initial concentration of 1 mg/L of both metals. Even after seven years of operation, the fly-ash media exhibited roughly two-thirds of the initial P retention, while Zn and Cu retention were essentially unchanged. The equilibrium concentrations of Pb were below the detection limit of 0.01 ppm for all initial Pb concentrations (1, 3, 10, 20 and 30 mg/L). In effect, the Pb removal was 100%. Thus, while it is not possible to define a Pb adsorption isotherm, the aged fly-ash media clearly has significant Pb retention.

Non-Linear Isotherm Models for P sorption

Figure 4.1 shows Langmuir and Freundlich adsorption isotherms for filter media samples at four different BRC while Table 4.4 lists the estimated Langmuir and Freundlich isotherm parameters, correlation coefficients (r^2) and related standard errors (S.E.) for each parameter. Both Langmuir and Freundlich isotherms fitted well with the experimental data. As shown in Table 4.4 and Figure 4.1, higher correlation coefficients (r^2) were obtained by fitting experimental data to the Freundlich isotherm ($r^2 > 0.945$) than that into Langmuir isotherm ($r^2 > 0.921$). Also, the values of S.E. for each parameter obtained in the Freundlich isotherm were lower than the Langmuir. Thus, the Freundlich isotherm generated a better fit to the experimental data.

A comparison of the amount of phosphorus sorbed at equilibrium with the initial material of sand and 5% fly-ash filter media with the batch experiment results from Zhang et al. (2008a) is presented in Table 4.5. The amount of phosphorus sorbed by the filter media in BRC after seven years of operation was around half (160 mg/kg) of the initial sorbed amount (350 mg/kg) as shown in Figure 4.2.

The results of P desorption from the filter media samples analyzed from the four BRC are presented in Figure 4.3. It was noted that with the P initial concentration of 1, 3, and 10 mg/L, the average P desorbed was 10% to 16% of the sorbed P, with the P initial concentration of 20 and 30 mg/L, the average P desorbed was 24%. Thus, desorption of P from fly-ash amended filter media for the influent concentration of 1 to 10 mg/L, after seven years of operation was 10 % to 16% of sorbed P, which predicts the long term P retention capacity of fly-ash amended filter media with very low P desorption even after seven years of operation.

Non-linear Isotherm Models for Metals Zn and Cu

Figure 4.4 and 4.5 presents, the Langmuir and Freundlich adsorption isotherms of Zn and Cu for the filter media samples at the four BRC, while Table 4.6 lists the Langmuir and Freundlich parameters and corresponding correlation coefficients (r^2), and related standard error (S.E.). Both nonlinear Langmuir and Freundlich isotherms fitted well with the experimental data. In Table 4.6 and Figure 4.4, the sorption of Zn using the Freundlich had a higher correlation coefficient (r^2 > 0.958) than the Langmuir (r^2 > 0.922), also values of S.E. for each parameter obtained in Freundlich was lower than the Langmuir. Thus, it was noted that with a higher correlation coefficient and lower S.E., the Freundlich fit better than the Langmuir for Zn sorption. In Table 4.6 and Figure 4.5., the sorption of Cu using the Langmuir had a higher S.E for each parameter than that of the Freundlich. With lower S.E., for each parameter the Freundlich fitted better than the Langmuir for Cu sorption.

The results of Zn and Cu desorption from the filter media samples are presented in Figures 4.6 and 4.7. With the Zn initial concentration of 1, 3, and 10 mg/L, the average Zn desorbed was 0.1% to 0.3% of the sorbed Zn, while with Zn initial concentration of 20, 30 mg/L, the average Zn desorbed was 0.33%. For Cu initial concentration of 1, 3, and 10 mg/L, the average Cu desorbed was 0.2% to 0.4% of the sorbed Cu with the Cu initial concentration of 20, 30 mg/L, the average Cu desorbed was 0.6%. Thus, desorption of Zn and Cu from fly-ash amended filter media for the influent concentration of 1 to 30 mg/L, after seven years of operation was less than 1% and negligible. Therefore, Zn and Cu metal sorption in fly-ash amended filter media may be considered irreversible and can provide long-term metal retention.

Phosphorus and Zn sorption from Flow-Through Experiments

The discrete P and Zn removal under the flow through condition of influent concentration of 1 mg/L P and Zn and RT of 8 min was described as a function of P and Zn added (x in Eq.10) to the materials using the exponential model as described by Stoner et al. (2012),

$$\text{Discrete P and Zn removal} = be^{mx} \qquad (7)$$

where b is the intercept and m is the slope coefficient for this relationship. Discrete P and Zn removal curve of fly-ash amended filter media samples analyzed through flow-through setting are presented in Figure 4.8 and 4.9. Maximum P and Zn added (x) and cumulative P and Zn removed (sorption capacity of material tested) were calculated using,

$$\text{Maximum P and Zn added (x)} = \left(\frac{\ln b}{-m}\right) \tag{8}$$

$$\text{Cumulative P and Zn removed (\%)} = \left(\frac{\int_0^x (be^{mx})dx}{x}\right) \tag{9}$$

Insertion of the maximum amount of P and Zn added determined from Eq.8 into t Eq. 9 results in the total amount of P and Zn predicted to be removed by the filter material under the *RT* of 8 min and inflow P and Zn concentration of 1 mg/L. Using the percent cumulative P and Zn removed and maximum P added, the P and Zn sorbed (mg/kg) by the fly-ash amended filter media at the flow-through setting were estimated. The estimated flow-through P sorption capacity of aged sand and 5% fly-ash filter media after seven years in operation at four BRC were (a) 17.7 mg/kg, (b) 14.10 mg/kg, (c) 22.1 mg/kg and (d) 45.5 mg/kg. Similarly, the estimated flow-through Zn sorption capacity of the filter media were (a) 88.0 mg/kg, (b) 43.8 mg/kg, (c) 49.8 mg/kg, and (d) 205 mg/kg. In the field these filter media are exposed to longer retention times and should display higher sorption capacity than that of flow-through setting of 8 min retention time.

CONCLUSIONS

The adsorption data were fitted by both Langmuir and Freundlich isotherm. Both the Langmuir and Freundlich fit the adsorption data satisfactorily ($r^2 > 0.9$). However, the Freundlich generated a better fit to the adsorption data. Even after seven years of operation, the fly-ash media exhibited P removal roughly two-thirds of the initial, while Zn and Cu were essentially unchanged. The amount of phosphorus sorbed by the filter media in the BRC after seven years of operation was around half (160 mg/g) to the initial sorbed amount (350 mg/g) tested by Zhang et al. (2008a). It was noted that with the phosphorus initial concentration of 1, 3, and 10 mg/L, the sand/fly-ash filter media after seven years of operation released an average of 10%, 13% and 16% of the sorbed phosphorus. This predicts strong P retention of the fly-ash amended filter media even after seven years of operation. The desorption of Zn and Cu at the initial concentration of 1, 3, and 10 mg/L was only 0.1% to 0.3% of the sorbed Zn and 0.2% to 0.4% of the sorbed Cu. At the higher initial concentration of 30 mg/L of Zn and Cu, the filter media released only 0.3% of sorbed Zn and 0.6% of sorbed Cu. Thus, desorption of Zn and Cu from the fly-ash amended filter media after seven years was negligible. Therefore, the phosphorus and metal sorption in fly-ash amenedfilter media may be considered irreversible and should provide long-term phosphorus and metal retention.

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Table 4.1. Design summary of bioretention cell at Grove, OK (Chavez et al. 2015).

Site	**Grand Lake Association (GLA)**	**Grove High School (GHS)**	**Elm Creek Plaza (ECP)**	**Spicer Residence (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
Land Cover % Impervious	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

Table 4.2**.** Adsorption of phosphorus and metal on filter media at phosphorus and metal initial concentrations of 1, 3, 10, 20, and 30 mg/L.

C_o (mg/L)	Element	Bioretention Cell Location							
		ECP		GLA		GHS		SR	
		C_e (mg/L)	q_e (mg/kg)	C_e (mg/L)	q_e (mg/kg)	C_e (mg/L)	q_e (mg/kg)	C_e (mg/L)	q_e (mg/kg)
1	P	0.46	10.8	0.365	12.7	0.37	12.6	0.42	11.6
3		1.15	36.9	1.32	33.6	1.26	34.7	1.34	33.1
10		5.44	91.2	6.62	67.6	7.17	56.6	6.54	69.1
20		14.6	106	14.5	109	14.8	103	13.3	132
30		22.8	143	22.0	159	22.7	145	20.9	181
1	Zn	0.02	19.6	0.02	19.6	0.01	19.7	0.01	19.8
3		0.02	59.6	0.025	59.5	0.02	59.6	0.03	59.4
10		0.565	188	1.85	163	2.55	149	0.28	194
20		3.29	334	4.72	305	5.50	289	2.37	352
30		9.29	414	10.3	392	12.9	340	5.75	485
1	Cu	0.05	19.8	0.03	19.2	0.03	19.4	0.015	19.7
3		0.01	59.7	0.01	59.8	0.03	59.4	0.03	59.4
10		0.74	185	0.125	197	0.70	186	0.08	198
20		6.92	261	0.485	390	6.25	275	0.32	393
30		9.89	402	2.70	545	9.45	411	2.23	555

C_e = Equilibrium concentration, q_e = amount of P, Zn and Cu adsorbed, C_o = Initial concentration.

