IMPROVEMENT OF PHOSPHORUS AND HEAVY METALS RETENTION IN STORMWATER TREATMENT

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CHAPTER I

INTRODUCTION, REVIEW, AND OBJECTIVES

Introduction

Over the past three decades, with the enactment of Clean Water Act (CWA) and the implementation of National Pollutant Discharge Elimination System (NPDES), the United States has made tremendous gain in the control of point source pollution from industries and sewage treatment plants. However, with those reductions non-point source (NPS) pollution has become the Nation's largest impairment source of water quality (USEPA, 1996). According to the National Water Quality Inventory 2000 Report, NPS pollution remains the leading source of impairment (USEPA, 2002).

NPS pollution typically occurs when the runoff from rainfall, snowmelt, or irrigation mobilizes pollutants and transports them to receiving water bodies. NPS pollution by its nature is diffusive and widespread. The National Water Quality Inventory 2000 Report lists agriculture as the leading contributor to the pollution of rivers, streams, and lakes. Urban runoff is the second largest impairment source for estuaries and the third largest pollution source for lakes (USEPA, 2002).

Stormwater runoff degrades water quality by changing the chemistry and hydrology of water bodies. The increased area of impervious surface from urbanization elevates runoff volume and peak flow, which in turn may cause flooding and increase stream erosion. The pollutants in stormwater runoff may also cause water quality problems by altering the chemical composition and aquatic habitat of water bodies. The Nationwide Urban Runoff Program (NURP) study conducted by the EPA indicated that stormwater runoff contains a wide spectrum of pollutants (USEPA, 1983). However, the level of pollutants varies from site to site and event to event. Stormwater runoff from "hot spots" such as parking lots, heavily traveled roads, car washes, and fertilized lawns may have a significant level of pollutants. For example, in an urban highway runoff in Cincinnati, Ohio, the event mean concentration (EMC) of total Zn ranged from 459 to 15,244 μg/L, total Cu from 43 to 325 μg/L, and total Pb from 31 to 97 μg/L (Sansalone and Buchberger, 1997). In a study in Queensland, Australia, the median first flush concentration of pollutants in the runoff from 21 road sites had total Zn from 160 to 1,850 μg/L, total Cu from 30 to 305 μg/L, total Pb from 50 to 575 μg/L, total phosphorus (TP) from 190 to 1,800 μg/L, and TKN from 1,600 to 11,000 μg/L (Drapper et al., 2000). In Wisconsin, the runoff from fertilized lawns had levels of TKN of 8.6 mg/L, TP of 4.02 mg/L, and dissolved phosphorus of 0.93 mg/L (Garn, 2002).

With the recognition of pollution from stormwater, under the amendment of CWA in 1987, CWA section 402(p), NPDES was required to cover the stormwater from municipal separate storm sewer systems (MS4s) serving a population more than 100,000, exposed to industrial activity, or contributing to the violation of water quality standards. Coming in effect on March 2003, the NPDES stormwater regulation final rule extended the coverage to stormwater discharge from smaller MS4s in urbanized area or construction sites disturbing one to five acres. The final rule also required the implementation of nonstructural or structural best management practices (BMPs) to reduce the pollutant loading from stormwater runoff (USEPA, 1999b).

To mitigate the adverse impact of stormwater runoff to water bodies, various structural BMPs have been developed. These practices include detention and infiltration ponds, vegetative filter strips, infiltration trenches, biofiltration swales, and bioretention cells. Bioretention cells are a relatively new technology, which were first developed in the early 1990's by Prince George's County, Department of Environmental Resources (PGDER) in Maryland. By definition, "bioretention is a terrestrial-based (up-land as opposed to wetland), water quality and water quantity control practice using the chemical, biological and physical properties of plants, microbes and soils for removal of pollutants from storm water runoff" (PGDER, 2002). Bioretention cells are a source control BMP because they are usually installed near the runoff source. Stormwater runoff from parking lots, road pavements, and residential areas are directed to bioretention cells for treatment before discharging to the natural water course or storm sewer. This source control practice is generally more cost-effective than the traditional end-pipe control structures (USEPA, 2000). Bioretention cells are particularly suitable to treat the runoff from "hot spots". Because of its design flexibility, appealing landscape aesthetics, and perceived effectiveness for reduction of pollutants, bioretention has gained popularity.

Field and laboratory studies have been undertaken by several researchers to determine pollutant removal of bioretention cells. Bioretention cells could remove heavy metals, oil and grease, and total suspended solids (TSS) almost completely, while the removal of ammonia and nitrate were low, and the production of nitrate was common (Davis et al., 2001, 2003; Hsieh and Davis, 2003, 2005a, 2005b). Kim et al. (2003) investigated the denitrification process in an anoxic zone incorporated in bioretention cells. Their study indicated that a well-designed anoxic zone in bioretention cells may be effective to remove nitrate. The removal of phosphorus was highly variable, and in some cases the production of phosphorus was also noted (Hsieh and Davis, 2003, 2005b; Hunt and Jarrett, 2003). Hunt and Jarrett (2003) asserted that high P-index soils in bioretention cells might contribute to the production of phosphorus. However, it might also be attributed to the low phosphorus retention capacity of the soils placed in bioretention cells. So far little effort has been made to enhance the phosphorus removal of bioretention.

Considering the elevated heavy metals concentration in stormwater runoff from "hot spots", the removal of heavy metals in bioretention cells or other stormwater infiltration systems is important. Soils are usually used as filter media in stormwater BMPs, and transport of heavy metals is associated with their properties (Liu et al., 2005). For example, some sandy soils have a low attenuation capacity of heavy metals (Liu et al., 2005; Zhang et al., 2003). Thus, there is the risk of contamination of receiving water bodies after the filter media is saturated by metals. Actually, in some stormwater infiltration systems, the downward transport of heavy metals occurred due to insufficient heavy metals retention of soils, exposure to high NaCl concentration from de-icing salts, or preferential flow (Mason et al., 1999; Norrström and Jacks, 1998). In a study conducted by Norrström and Jacks (1998), the groundwater 4.5 meter below the surface was found to be polluted by Pb. Therefore, it is important to assure that filter media have adequate heavy metals sorption capacity when designing stormwater infiltration systems.

From the previously referenced research, two specific concerns need to be addressed. First, enhancing the phosphorus removal in bioretention cells is essential.

Second, there is a need to improve the retention of heavy metals. The following review addresses these two subjects in detail.

Phosphorus Removal

Phosphorus is a limiting nutrient in some receiving waters, and accumulation of phosphorus in stagnant surface waters may lead to eutrophication (Correll, 1998). Stormwater runoff can transport a significant load of phosphorus. Lawns and streets were identified as the largest sources of total and dissolved phosphorus (Garn, 2002; Waschbusch et al., 1999). Phosphorus in runoff can be divided into particulate phosphorus and dissolved phosphorus. Particulate phosphorus can be readily removed by settling and infiltration in bioretention cells. Orthophosphate, one major form of dissolved phosphorus, is the only form which can be easily assimilated by plants directly. It is conservative and mobile when infiltrating through some soil media (Mason et al., 1999).

Tremendous effort has been put into phosphorus removal in wastewater treatment. The developed approaches can be categorized as chemical and biological processes. Generally, to accomplish biological phosphorus removal, phosphorus-storing bacteria are encouraged in an anaerobic zone in the presence of the abundant biodegradable soluble COD (bsCOD) followed by an aerobic zone (Tchobanoglous et al., 2003). Apparently, bsCOD is scarce in stormwater runoff. BOD_5 in stormwater runoff was only about 9 mg/L according to the NURP study (USEPA, 1983), which is far below the requirement of biological phosphorus removal process. Therefore, biological phosphorus removal can be excluded from consideration, which leaves chemical processes the only options. Phosphate precipitation has been the main mechanism to remove phosphorus by adding lime, alum, and iron to wastewater (Tchobanoglous et al., 2003). Recent studies indicated that other materials such as activated alumina, layered double hydroxide, and polymeric ligand exchanger are also able to remove phosphorus efficiently through adsorption and ion exchange (Hano et al., 1997; Seida and Nakano, 2002; Zhao and Sengupta, 1998). However, particular attention has been focused on searching for economical sorptive materials. Fly ash, slag, red mud, gas concrete, and cement have been reported to be effective at removing phosphorus (Agyei et al., 2002; Akay et al., 1998; Cheung and Venkitachalam, 2000; Johansson and Gustafsson, 2000; Oguz et al., 2003; Ugurlu and Salman, 1998). Expanded shale also demonstrated good phosphorus removal efficiency (Forbes et al., 2004). These materials are usually complexes of various compounds. The mechanisms of phosphorus removal are the combination of adsorption, ion exchange, and precipitation, which are practically lumped as sorption process.

Cost-effective sorptive materials are particularly needed in stormwater BMPs because stormwater programs are usually budget-constrained. Fly ash is the waste product of burning coal in power plants. Expended shale is a porous material manufactured by firing shale at 2000 °F. Based on the literature, these two materials could possibly be used to improve the phosphorus removal of bioretention cells (Agyei et al., 2002; Cheung and Venkitachalam, 2000; Forbes et al., 2004; Ugurlu and Salman, 1998).