Table 4.3. Phosphorus and metal removal efficiencies of filter media from 2014 and 2007 batch experiments.

C_o (mg/L)	Average Removal (%)														
	Bioretention Cell Location														
	ECP			GLA			GHS			SR			[a]Initial Sample		
	P	Zn	Cu	P	Zn	Cu	P	Zn	Cu	P	Zn	Cu	P	Zn	Cu
1	60	98	99	63	98	97	63	99	97	58	99	98	87	97	92
3	58	99	99	56	99	99	57	99	99	55	99	99	91	NA	NA
10	36	94	92	38	81	98	28	75	93	54	97	99	NA	NA	NA

[a] Results from Zhang et al. (2008 a), NA = Not available, C_o= Initial Concentration

Table 4.4. Langmuir and Freundlich isotherm parameters obtained by non-linear regression for phosphorus adsorption of filter media from 2014 and 2007 batch experiments at four bioretention cells at Grove, OK.

Model	Parameters	Bioretention Cell Location								
		ECP		GLA		GHS		SR		
		Value	S.E	Value	S.E	Value	S.E	Value	S.E	Initial Sample [a]
Langmuir	q_m(mg/kg)	157	17.8	383	189	431	326	491	178	385
	b (L/kg)	0.225	0.085	0.031	0.023	0.021	0.023	0.028	0.015	2.89
Freundlich	K_F (L/kg)	31.2	8.23	19.4	4.22	16.98	5.2	19.2	3.25	203
	n	2.02	0.403	1.49	0.172	1.476	0.233	1.35	0.111	0.295

[a] Estimated isotherm parameter of sand with 5% fly ash sample (Zhang et al. 2008 a), S.E.= Standard Error.

Table 4.5. Phosphorus adsorption of filter media from 2014 and 2007 batch experiments.

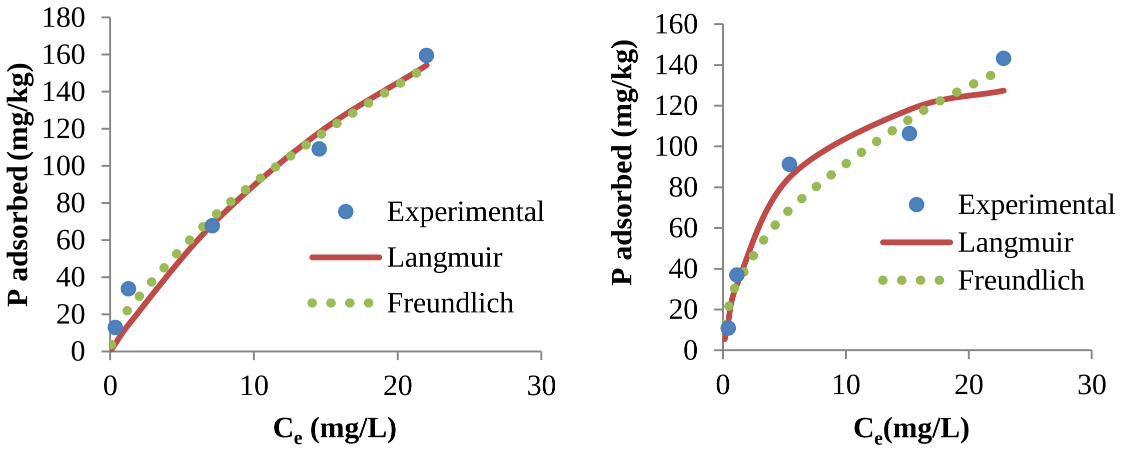
	Bioretention Cell Location									
	ECP		GLA		GHS		SR		Initial Sample[a]	
C_o (mg/L)	C_e	q_e	C_e	q_e	C_e	q_e	C_e	q_e	C_e	q_e
1	0.460	10.8	0.365	12.7	0.37	12.6	0.420	11.6	-	-
3	1.15	36.9	1.32	33.6	1.26	34.7	1.34	33.1	0.03	67.3
10	5.44	91.2	6.62	67.6	7.17	56.6	6.54	69.1	0.11	112
20	14.6	106	14.5	109	14.8	103	13.3	132	0.66	197
30	22.8	143	22.0	159	22.7	145	20.9	181	9.76	350

C_o = Initial concentration, C_e = Equilibrium concentration (mg/L), q_e = Amount of phosphorus adsorbed (mg/kg), [a]Phosphorus adsorption results from batch experiment (Zhang et al. 2008 a).

Table 4.6. Langmuir and Freundlich isotherm parameters obtained by nonlinear regression for Zn and Cu adsorption of filter media from 2014 and 2007 batch experiments at four bioretention cells at Grove, OK.

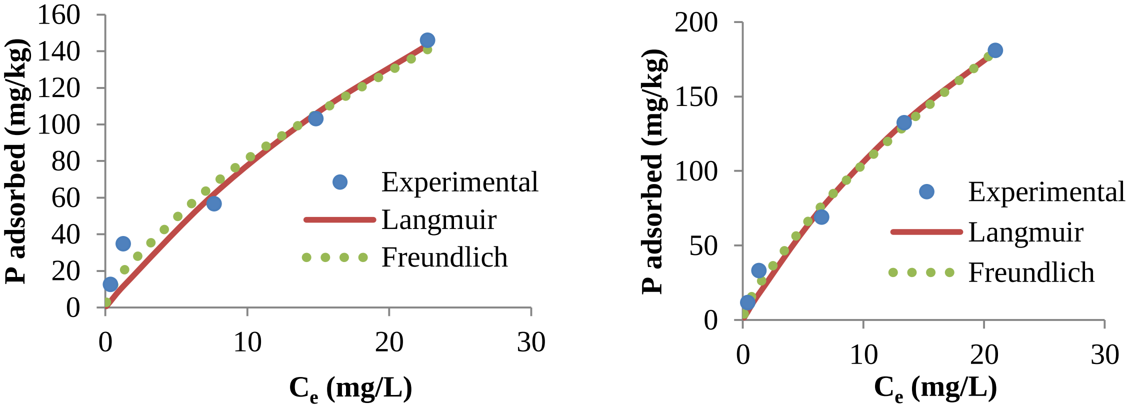
Model	Metal	Parameters	Bioretention Cell Location							
			ECP		GLA		GHS		SR	
			Value	S.E	Value	S.E	Value	S.E	Value	S.E
Langmuir	Zn	q_m (mg/kg)	432	31.8	551	96.1	470	101.00	480	39.9
		b (L/kg)	1.34	0.433	0.246	0.105	0.227	0.127	2.22	0.843
	Cu	q_m (mg/kg)	365	53.10	605	40.5	380	50.6	609	31.9
		b (L/kg)	1.35	0.952	3.6	0.818	1.32	0.859	5.25	0.909
Freundlich	Zn	K_F (L/kg)	200	21.1	142	17.8	126	24.0	251	19.0
		n	0.443	0.443	2.26	0.322	2.51	0.548	2.59	0.321
	Cu	K_F (L/kg)	157	31.2	392	42.7	160	28.4	433	42.0
		n	2.74	0.709	2.55	0.518	2.59	0.584	2.57	0.591

S.E. = Standard errors.



Site GLA

Site ECP



Site GHS

Site SR

Figure 4.1. Non-linear isotherm for phosphorus adsorption by filter media samples at four bioretention cells at Grove, OK.

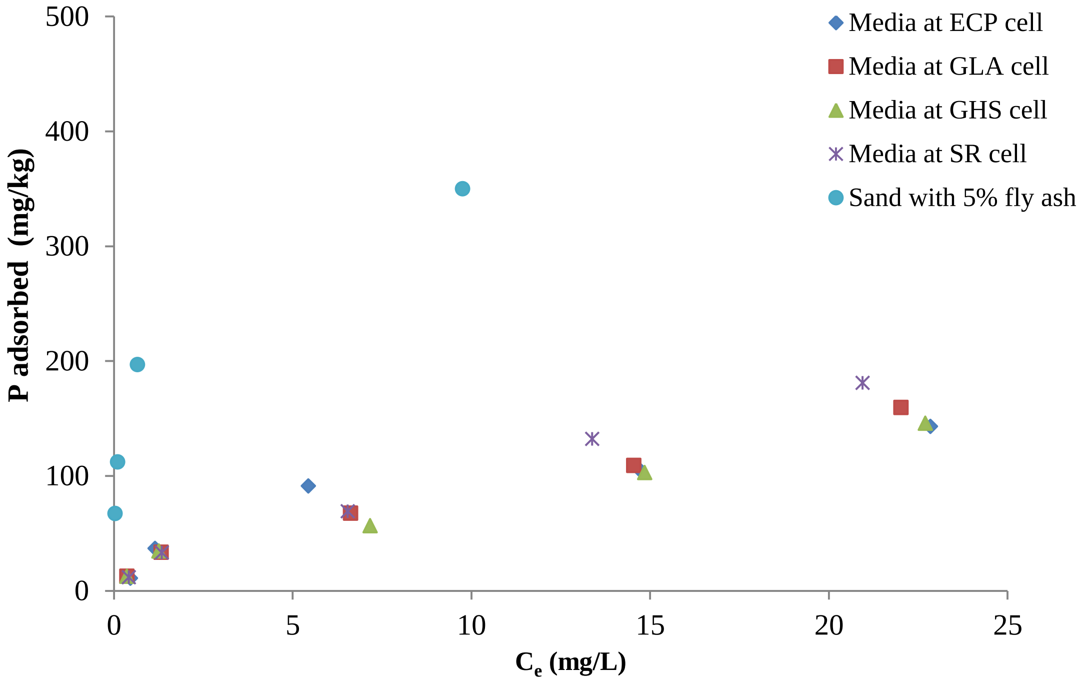
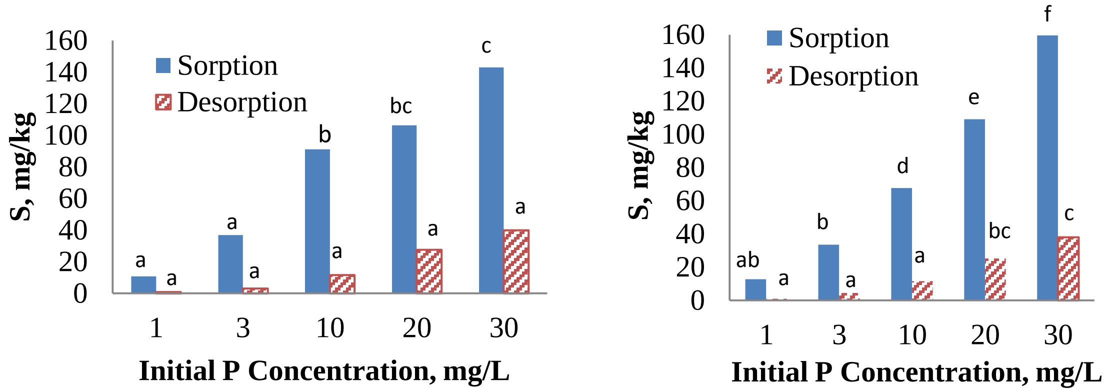


Figure 4.2. Phosphorus adsorption on sand with 5% fly ash in 2007 (Zhang et al. 2008 a) and after seven years of operation in 2014 at four bioretention cells at Grove, OK.



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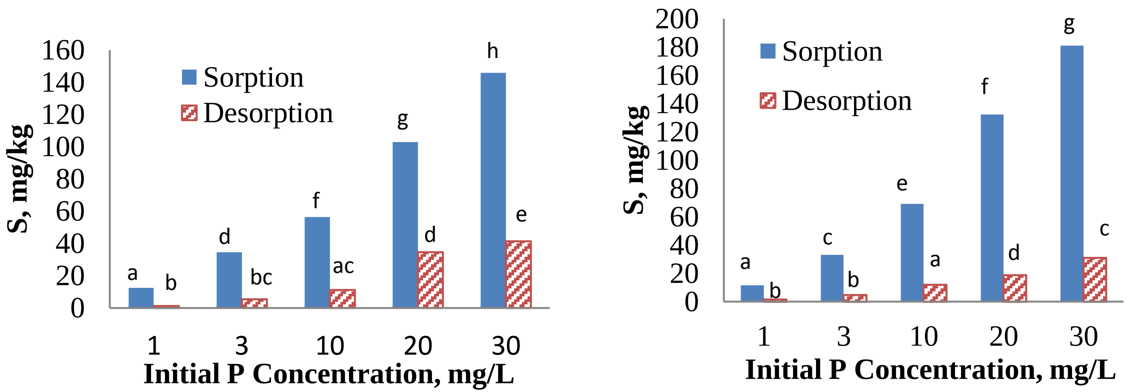
Site GLA

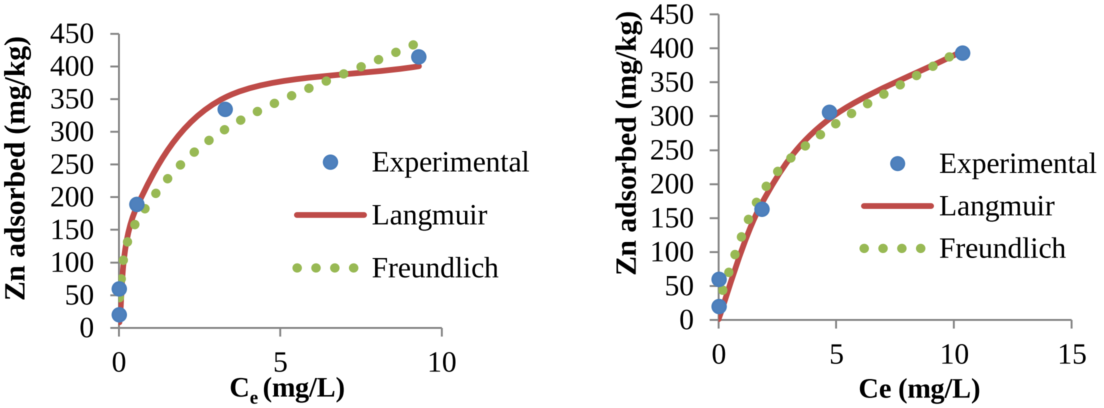


Site GHS

Site SR

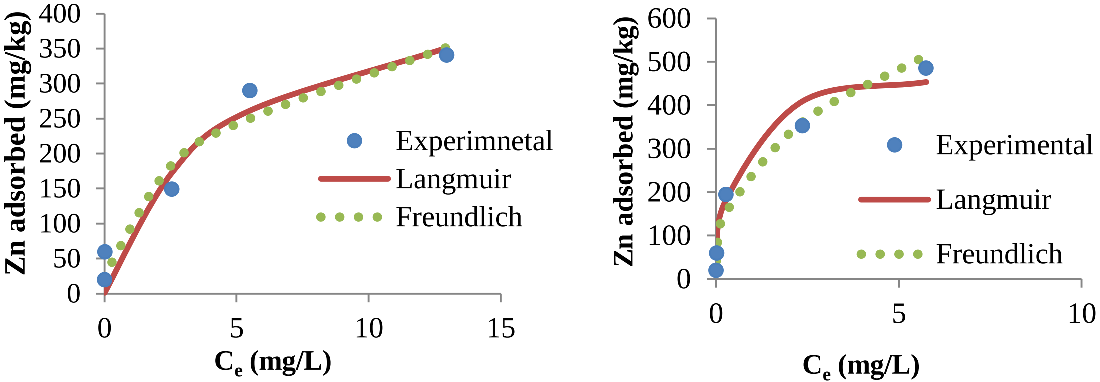
Figure 4.3. Amount of P sorbed and desorbed from filter media samples at four BRC at five initial P concentrations ranging from 1 to 30 mg/L.

Different lower-case letters represent statistically significant difference between sorption and desorption, based on Tukey’s HSD test. ($p < 0.05$).



Site ECP

Site GLA



Site GHS

Site SR

Figure 4.4. Non-linear isotherm for Zn adsorption by filter media at four bioretention cells at Grove, OK.