Heavy Metals Retention

As discussed before, high levels of heavy metals exist in the stormwater runoff from "hot spots". Structural BMPs such as infiltration ponds, bioretention cells, and other engineered devices have been developed to remove heavy metals from stormwater runoff (Davis et al., 2003; Mason et al., 1999; Norrström and Jacks, 1998; Sansalone and Buchberger, 1995; Sonstrom et al., 2002). Davis et al. (2003) found that the affinity of heavy metals in a sandy loam soil follows an order of Pb>Cu>Zn. Recently, effort has been made to compare sorption capacity of various filter media for Cu, Cd, Pb, and Zn (Liu et al., 2005).

With the adequate information, it can be assured that the heavy metals sorption capacity of filter media will not be exhausted in the lifetime of system. Fly ash, as a cost-effective material, can effectively remove boron (Polat et al., 2004) and heavy metals such as Cu, Cd, Zn, Cr, Hg, Pb, and Ni (Ayala et al., 1998; Bayat et al., 2002; Banerjee et al., 2003, 2004; Erol et al., 2005). There is a potential to amend soils with fly ash to improve their heavy metals retention capacity.

Hydraulic Conductivity

For bioretention cells or other stormwater infiltration systems, the infiltration capacity of filter media is an important parameter. It is not recommended to leave water in the ponding area of bioretention cells for longer than four days because it restricts the use of water-intolerant plants and encourages the breeding of mosquitoes and other insects (USEPA, 1999a). Saturated hydraulic conductivity is an index of the infiltration capacity of filter media. Hydraulic conductivity consideration should be integrated into the overall design of bioretention cells. The hydraulic conductivity of bioretention media has to be adequate to drain the water in bioretention cells within an appropriate time, for example, four days. Depending on the allowable depth of ponding water, the required hydraulic conductivity of media may vary in bioretention cells. PGDER (2002) recommends that the infiltration rate should be greater than 2.54 cm/hr (1 inch/hr) in a bioretention cell intended for runoff infiltration. The infiltration rate could be directly associated with hydraulic conductivity by the Darcy's law and estimated from hydraulic conductivity and hydraulic gradient. When the hydraulic gradient is equal to one, the infiltration rate is equal to the hydraulic conductivity. Hunt (2003) suggested that the desired range of hydraulic conductivity in bioretention cells is 1.26 cm/hr to 5.04 cm/hr (0.5 to 2.0 in/hr). However, the hydraulic conductivity requirement depends on the design of bioretention cells. If an underdrain is installed at the bottom of the cells to guarantee the adequate drainage, a hydraulic conductivity of 0.42 cm/hr (0.17 in/hr) would drain 30 cm (1 ft) ponding water within 72 hours. Other infiltration systems may have different infiltration rate requirements.

Objectives

This research pursues two objectives. One objective is to find a cost-effective filter media with high phosphorus sorption capacity and adequate hydraulic conductivity to enhance the phosphorus removal in bioretention cells. The second objective is to evaluate the improvement of heavy metals retention of sandy soils by soil amendments.

For improving phosphorus removal, the tasks are:

1) Determine the distribution coefficient of phosphorus in two Oklahoma soils, five other materials, and various soil amendments by batch sorption experiments,

2) Investigate the change in hydraulic conductivity of soil with the addition of fly ash,

3) Determine sorption isotherms and desorption on selected materials,

4) Conduct column flow-through experiments on selected materials to obtain breakthrough curves (BTCs) and fit BTCs with a linear equilibrium convection-dispersion transport model to estimate retardation factor.

For improving heavy metals retention, the tasks are:

1) Determine the distribution coefficient of heavy metals in three Oklahoma soils and fly ash,

2) Conduct column leaching experiments on selected materials to obtain BTCs,

3) Obtain non-eluted metals distribution in the column cores and model transport of heavy metals in the selected materials.

The objectives of this research are addressed in Chapter II and Chapter III. Chapter II investigates the feasibility of improving the phosphorus removal in bioretention cells by amending soils. Chapter III evaluates the enhancement of heavy metals retention by soil amendments.

Future Recommendations

The objectives of this research have been fully accomplished, which are presented in Chapter II and Chapter III. The results provide useful information to improve phosphorus and heavy metals retention when designing bioretention cells or other stormwater infiltration systems. Future studies should focus on the following areas.

1) Pilot bioretention cells with the incorporation of sand/fly ash infiltration layers should be studied. Synthetic stormwater runoff should be applied into the pilot bioretention cells to investigate the removal of pollutants, especially phosphorus and heavy metals, on a multiple-event scale.

2) Field studies should be conducted to evaluate the performance of bioretention cells. Inflow and outflow should be monitored to evaluate the pollutant reduction of bioretention cells.