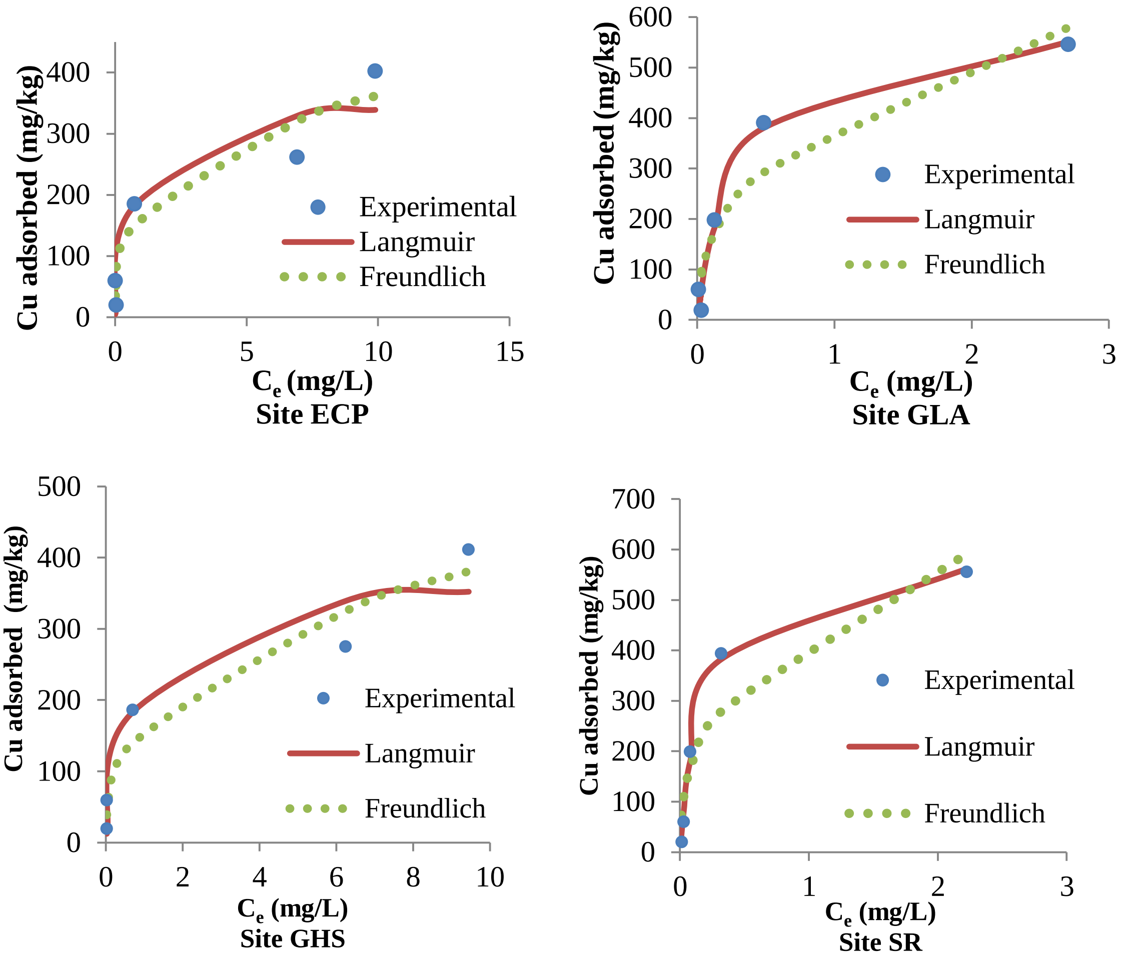


Figure 4.5. Non-linear isotherm for Cu adsorption by filter media at four bioretention cells at Grove, OK.

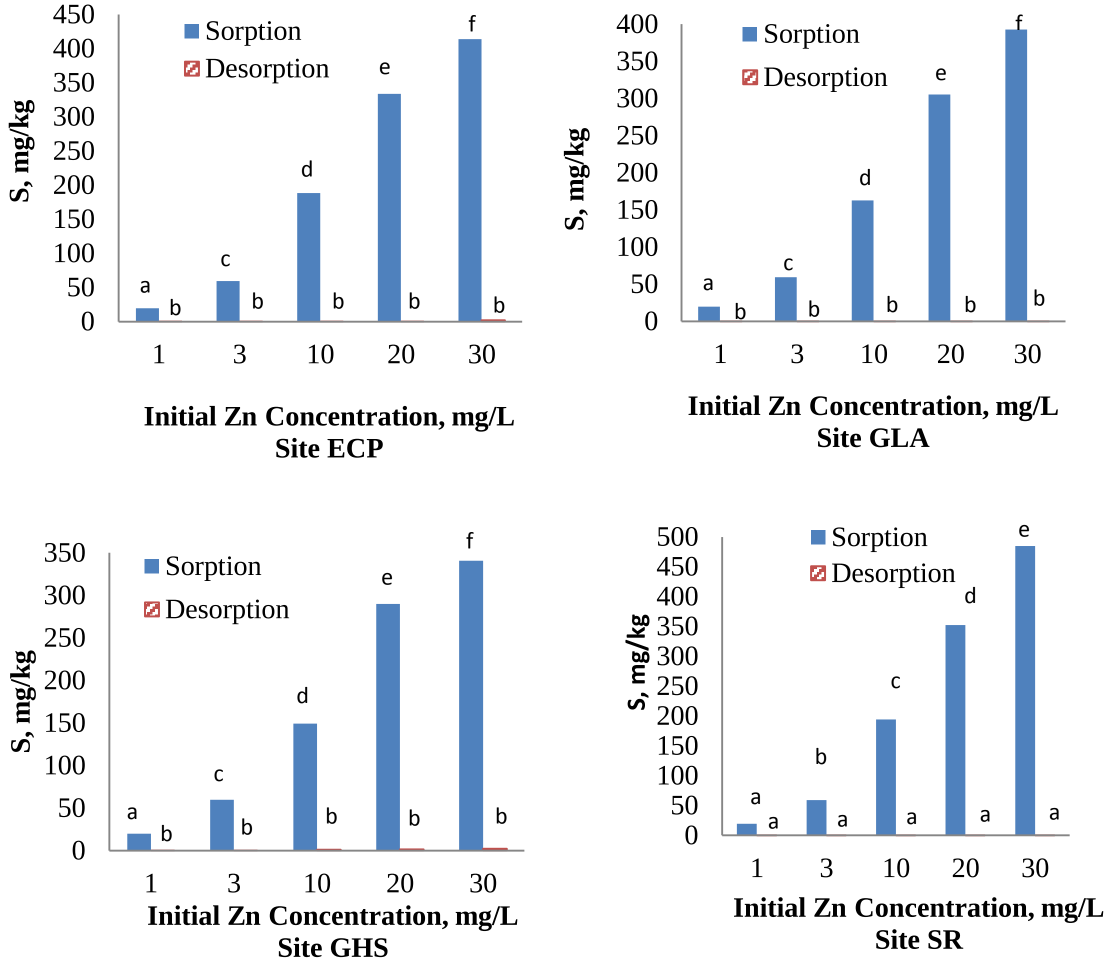


Figure 4.6. Amount of Zn sorbed and desorbed from filter media samples at four bioretention cells at five initial concentrations ranging from 1 to 30 mg/L.

Different lower-case letters represent statistically significant difference between sorption and desorption, based on Tukey’s HSD test.($p < 0.05$).

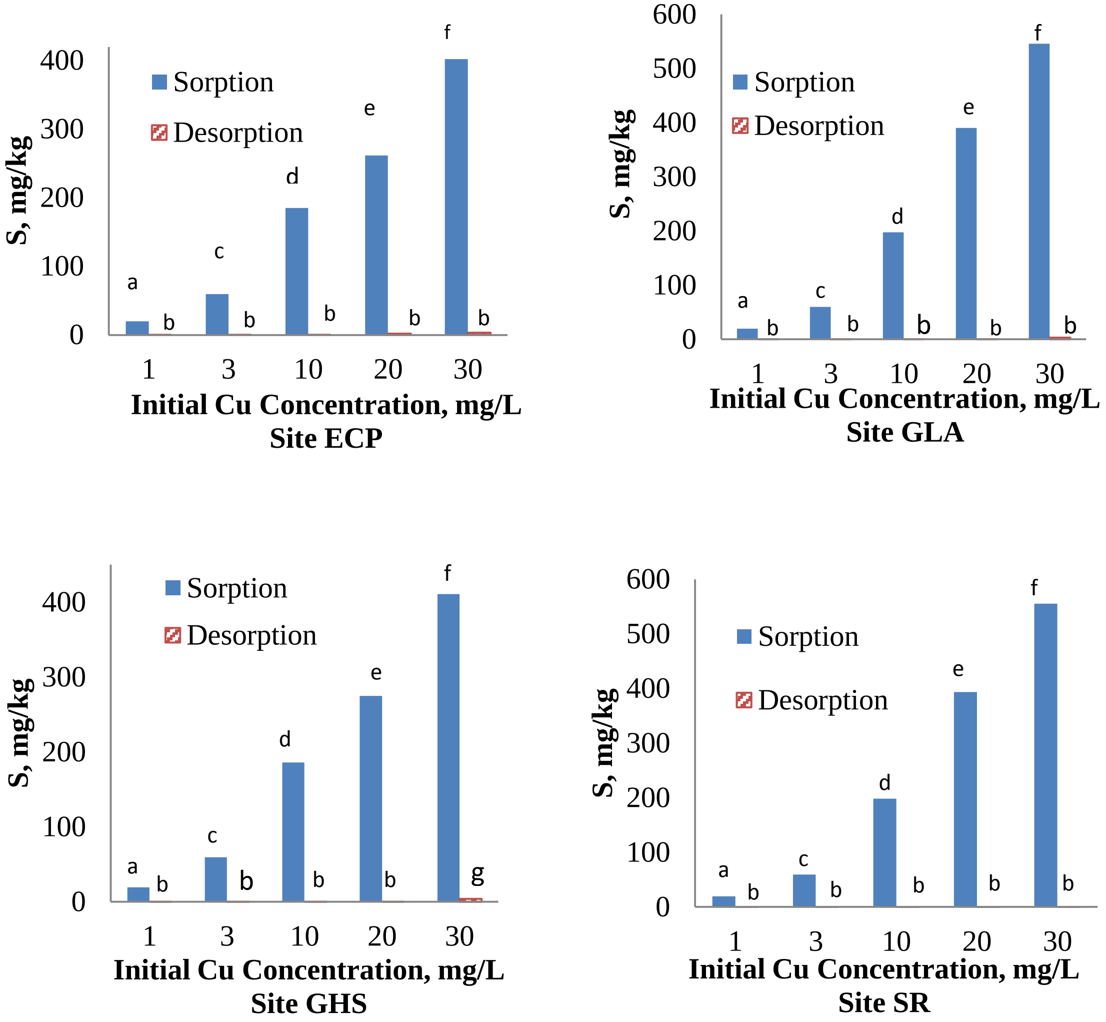


Figure 4.7. Amount of Cu sorbed and desorbed from filter media at four bioretention cells at five initial concentrations ranging from 1 to 30 mg/L.

Different lower-case letters represent statistically significant difference between sorption and desorption, based on Tukey's HSD test. ($p < 0.05$).

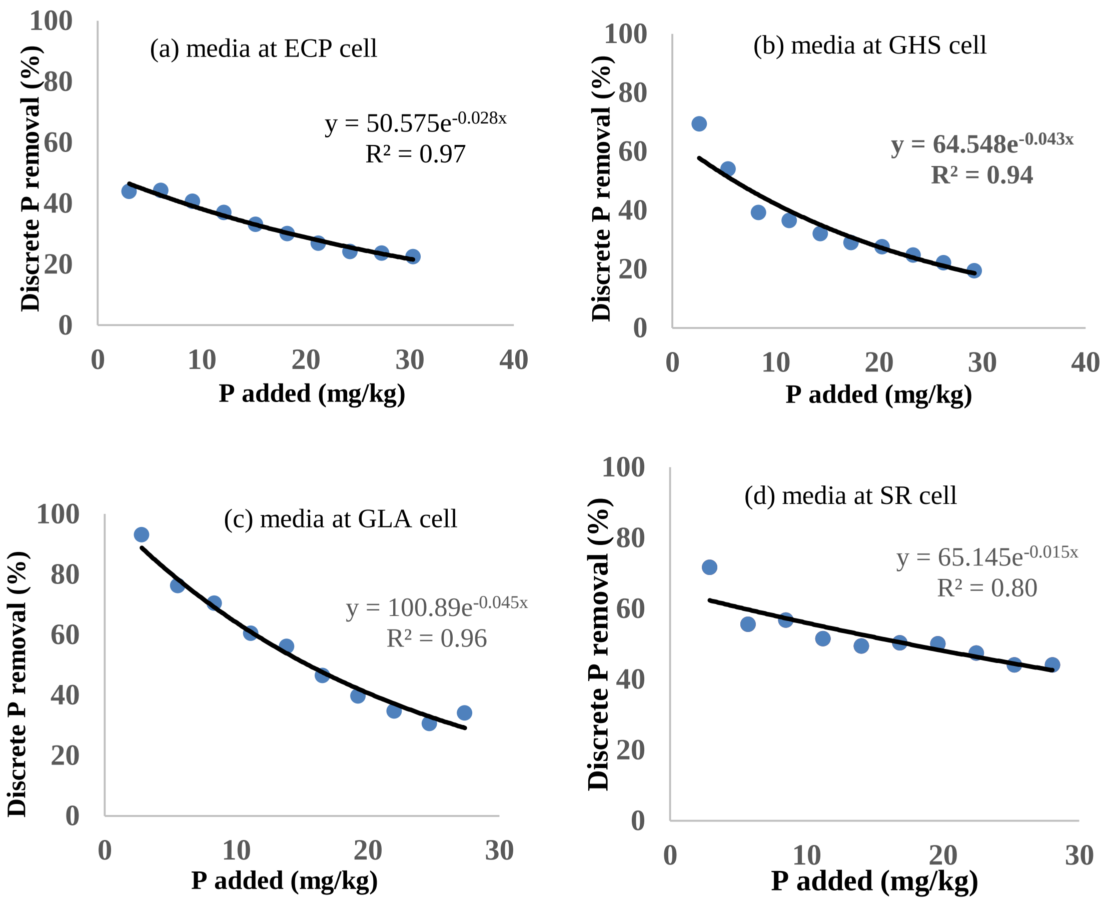


Figure 4.8**.** Experimentally determined flow-through P removal curves for filter media at four bioretention cells at Grove, OK, with a 1 mg/L inflow P solution.

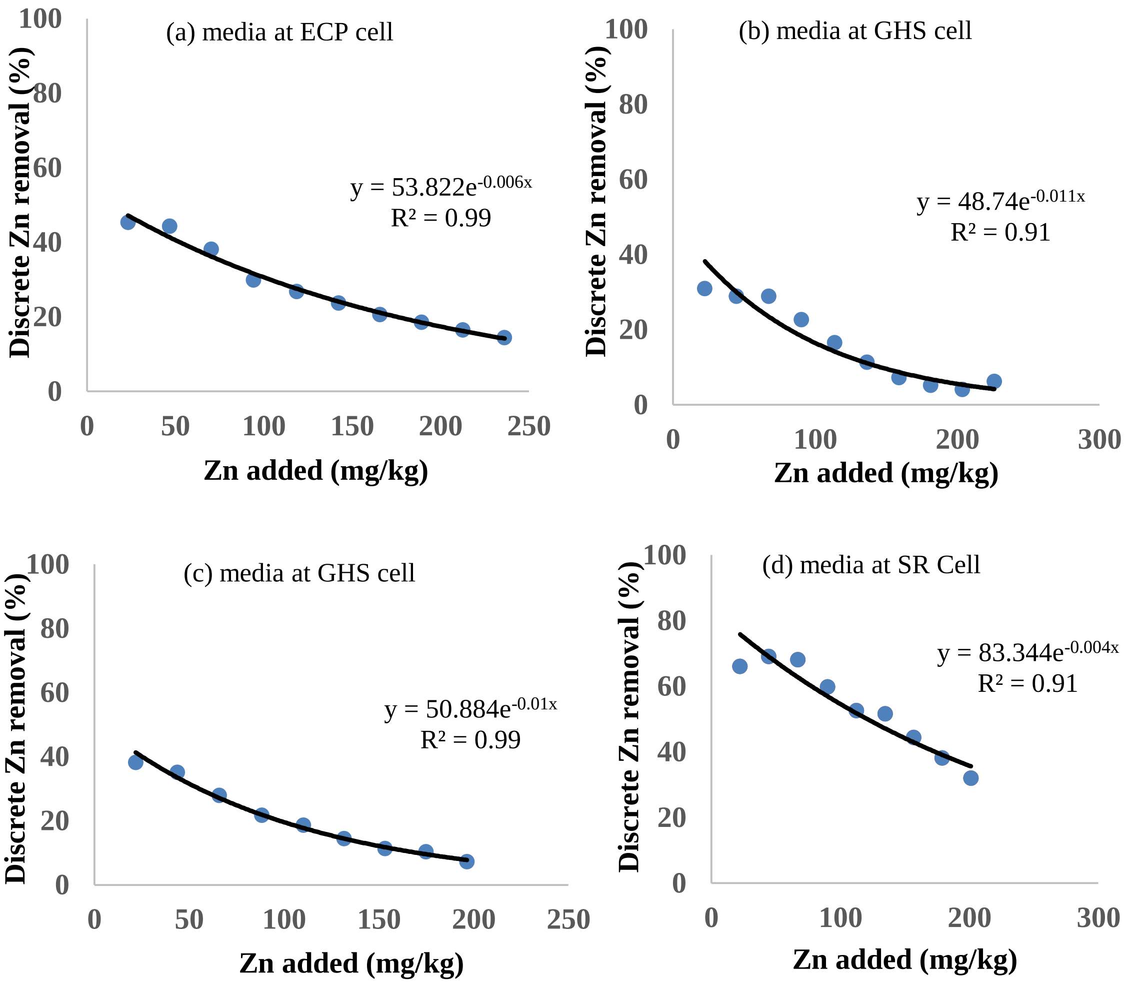


Figure 4.9. Experimentally determined flow-through Zn removal curves for aged sand with 5% fly-ash filter media at four different BRC at Grove, OK, with a 1 mg/L inflow Zn solution.

APPENDEX

Appendix A

Data from core sample analysis

Table A1. Phosphorus concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-P (mg/kg)	WS-P (mg/kg)	M3-P (mg/kg)
ECP	1	0-15	268	1.41	29.2
	1	15-30	318	1.15	5.22
	1	30-45	503	1.21	6.25
	1	45-60	550	1.25	7.45
	2	0-15	395	1.86	24.6
	2	15-30	500	1.06	6.64
	2	30-45	565	1.28	6.90
	2	45-60	448	1.17	6.52
	3	0-15	170	1.50	22.9
	3	15-30	490	0.92	6.71
	3	30-45	455	1.21	7.77
	3	45-60	471	1.32	8.23
	4	0-15	273	1.55	35.9
	4	15-30	580	1.15	7.07
	4	30-45	580	1.01	6.69
	4	45-60	143	0.76	21.5
	5	0-15	365	1.08	25.1
	5	15-30	538	0.92	7.51
	5	30-45	380	0.45	7.0
	5	45-60	568	1.69	7.01
	6	0-15	383	1.29	27.9
	6	15-30	380	0.62	6.11
	6	30-45	203	0.73	6.02
	6	45-60	380	0.93	6.82

T-P = Total phosphorus concentration from total soil digestion

WS-P = Water soluble phosphorus concentration from water soluble extraction

M3-P = Mehlich-3 phosphorus concentration from Mehlich -3 extraction

ECP = Elm Creek Plaza. Lab detection limit (D.L) = 0.01 mg/L.