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CHAPTER II

IMPROVEMENT OF PHOSPHORUS RETENTION BY SOIL AMENDMENT

Abstract

Phosphorus removal in bioretention cells has been highly variable. The objective of this study was to find filter media with high phosphorus sorption and adequate hydraulic conductivity. Batch sorption experiments were conducted to screen filter media. With the incorporation of fly ash, the phosphorus sorption of two Oklahoma soils, Teller loam and Dougherty sand, was increased significantly. Fly ash addition decreased the hydraulic conductivity of the sand exponentially. Maximum sorption capacity predicted by Langmuir isotherms was only 23.8 mg/kg for Dougherty sand, but 385 mg/kg for Dougherty sand with 5% by weight fly ash, and 82.0 mg/kg for expanded shale. Dougherty sand released most sorbed phosphorus while the phosphorus released by the sand/fly ash mixture was negligible. A linear equilibrium convection-dispersion transport model was applied to estimate retardation factors by fitting observed breakthrough curves (BTCs) obtained from column flow-through experiments. The phosphorus BTC of Dougherty sand suggested its retardation factor to be close to one, while retardation factors of Dougherty sand with 2.5% and 5% fly ash, and expanded shale were 199, 470, and 15.7, respectively. The incorporation of a sand/fly ash layer in bioretention cells could improve the phosphorus removal dramatically.

Keywords: Best management practice; Bioretention; Stormwater; Runoff; Phosphorus; Sorption; Hydraulic conductivity; Fly ash; Transport; Retardation

Introduction

According to the National Water Quality Inventory 2000 Report, non-point source (NPS) pollution is responsible for the pollution of 39% of the rivers, 45% of the lakes, and 51% of the estuaries in assessed water bodies in the United States (USEPA, 2002). Urban stormwater runoff, one of the main sources of NPS pollution, is the second largest pollution source for estuaries and the third largest for lakes (USEPA, 2002). Phosphorus (P) has been long recognized as a limiting nutrient in some stagnant surface waters (Correll, 1998). Overenrichment of phosphorus in lakes, reservoirs, and stream backwater may lead to eutrophication. Stormwater runoff, especially the runoff from streets, fertilized lawns, and golf courses, can transport a significant phosphorus load (Garn, 2002; Moss et al., 2006; Waschbusch et al., 1999). In Wisconsin, the runoff from fertilized lawns had total phosphorus of 4 mg/L, and dissolved phosphorus of 0.93 mg/L (Garn, 2002). In Oklahoma, the runoff from golf course fairways had dissolved phosphorus as high as 8 mg/L (Moss et al., 2006). Thus, phosphorus reduction from stormwater runoff may be of significance to protect the quality of recipient water bodies.

Since bioretention cells appeared in the early 1990's as a measure to control the quality and the quantity of stormwater runoff, this stormwater best management practice (BMP) has gained popularity because of its design flexibility, appealing landscape aesthetics, and perceived effectiveness for reduction of pollutants. Field and laboratory studies on pollutant removal of bioretention cells have been undertaken by several researchers (Davis et al., 2001, 2003; Hsieh and Davis, 2003, 2005a, 2005b; Hunt, 2003).

Davis et al. (2003) and Hsieh and Davis (2003, 2005b) reported that bioretention can remove heavy metals, oil and grease, and total suspended solids (TSS) efficiently. However, the removal of phosphorus has been highly variable in the previous research, and in some cases the production of phosphorus was noted (Hsieh and Davis, 2003; Hunt, 2003). Hunt (2003) argued that high P-index soils placed in the cells might contribute to the production of phosphorus. Hsieh and Davis (2005a) evaluated and optimized bioretention media, but the removal of phosphorus, ranging from 4% to 85%, was still variable and not satisfactory. So far little effort has been made to improve the phosphorus removal in bioretention cells.

The primary mechanisms of phosphorus retention in bioretention cells are filtration, biological uptake, and storage in planting soils and filter media (PGDER, 2002). Phosphorus sorption is most often positively related to soil properties such as Al, Fe, and Ca content (Arias et al., 2001; Detenbeck and Brezonik, 1991; Dubus and Becquer, 2001; McDowell and Condron, 2001; Villapando and Graetz, 2001). Therefore, it is possible to improve the phosphorus sorption capacity of soils through amending soils.

Various materials have been used to remove phosphorus through mechanisms such as adsorption, ion exchange, and precipitation in wastewater treatment. Alum, lime, and iron are commonly used in chemical phosphorus precipitation. However, many researchers expressed an interest in finding more economical sorptive materials. Fly ash, expanded shale, slag, red mud, gas concrete, and cement can remove phosphorus effectively (Agyei et al., 2002; Akay et al., 1998; Cheung and Venkitachalam, 2000; Forbes et al., 2004; Johansson and Gustafsson, 2000; Oguz et al., 2003; Ugurlu and Salman, 1998). Fly ash, the waste product of burning coal, is abundant and inexpensive.

Expanded shale, a porous material manufactured by firing shale at 2000 °F, is also readily available but at greater cost. Little research has been undertaken on the applicability of fly ash and expanded shale in the treatment of runoff.

Hydraulic conductivity is another important parameter for filter media in bioretention cells. It is not recommended to leave water in the ponding area of bioretention cells for longer than four days because it restricts the use of water-intolerant plants and encourages the breeding of mosquitoes and other insects (USEPA, 1999). Thus, the hydraulic conductivity of media has to be adequate to drain the water in bioretention cells within four days. Hunt (2003) suggested that the desired range of hydraulic conductivity in bioretention cells is 1.26 cm/hr to 5.04 cm/hr. However, the requirement of hydraulic conductivity depends on the design of bioretention cells. For example, if an underdrain is installed at the bottom of the cells to guarantee a proper drainage, a hydraulic conductivity of 0.42 cm/hr would drain 30 cm ponding water within 72 hours.

The objective of the present research was to find filter media with both high phosphorus sorption capacity and adequate hydraulic conductivity to improve the phosphorus removal in bioretention cells. First, the phosphorus distribution coefficients (K_d) of two Oklahoma soils, Teller loam and Dougherty sand, and other materials, fly ash, peat moss, limestone, and expanded shales were determined through batch sorption experiments to screen filter media. Results revealed the potential of fly ash as a soil additive and expanded shale as a filter medium. The hydraulic conductivity of filter media was measured by a falling head permeameter. Sorption isotherms and desorption experiments were conducted to further characterize the phosphorus sorption and desorption of Dougherty sand, its mixture with fly ash, and expanded shale. To obtain phosphorus breakthrough curves (BTCs), column flow-through experiments were conducted on Dougherty sand, its mixture with 2.5% and 5% by weight fly ash (D+2.5%F and D+5%F), and expanded shale. Phosphorus BTCs were fitted by a linear equilibrium, convection-dispersion transport model to estimate retardation factors. Results were combined to identify the best filter media for the phosphorus removal in bioretention cells.

Materials

Teller loam (Thermic Udic Argiustoll) and Dougherty sand (Thermic Arenic Haplustalf) were collected from field locations in Payne County, Oklahoma. Soil samples were air dried and passed through a 2 mm sieve before use. Fly ash was obtained from the Sooner Power Plant at Red Rock, Oklahoma. The fuel source of the Sooner Power Plant is a sub-bituminous coal from the Power River Basin, Wyoming. Fly ashes from power plants burning different types of fuels may differ in chemical compositions. Table 1 lists the chemical compositions for the fly ash used in this study as determined by X-ray fluorescence (XRF) analyzer (Philips PW-2400) at Activation Laboratories Ltd., Ontario, Canada. The fly ash is class C fly ash with quicklime more than 10%. Limestone was taken from a local aggregate supplier and crushed to pass a 2 mm sieve. Peat moss was commercially obtained from Premier Horticulture Inc., PA and ground to pass a 2 mm sieve. Two expanded shales were obtained from two plants of Buildex Inc., KS, located at Marquette, KS and New Market, MO, and labeled as M-shale and N-shale, respectively. All materials were tested by the Soil, Water and Forage Analytical Laboratory (SWFAL) in the Department of Plant and Soil Sciences, Oklahoma

State University in accordance with the procedures of ASA and SSSA (ASA and SSSA, 1986; SSSA and ASA, 1996). Teller loam contains 52% sand, 31% silt, and 17% clay. Dougherty sand has 98% sand and 2% silt plus clay. Other relevant properties of materials are presented in Table 2.

Methods

Distribution Coefficients and Removal Efficiency

Two grams of sorbent were placed in 50 mL polypropylene centrifuge tubes with 40 mL solution containing 1 mg/L P as sodium phosphate ($Na_3PO_4·12H_2O$) (0.05 solid/water ratio). Solution ionic strength was fixed with 0.01 mol/L potassium chloride (KCl). The tubes were shaken on a rotary agitator at 30 RPM and 23±2 °C for 24 hrs. Then the suspensions were centrifuged and the pH measured. The supernatants were filtered through a 0.45 μm Glass/Nylon filter, acidified, and then analyzed for phosphorus by ICP-AES. Phosphorus distribution coefficients (K_d) (ASTM, 2004) and removal efficiency (P removal, %) were calculated as:

$$K_d = \frac{(C_0 - C)V}{M_s C} \qquad (1)$$

$$\text{P removal, \%} = 100(C_0 - C)/C_0 \qquad (2)$$

where K_d (mL/g) is distribution coefficient, C_0 (mg/L) is the initial phosphorus concentration in the blank, C (mg/L) is the equilibrium phosphorus concentration in the solution, V (mL) is the volume of solution, and M_s (g) is the mass of sorbent.