Table A2. Phosphorus concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-P (mg/kg)	WS-P (mg/kg)	M3-P (mg/kg)
GLA	1	0-15	255	4.74	34.5
	1	15-30	268	0.72	18.6
	1	30-45	155	2.25	24.3
	1	45-60	205	1.62	18.4
	2	0-15	325	2.44	28.2
	2	15-30	223	0.59	14.4
	2	30-45	358	2.39	17.9
	2	45-60	235	1.84	16.5
	3	0-15	365	3.1	38.0
	3	15-30	180	0.6	15.2
	3	30-45	203	0.42	21.1
	3	45-60	218	1.89	27.8
	4	0-15	308	1.06	24.2
	4	15-30	200	0.73	13.3
	4	30-45	315	1.06	22.3
	4	45-60	238	2.14	41.8
	5	0-15	298	1.91	27.6
	5	15-30	180	0.79	15.4
	5	30-45	225	2.47	36.1
	5	45-60	173	1.02	27.8
	6	0-15	190	2.75	27.1
	6	15-30	195	0.94	16.3
	6	30-45	278	0.23	38.4
	6	45-60	168	0.48	22.8

T-P = Total phosphorus concentration from total soil digestion

WS-P = Water soluble phosphorus concentration from water soluble extraction

M3-P = Mehlich-3 phosphorus concentration from Mehlich -3 extraction

GLA = Grand Lake Association

Table A3. Phosphorus concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-P (mg/kg)	WS-P (mg/kg)	M3-P (mg/kg)
GHS	1	0-15	493	1.80	41.0
	1	15-30	248	0.51	18.1
	1	30-45	260	0.40	15.0
	1	45-60	288	0.53	39.5
	2	0-15	433	1.89	31.2
	2	15-30	363	0.63	15.5
	2	30-45	288	1.19	16.9
	2	45-60	293	1.31	27.1
	3	0-15	358	1.79	36.1
	3	15-30	320	0.62	19.6
	3	30-45	310	0.80	9.69
	3	45-60	275	0.63	29.1
	4	0-15	228	0.98	22.4
	4	15-30	243	0.80	12.3
	4	30-45	285	1.07	15.1
	4	45-60	275	0.60	23.9
	5	0-15	215	1.33	33.5
	5	15-30	240	0.68	12.9
	5	30-45	250	1.38	22.6
	5	45-60	285	0.90	32.9
	6	0-15	263	1.45	43.9
	6	15-30	263	0.78	14.5
	6	30-45	305	0.76	20.8
	6	45-60	287	0.85	25.9

T-P = Total phosphorus concentration from total soil digestion

WS-P = Water soluble phosphorus concentration from water soluble extraction

M3-P = Mehlich-3 phosphorus concentration from Mehlich -3 extraction

GHS = Grove High School

Table A4. Phosphorus concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-P (mg/kg)	WS-P (mg/kg)	M3-P (mg/kg)
SR	1	0-15	388	7.63	37.9
	1	15-30	433	1.14	7.21
	1	30-45	433	0.93	6.33
	1	45-60	180	1.12	29.6
	2	0-15	623	5.24	59.9
	2	15-30	208	0.82	15.9
	2	30-45	160	1.29	9.39
	2	45-60	198	1.66	28.9
	3	0-15	158	4.59	30.8
	3	15-30	185	1.38	11.7
	3	30-45	108	2.06	5.82
	3	45-60	83	1.02	27.4
	4	0-15	265	5.42	25.2
	4	15-30	790	0.21	8.76
	4	30-45	485	0.52	6.26
	4	45-60	293	2.86	21.7
	5	0-15	210	6.71	19.8
	5	15-30	193	1.3	8.23
	5	30-45	373	1.37	7.80
	5	45-60	728	0.5	6.58
	6	0-15	230	4.69	65.2
	6	15-30	680	1.36	6.20
	6	30-45	765	0.32	9.85
	6	45-60	410	0.24	9.82

T-P = Total phosphorus concentration from total soil digestion

WS-P = Water soluble phosphorus concentration from water soluble extraction

M3-P = Mehlich-3 phosphorus concentration from Mehlich -3 extraction

SR = Spicer Residence

Table A5. Zn concentration on core samples from three different extraction methods.

Site	Sample set	Depth (cm)	T-Zn (mg/kg)	WS-Zn (mg/kg)	M3-Zn (mg/kg)
ECP	1	0-15	69.9	0.70	14.2
	1	15-30	26.8	0.31	4.85
	1	30-45	32.0	0.37	4.69
	1	45-60	28.8	0.39	3.98
	2	0-15	161	0.59	60.0
	2	15-30	32.5	0.31	4.94
	2	30-45	29.7	0.24	4.06
	2	45-60	28.5	0.10	3.90
	3	0-15	42.7	0.29	9.54
	3	15-30	31.9	0.05	4.23
	3	30-45	30.8	0.18	4.23
	3	45-60	31.0	0.19	4.50
	4	0-15	117	0.23	44.5
	4	15-30	31.4	0.05	3.79
	4	30-45	31.8	0.05	3.31
	4	45-60	22.2	0.05	3.12
	5	0-15	154	0.24	57.0
	5	15-30	31.0	0.10	3.97
	5	30-45	32.3	0.05	3.90
	5	45-60	32.4	0.05	4.18
	6	0-15	105	0.34	29.5
	6	15-30	27.0	0.05	4.43
	6	30-45	41.0	0.10	3.63
	6	45-60	40.5	0.10	3.80

T-Zn = Total zinc concentration from total soil digestion

WS-P = Water soluble zinc concentration from water soluble extraction

M3-P = Mehlich-3 zinc concentration from Mehlich -3 extraction

ECP = Elm Creek Plaza

Laboratory detection limit for metals were 0.01 mg/L

Table A6. Zn concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Zn (mg/kg)	WS-Zn (mg/kg)	M3-Zn (mg/kg)
GLA	1	0-15	47.2	0.43	10.3
	1	15-30	37.2	0.13	4.62
	1	30-45	20.4	0.11	3.94
	1	45-60	19.3	0.05	4.17
	2	0-15	37.4	0.38	9.74
	2	15-30	27.7	0.20	5.23
	2	30-45	33.2	0.12	4.28
	2	45-60	32.4	0.27	3.79
	3	0-15	54.3	0.54	15.2
	3	15-30	37.4	0.1	4.75
	3	30-45	36.4	0.3	5.74
	3	45-60	29.8	0.33	2.63
	4	0-15	50.4	0.49	15.0
	4	15-30	35.6	0.21	5.43
	4	30-45	29.1	0.18	4.67
	4	45-60	29.0	0.1	3.22
	5	0-15	50.8	0.41	15.7
	5	15-30	36.7	0.22	4.67
	5	30-45	25.5	0.34	4.09
	5	45-60	28.8	0.25	3.28
	6	0-15	40.8	0.63	9.94
	6	15-30	38.3	0.23	4.84
	6	30-45	28.1	0.60	3.81
	6	45-60	24.0	0.23	2.80

T-Zn = Total zinc concentration from total soil digestion

WS-P = Water soluble zinc concentration from water soluble extraction

M3-P = Mehlich-3 zinc concentration from Mehlich -3 extraction

GLA = Grand Lake Association

Table A7. Zn concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Zn (mg/kg)	WS-Zn (mg/kg)	M3-Zn (mg/kg)
GHS	1	0-15	149.5	0.49	123
	1	15-30	53.0	0.32	15.7
	1	30-45	27.1	0.05	5.51
	1	45-60	26.8	0.14	4.18
	2	0-15	158.0	0.48	70.5
	2	15-30	63.3	0.15	25.4
	2	30-45	26.1	0.1	5.39
	2	45-60	23.4	0.2	4.30
	3	0-15	132.1	0.49	154
	3	15-30	91.6	0.3	8.35
	3	30-45	33.4	0.11	5.63
	3	45-60	26.5	0.1	4.34
	4	0-15	81.1	0.54	30.8
	4	15-30	19.7	0.26	5.64
	4	30-45	22.7	0.05	4.13
	4	45-60	23.5	0.10	4.12
	5	0-15	60.6	0.28	31.9
	5	15-30	25.1	0.2	4.91
	5	30-45	24.5	0.16	4.41
	5	45-60	24.5	0.10	4.16
	6	0-15	174.9	0.46	48.4
	6	15-30	22.3	0.17	5.04
	6	30-45	23.8	0.05	4.53
	6	45-60	23.0	0.05	4.52