The pH effect on phosphorus sorption of fly ash was investigated to better understand the underlying sorption mechanisms of fly ash. The pH of a series of fly ash sorption suspensions was varied by concentrated sulfuric acid (H_2SO_4). Following the same protocol mentioned above, phosphorus K_d and removal efficiency of the fly ash under a wide pH range were measured. Phosphorus K_d and removal efficiency were also determined for the mixtures of Teller loam or Dougherty sand with various levels of fly ash to examine the effect of fly ash addition on phosphorus sorption of soils.

Hydraulic Conductivity

A falling head permeameter (McWhorter and Sunada, 1977) was used to determine the saturated hydraulic conductivity (K_s) of Teller loam, Dougherty sand, expanded shale, and the mixtures of Dougherty sand with various levels of fly ash. A 4.0 cm inner diameter and 15 cm long acrylic column was packed with each material. Average bulk density was 1.28 g/cm^3 for Teller loam, 1.50 g/cm^3 for Dougherty sand, 0.87 g/cm^3 for expanded shale, and 1.58 to 1.73 g/cm^3 for the Dougherty sand/fly ash mixtures. The column was connected to a glass tubing reservoir containing 0.01 mol/L calcium sulfate ($CaSO_4$) solution. Water flowed upward through the column, and the hydraulic gradient ranged from 2.03 m/m to 3.79 m/m.

Due to the pozzolanic nature of fly ash and hydration reactions, the hydraulic conductivity of the sand/fly ash mixtures may decrease with extended saturation period. To assess the effect of saturation period on the hydraulic conductivity of the sand/fly ash mixtures, Dougherty sand, D+2.5%F, and D+5%F were kept in saturation in the testing columns for 28 days and the hydraulic conductivity measured periodically. Dougherty sand was examined for comparison in this case.

Sorption Isotherm and Desorption

Two grams of Dougherty sand, D+5%F, and M-shale were placed into 50 mL polypropylene centrifuge tubes. Forty mL 0.01 mol/L KCl solution containing 1, 3, 6, or 11 mg/L P was added to each Dougherty sand and M-shale sample, while 3, 6, 11, or 29 mg/L P was added to each D+5%F sample. The sorption procedure was the same to the aforementioned procedure. Data were fitted to the linear form of Langmuir equation by a linear regression and Freundlich equation by a nonlinear regression. The isotherm equations are:

$$\frac{C}{S} = \frac{C}{S_m} + \frac{1}{S_m b} \tag{3}$$

$$S = K_f C^n \tag{4}$$

where S (mg/kg) is the amount of phosphorus sorbed per unit mass, and S_m, b, K_f, and n are adjustable parameters.

Langmuir and Freundlich equations have been commonly used to evaluate the phosphorus sorption capacity of materials (Arias et al., 2001; Dubus and Becquer, 2001; Forbes et al., 2004; McDowell and Condron, 2001; Vallapando and Graetz, 2001). In the Langmuir equation, S_m represents the maximum sorption capacity of materials, and b is an empirical constant related to the sorption energy. In the Freundlich equation, the distribution coefficient (K_f) provides a measure of sorption capacity.

Desorption describes the tendency of materials releasing sorbed phosphorus under diluted concentrations. Phosphorus desorption experiments were conducted on these three materials following the sorption experiments. Initial phosphorus concentration was extended to 114 mg/L for D+5%F. After removing the previous solution from the tubes 20 mL 0.01 mol/L KCl solution free of P was added. The tubes were shaken thoroughly to disperse the sorbent and placed on the rotary agitator for another 24 hr at 23 ± 2 °C. Then the same procedures of separation and analysis used in the sorption experiment were conducted.

Column Flow-through Experiments and Transport Modeling

Dougherty sand, D+2.5%F, D+5%F and M-shale were packed into acrylic columns with 14.4 cm inner diameter and 14.3 cm long. Influent containing 1 mg/L P in deionized water passed upward through the columns with a loading rate of 3 cm/hr. Influent and effluent samples were collected periodically, and their pH was measured. Effluent samples were turbid in the early period of experiments for Dougherty sand and M-shale. Those samples were centrifuged to remove suspended particles. The test on Dougherty sand lasted 13 days and produced about 150 L of effluent. Other experiments lasted three weeks, and approximately 240 L of effluent was produced. All samples were acidified and analyzed for phosphorus by ICP-AES.