T-Zn = Total zinc concentration from total soil digestion

WS-P = Water soluble zinc concentration from water soluble extraction

M3-P = Mehlich-3 zinc concentration from Mehlich -3 extraction

GHS = Grove High School

Table A8. Zn concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Zn (mg/kg)	WS-Zn (mg/kg)	M3-Zn (mg/kg)
SR	1	0-15	33.3	2.21	10.7
	1	15-30	24.8	0.42	4.38
	1	30-45	26.5	0.11	4.11
	1	45-60	22.3	0.05	3.09
	2	0-15	53.1	1.82	20.4
	2	15-30	22.3	0.17	3.22
	2	30-45	20.3	0.18	2.30
	2	45-60	20.2	0.05	3.05
	3	0-15	45.9	2.37	15.4
	3	15-30	14.0	0.21	2.85
	3	30-45	8.8	0.29	1.74
	3	45-60	6.6	0.25	1.47
	4	0-15	48.8	2.16	15.1
	4	15-30	26.8	0.05	4.04
	4	30-45	26.1	0.05	4.04
	4	45-60	20.8	0.16	3.47
	5	0-15	49.7	2.24	13.3
	5	15-30	20.0	0.24	2.91
	5	30-45	24.8	0.11	3.71
	5	45-60	27.8	0.05	3.14
	6	0-15	48.5	1.78	13.3
	6	15-30	2.0	0.13	3.85
	6	30-45	29.4	0.05	3.44
	6	45-60	22.0	0.05	3.30

T-Zn = Total zinc concentration from total soil digestion

WS-P = Water soluble zinc concentration from water soluble extraction

M3-P = Mehlich-3 zinc concentration from Mehlich -3 extraction

SR = Spicer Residence

Table A9. Cu concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Cu (mg/kg)	WS-Cu (mg/kg)	M3-Cu (mg/kg)
ECP	1	0-15	10.1	0.10	4.80
	1	15-30	14.8	0.01	3.87
	1	30-45	23.0	0.01	4.26
	1	45-60	23.6	0.01	4.34
	2	0-15	12.3	0.01	4.62
	2	15-30	21.0	0.01	3.63
	2	30-45	23.9	0.01	4.55
	2	45-60	24.0	0.01	4.48
	3	0-15	7.09	0.01	4.57
	3	15-30	21.3	0.01	3.58
	3	30-45	19.8	0.01	4.75
	3	45-60	19.8	0.01	4.85
	4	0-15	9.6	0.01	4.90
	4	15-30	25.1	0.01	3.25
	4	30-45	25.6	0.01	3.03
	4	45-60	26.4	0.01	1.75
	5	0-15	13.1	0.10	4.89
	5	15-30	22.9	0.10	3.27
	5	30-45	26.9	0.01	4.35
	5	45-60	27.3	0.10	4.97
	6	0-15	13.7	0.10	3.82
	6	15-30	16.3	0.10	2.71
	6	30-45	9.4	0.10	3.21
	6	45-60	17.9	0.10	3.21

T-Cu = Total copper concentration from total soil digestion

WS-Cu = Water soluble copper concentration from water soluble extraction

M3-Cu = Mehlich-3 copper concentration from Mehlich -3 extraction

ECP = Elm Creek Plaza

Table A10. Cu concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Cu (mg/kg)	WS-Cu (mg/kg)	M3-Cu (mg/kg)
GLA	1	0-15	5.90	0.1	2.62
	1	15-30	9.45	0.1	1.07
	1	30-45	6.20	0.1	2.12
	1	45-60	11.2	0.01	3.52
	2	0-15	12.2	0.01	5.05
	2	15-30	6.91	0.01	2.2
	2	30-45	12.5	0.01	2.48
	2	45-60	9.16	0.01	3.23
	3	0-15	8.0	0.01	2.43
	3	15-30	5.85	0.01	1.35
	3	30-45	6.68	0.01	1.01
	3	45-60	9.88	0.01	1.35
	4	0-15	7.05	0.01	2.36
	4	15-30	8.43	0.01	1.78
	4	30-45	8.64	0.05	2.08
	4	45-60	9.90	0.01	2.13
	5	0-15	6.94	0.01	2.63
	5	15-30	8.92	0.01	1.83
	5	30-45	9.47	0.01	2.14
	5	45-60	10.9	0.01	1.97
	6	0-15	6.40	0.01	2.83
	6	15-30	9.12	0.01	1.74
	6	30-45	11.3	0.01	1.54
	6	45-60	7.63	0.01	1.64

T-Cu = Total copper concentration from total soil digestion

WS-Cu = Water soluble copper concentration from water soluble extraction

M3-Cu = Mehlich-3 copper concentration from Mehlich -3 extraction

GLA = Grand Lake Association

Table A11. Cu concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Cu (mg/kg)	WS-Cu (mg/kg)	M3-Cu (mg/kg)
GHS	1	0-15	7.81	0.01	3.79
	1	15-30	4.75	0.01	2.32
	1	30-45	6.11	0.01	2.19
	1	45-60	5.71	0.01	2.39
	2	0-15	5.58	0.01	3.34
	2	15-30	4.70	0.01	1.86
	2	30-45	4.75	0.01	2.66
	2	45-60	6.61	0.01	2.25
	3	0-15	6.04	0.01	2.80
	3	15-30	5.17	0.01	1.81
	3	30-45	9.83	0.01	2.4
	3	45-60	8.28	0.05	2.08
	4	0-15	2.53	0.01	2.62
	4	15-30	3.47	0.01	1.73
	4	30-45	5.28	0.01	1.87
	4	45-60	5.20	0.01	1.4
	5	0-15	1.03	0.01	2.51
	5	15-30	3.68	0.01	1.83
	5	30-45	3.62	0.01	1.92
	5	45-60	3.80	0.01	1.9
	6	0-15	3.57	0.01	2.58
	6	15-30	4.34	0.01	1.06
	6	30-45	5.20	0.01	1.05
	6	45-60	4.95	0.01	1.23

T-Cu = Total copper concentration from total soil digestion

WS-Cu = Water soluble copper concentration from water soluble extraction

M3-Cu = Mehlich-3 copper concentration from Mehlich -3 extraction

GHS = Grove High School

Table A12. Cu concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Cu (mg/kg)	WS-Cu (mg/kg)	M3-Cu (mg/kg)
SR	1	0-15	9.57	1.58	3.33
	1	15-30	14.6	0.17	1.64
	1	30-45	15.2	0.01	1.66
	1	45-60	17.3	0.01	2.41
	2	0-15	20.7	0.15	7.11
	2	15-30	6.06	0.01	1.66
	2	30-45	5.12	0.01	1.85
	2	45-60	7.52	0.01	2.37
	3	0-15	4.17	0.01	1.42
	3	15-30	6.45	0.01	1.62
	3	30-45	3.06	0.01	1.14
	3	45-60	9.0	0.01	0.77
	4	0-15	8.0	0.01	4.37
	4	15-30	26.2	0.01	4.25
	4	30-45	17.1	0.01	4.0
	4	45-60	18.8	0.01	3.62
	5	0-15	5.91	0.01	1.82
	5	15-30	5.62	0.01	2.1
	5	30-45	12.9	0.01	3.05
	5	45-60	24.8	0.01	3.55
	6	0-15	8.13	0.01	3.23
	6	15-30	22.3	0.01	3.05
	6	30-45	27.7	0.01	3.76
	6	45-60	22.5	0.01	3.44

T-Cu = Total copper concentration from total soil digestion

WS-Cu = Water soluble copper concentration from water soluble extraction

M3-Cu = Mehlich-3 copper concentration from Mehlich -3 extraction

SR = Spicer Residence

Table A13. Pb concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Pb (mg/kg)	WS-Pb (mg/kg)	M3-Pb (mg/kg)
ECP	1	0-15	9.05	0.37	0.79
	1	15-30	6.75	0.10	0.10
	1	30-45	8.15	0.18	0.10
	1	45-60	7.775	0.10	0.10
	2	0-15	16.5	0.38	2.4
	2	15-30	8.50	0.19	0.10
	2	30-45	8.22	0.37	0.10
	2	45-60	7.12	0.18	0.10
	3	0-15	7.40	0.31	0.43
	3	15-30	7.57	0.10	0.01
	3	30-45	8.27	0.24	0.50
	3	45-60	8.24	0.24	0.10
	4	0-15	9.92	0.48	4.0
	4	15-30	8.27	0.24	0.01
	4	30-45	8.55	0.24	0.01
	4	45-60	5.60	0.24	0.01
	5	0-15	12.5	0.43	2.84
	5	15-30	7.72	0.16	0.01
	5	30-45	7.42	0.24	0.01
	5	45-60	7.47	0.24	0.01
	6	0-15	14.3	0.48	0.67
	6	15-30	7.35	0.24	0.10
	6	30-45	5.77	0.30	0.01
	6	45-60	5.87	0.29	0.10

T-Pb = Total lead concentration from total soil digestion

WS-Pb = Water soluble lead concentration from water soluble extraction

M3-Pb = Mehlich-3 lead concentration from Mehlich -3 extraction

ECP = Elm Creek Plaza

Table A14. Pb concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Pb (mg/kg)	WS-Pb(mg/kg)	M3-Pb (mg/kg)
GLA	1	0-15	19.1	0.01	4.02
	1	15-30	10.8	0.01	1.43
	1	30-45	5.63	0.01	0.01
	1	45-60	6.65	0.01	0.01
	2	0-15	17.65	0.01	4.68
	2	15-30	10.50	0.01	1.89
	2	30-45	6.00	0.01	0.01
	2	45-60	6.58	0.01	0.01
	3	0-15	17.7	0.01	4.88
	3	15-30	10.3	0.01	1.77
	3	30-45	13.9	0.01	2.82
	3	45-60	6.23	0.01	0.01
	4	0-15	18.4	0.01	5.97
	4	15-30	10.9	0.01	1.66
	4	30-45	8.68	0.01	0.01
	4	45-60	6.53	0.01	0.01
	5	0-15	18.0	0.01	6.1
	5	15-30	10.15	0.01	1.14
	5	30-45	6.15	0.01	0.01
	5	45-60	6.08	0.01	0.01
	6	0-15	20.3	0.01	4.96
	6	15-30	11.9	0.01	2.12
	6	30-45	6.03	0.1	0.01
	6	45-60	6.28	0.01	0.01

T-Pb = Total lead concentration from total soil digestion

WS-Pb = Water soluble lead concentration from water soluble extraction

M3-Pb = Mehlich-3 lead concentration from Mehlich -3 extraction

GLA = Grand Lake Association

Table A15. Pb concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Pb (mg/kg)	WS-Pb(mg/kg)	M3-Pb (mg/kg)
GHS	1	0-15	23.1	0.01	5.77
	1	15-30	11.8	0.01	0.01
	1	30-45	7.23	0.01	0.01
	1	45-60	6.98	0.01	0.01
	2	0-15	22.2	0.01	4.65
	2	15-30	14.7	0.01	0.86
	2	30-45	6.23	0.01	0.01
	2	45-60	6.90	0.01	0.01
	3	0-15	21.2	0.01	7.13
	3	15-30	21.4	0.01	0.43
	3	30-45	9.08	0.01	0.05
	3	45-60	7.85	0.01	0.05
	4	0-15	22.8	0.01	1.65
	4	15-30	4.83	0.01	0.01
	4	30-45	6.73	0.01	0.01
	4	45-60	6.52	0.01	0.01
	5	0-15	22.1	0.01	1.65
	5	15-30	6.10	0.01	0.01
	5	30-45	6.00	0.01	0.01
	5	45-60	5.89	0.01	0.01
	6	0-15	21.8	0.01	2.53
	6	15-30	5.38	0.01	0.01
	6	30-45	6.10	0.01	0.01
	6	45-60	6.23	0.01	0.01

T-Pb = Total lead concentration from total soil digestion

WS-Pb = Water soluble lead concentration from water soluble extraction

M3-Pb = Mehlich-3 lead concentration from Mehlich -3 extraction

GHS = Grove High School

Table A16. Pb concentration on core samples from three different extraction methods

Site	Sample set	Depth (cm)	T-Pb (mg/kg)	WS-Pb (mg/kg)	M3-Pb (mg/kg)
SR	1	0-15	16.5	0.91	1.85
	1	15-30	5.83	0.01	0.01
	1	30-45	5.60	0.01	0.01
	1	45-60	5.50	0.01	0.05
	2	0-15	20.3	0.18	3.27
	2	15-30	8.43	0.01	0.10
	2	30-45	21.7	0.01	1.55
	2	45-60	6.05	0.01	0.01
	3	0-15	15.3	0.27	1.93
	3	15-30	4.45	0.01	0.01
	3	30-45	1.65	0.01	0.01
	3	45-60	2.30	0.01	0.01
	4	0-15	15.0	1.98	1.70
	4	15-30	6.38	0.01	0.01
	4	30-45	5.50	0.01	0.01
	4	45-60	5.63	0.01	0.01
	5	0-15	16.7	0.15	2.26
	5	15-30	5.43	0.01	2.12
	5	30-45	14.8	0.01	0.01
	5	45-60	7.70	0.01	0.01
	6	0-15	15.6	0.19	0.01
	6	15-30	7.90	0.01	0.01
	6	30-45	6.85	0.01	0.01
	6	45-60	5.80	0.01	0.01

T-Pb = Total lead concentration from total soil digestion

WS-Pb = Water soluble lead concentration from water soluble extraction

M3-Pb = Mehlich-3 lead concentration from Mehlich -3 extraction

SR = Spicer Residence

Table A17. Listing of storm events, rainfall, flow volume, and flow reduction at the Elm Creel Plaza (ECP) bioretention cell.

Event Date	Precipitation [mm (in)]	Inlet Volume (ft^3)	Underdrain Volume (ft^3)	Volume Reduction (%)
26-May-14	6.1 (0.24)	539	170	68%
5-Jun-14	19.1 (0.75)	595.3	148.1	75%
9-Jun-14	17.0 (0.67)	706.1	162	77%
23-Jun-14	17.0 (0.67)	455.3	110.6	76%
7-Aug-14	14.2 (0.56)	426.4	72.9	83%
2-Oct-14	45.0 (1.77)	1349.8	709.3	47%
10-Oct-14	29.7 (1.17)	5093.5	2320	54%
23-Oct-14	97.3 (3.83)	163.3	52.2	68%
26-Mar-15	35.6 (1.40)	1517	385.3	75%
1-Apr-15	7.1 (0.28)	268	29.2	89%
2-Apr-15	13.0 (0.51)	569.4	123.7	78%
8-May-15	7.4 (0.29)	159.9	14.4	91%
20-May-15	11.2 (0.44)	294.2	51.3	83%
29-May-15	19.1 (0.75)	586	78.8	87%
18-Jun-15	52.6 (2.07)	1394.5	144.3	90%
8-Jul-15	49.8 (1.96)	2092.3	855.4	59%
22-Jul-15	9.9 (0.39)	358.3	110.6	69%
6-Aug-15	10.9 (0.43)	379.7	115.4	70%
19-Aug-15	51.6 (2.03)	2122.5	729.1	66%
8-Sep-15	57.2 (2.25)	1442.3	646.2	55%

A positive percent reduction indicates flow reduction.

Table A18. Listing of storm events, rainfall, flow volume, and flow reduction at the Grand Lake Association (GLA) bioretention cell.

Event Date	Precipitation [mm (in)]	Inlet Volume (ft$^{3)}$	Underdrain Volume (ft3)	Flow Reduction %
5-Jun-14	24.9 (0.98)	1058.2	2853.3	-170%
23-Aug-14	11.7 (0.46)	363.4	72	80%
2-Sep-14	42.2 (1.66)	1051.4	3111.8	-196%
10-Oct-14	92.5 (3.64)	6105.5	3826.3	37%
4-Nov-14	36.1 (1.42)	312.7	3918	-1153%
26-Mar-15	29.2 (1.15)	1182.1	2943.1	-149%
1-Apr-15	17.5 (0.69)	506.4	1859.2	-267%
2-Apr-15	21.8 (0.86)	1012.6	3818	-277%
18-Jun-15	41.4 (1.62)	1015.5	3708.1	-265%
8-Jun-15	63.8 (2.51)	2272.6	857.8	62%
8-Sep-15	42.9 (1.69)	2272.6	857.8	62%

A positive percent reduction indicates flow reduction, while negative percent reduction indicates increase in flow volume.

Table A19. Listing of storm events, rainfall, flow volume, and flow reduction at the Grove High School (GHS) bioretention cell.

Event Date	Precipitation [mm (in)]	Inlet Volume (ft^3)	Underdrain Volume (ft^3)	Volume Reduction %
2-Sep-14	45.0 (1.77)	3884.5	NA	NA
18-Sep-14	19.8 (0.78)	937.6	NA	NA
3-Oct-14	30.2 (1.19)	2384.7	NA	NA
10-Oct-14	80.3 (3.16)	11182.3	NA	NA
4-Nov-14	30.0 (1.18)	807	NA	NA
26-Mar-14	33.3 (1.31)	3483.1	1769.4	49%
1-Apr-15	10.9 (0.43)	976.4	956.9	2%
2-Apr-15	18.0 (0.71)	1348.3	1769.1	-31%
8-May-15	7.9 (0.31)	150.2	480.2	-220%
20-May-15	1.8 (0.07)	340.4	460.3	-35%
29-May-15	20.1 (0.79)	1514.1	468.7	69%
18-Jun-15	36.3 (1.43)	2396.2	1149.9	52%
6-Aug-15	11.4 (0.45)	703.8	98.7	86%
19-Aug-15	13.2 (0.52)	4828.1	1184.3	75%
8-Sep-15	6.4 (0.25)	3859.9	786	80%

A positive percent reduction indicates flow reduction, while negative percent reduction indicates increase in flow volume.

NA = No samples and no flow were recorded due to ISCO auto samplers failure.

VITA

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