At each sampling point, the normalized concentration (C_e/C_i, C_e is the effluent concentration and C_i is the influent concentration) and the number of pore volume were calculated, and the BTCs were constructed. Phosphorus transport modeling was conducted by fitting BTCs using a one-dimensional linear equilibrium convection-dispersion transport model in CXTFIT 2.1 in the STANMOD software package (Simunek et al., Riverside, California), which was developed for evaluating solute transport in porous media using analytical solutions of the convection-dispersion equation by the U.S. Salinity Laboratory. It was assumed that there was no phosphorus production or decay. Retardation factors (R) and hydrodynamic dispersion coefficients (D) were estimated under the third-type inlet boundary and step input conditions. Column characteristics and modeling parameters are presented in Table 4.

Results and Discussion

Distribution Coefficients and Removal Efficiency

Measured phosphorus distribution coefficient (K_d) is summarized in Table 2. Fly ash had a phosphorus K_d an order of magnitude greater than expanded shale from Marquette, KS (M-shale) and three orders of magnitude greater than Dougherty sand. Therefore, for the materials studied fly ash was identified as a better additive to amend soils. It is interesting that expanded shales from two locations exhibited significantly different sorption capacity. The difference may be a result of the variation of physicochemical properties of expanded shales. Expanded shale from New Market, MO (N-shale) was excluded from the further experiments. M-shale, with the second highest phosphorus K_d, was also examined in the sorption isotherm, desorption, and column flow-through experiments. However, shale was not investigated as a soil additive.

As shown in Figure 1, the pH of sorption suspensions had an obvious effect on the phosphorus sorption of fly ash. Under the higher pH range, fly ash exhibited a high phosphorus sorption predominantly due to calcium phosphate precipitation (Evangelou, 1998). Fly ash in this study has 14,300 mg/kg exchangeable Ca (Table 2), which is at least one order of magnitude higher than that of the two soils. Calcium can dissolve from fly ash and form calcium phosphate precipitates (Agyei et al., 2002; Cheung and Venkitachalam, 2000; Ugurlu and Salman, 1998). Using X-ray diffraction Ugurlu and Salman (1998) directly observed the formation of calcium phosphate precipitate in the fly ash sample in a phosphorus column sorption experiment.

In Figure 1, when the pH decreased, the phosphorus sorption of fly ash dropped, reaching the low point at the pH of 8.6 with K_d of 42 mL/g and removal efficiency of

67.5%. Apparently, lowering pH greatly decreased the formation of calcium phosphate precipitates. However, as the pH continued to decrease, the phosphorus sorption increased again to reach a K_d of 931 mL/g and removal efficiency of 97.9% at pH of 5.2. This phenomenon indicated the contribution of Al and Fe compounds to phosphorus removal. Fly ash in this study contains 18.4% Al_2O_3 and 5.93% F_2O_3. Phosphate can either form oxide-phosphate complex or precipitate with Fe and Al ions under the slightly acidic pH range (Evangelou, 1998). Al and Fe oxide-rich soils actually demonstrated a very high phosphorus sorption capacity with Langmuir maximum sorption capacity ranging from 6,400 to 9,250 mg P/kg (Dubus and Becquer, 2001). A number of other studies also concluded the positive correlation between phosphorus sorption and Al and Fe content in a variety of soils (Detenbeck and Brezonik, 1991; McDowell and Condron, 2001; Villapando and Graetz, 2001).

When the pH shifted to the lower pH range, the phosphorus sorption decreased again (Figure 1). At the pH of 3.5, the extractable P of fly ash was released, which caused the negative values of K_d as -10.3 mL/g and removal efficiency as -106%. The reason might be the competitive interactions between metal cations and hydrogen ion. This observed pH-dependence of phosphorus sorption agrees with a number of other studies. Arias et al. (2001) believed that Ca content precipitates phosphate at the slightly alkaline conditions while Al and Fe contents are more important as the phosphate-fixing agents under the acidic conditions. Bastin et al. (1999) observed that phosphorus sorption of a synthetic iron oxide-gypsum compound remained unaltered at the pH values between 4 and 8, but increased significantly with the higher pH values such as 9.5 and 10. They argued that calcium phosphate precipitation occurred under the higher pH range resulted in this interesting phenomenon. Detenbeck and Brezonik (1991) found that the phosphorus removal was increased significantly when the pH was changed from 6.0 to 4.5 for sedimentary soils, which is similar to the trend in Figure 1. Overall, fly ash had high phosphorus sorption under a wide range of pH. At a pH range above 4.0, the minimum K_d and removal efficiency was 42 mL/g and 67.5%, respectively, which was still much higher than those of soils.

The addition of fly ash increased the phosphorus sorption of soils dramatically (Figure 2). With the addition of 5% fly ash, the K_d of Teller loam and Dougherty sand were elevated from 0.41 mL/g and 2.08 mL/g to 49.3 mL/g and 398 mL/g, and P removal increased from 2.0% and 9.4% to 71.4% and 94.2%, respectively. It was also noted that the change of phosphorus sorption of Dougherty sand was more significant than Teller loam. The reason for this phenomenon was not understood clearly. It might be attributed to the higher extractable P in Teller loam (Table 2), which is 71 mg/kg and four folds higher than Dougherty sand and fly ash. If this characteristic is similar to other sands, it would favor sand/fly ash mixtures in bioretention cells.

Hydraulic Conductivity

The hydraulic conductivity (K_s) of Teller loam, Dougherty sand, and M-shale was 0.30 cm/hr, 34 cm/hr, and 39 cm/hr, respectively. Fly ash had an extremely low hydraulic conductivity, which could not be measured by the procedure used. Due to its low hydraulic conductivity, Teller loam is not appropriate to be used in bioretention cells or amended with fly ash. The hydraulic conductivity of Dougherty sand and its mixtures with various levels of fly ash are presented in Figure 3. The hydraulic conductivity dropped exponentially with increasing fly ash content. To keep the hydraulic conductivity of amended soils higher than 2.54 cm/hr, the incorporation rate of fly ash should be less than 6% calculated from the exponential relationship (Figure 3). Thus, D+2.5%F and D+5%F were selected for further experiments, but only D+5%F was investigated in sorption isotherm and desorption experiments along with Dougherty sand and M-shale.

The change of hydraulic conductivity over extended saturation period for Dougherty sand, D+2.5%F, and D+5%F is shown in Figure 4. The trends were totally different for Dougherty sand and the sand/fly ash mixtures. Hydraulic conductivity of Dougherty sand dropped slightly first, and then recovered to the previous level. However, the hydraulic conductivity of D+2.5%F and D+5%F decreased rapidly at the first 24 hours, and then was stabilized after 14 days. Because of the pozzolanic reactions occurred in the water-saturated sand/fly ash mixtures, the permeability of D+2.5%F and D+5%F was decreased. The stabilization of hydraulic conductivity after 14 days indicated the end of the pozzolanic reactions. At the end of 28-day experiments, the hydraulic conductivity of D+2.5%F and D+5%F was 5.50 cm/hr and 0.91 cm/hr. This characteristic of the sand/fly ash mixtures implies that their 4-day or 7-day hydraulic conductivity should be evaluated to ensure the adequate infiltration. With the final hydraulic conductivity of 0.91 cm/hr, D+5%F still possesses an adequate hydraulic conductivity to drain 30 cm ponding water within 33 hours.

Sorption Isotherm and Desorption

Sorption data for Dougherty sand, D+5%F, and M-shale fitted both Langmuir and Freundlich equations well (r^2>0.914). The fitted isotherms are shown in Figure 5 and the fitted parameters in Table 3. Dougherty sand with 5% fly ash had the highest Langmuir maximum sorption capacity (S_m) and Freundlich distribution coefficient (K_f), which were 385 mg/kg, and 203 L/kg, respectively (Table 3). Expanded shale also showed a degree of phosphorus sorption capacity with S_m of 82.0 mg/kg, and K_f of 52.9 L/kg. By comparing the observed sorption and the predicted sorption by Langmuir and Freundlich equations in Figure 6, it was noted that Freundlich equation fitted the observed sorption of D+5%F better than Langmuir equation.

The results of desorption are shown in Figure 7. Shale desorbed a small amount of sorbed phosphorus averaging 6.7% of the initially sorbed phosphorus. Dougherty sand with 5% fly ash released negligible phosphorus. However, Dougherty sand released a large amount of phosphorus averaging 42% of the initially sorbed phosphorus, which means that Dougherty sand cannot provide long-term phosphorus storage, and the sorbed phosphorus will be desorbed to water flow with low phosphorus concentration. Forbes et al. (2004) also reported that Mason sand has little phosphorus storage capacity comparing with expanded shale. It was noted that even when the phosphorus initial concentration was up to 114 mg/L, D+5%F still released a negligible amount of the sorbed phosphorus. Thus, the phosphorus sorption in D+5%F may be irreversible, and D+5%F can provide long-term phosphorus retention. M-shale can also exert a smaller, but significant long-term phosphorus retention.

Column Flow-through Experiments and Transport Modeling

In the column experiments, the mean influent pH was 6.7, and the mean effluent pH for Dougherty sand, D+2.5%F, D+5%F, and shale were 6.5, 9.8, 10.3, and 6.7, respectively. Total mass of input and output phosphorus are summarized in Table 4. Dougherty sand had little phosphorus retention with only 2% mass removal. Adding

2.5% and 5% fly ash in Dougherty sand increased the mass removal to 66% and 85%, respectively. Expanded shale exerted 40% mass removal. Overall, a Dougherty sand/fly ash mixture retained a large fraction of input phosphorus under continuous flow loading for more than 300 pore volumes. Breakthrough curves of phosphorus are presented in Figure 8. A phosphorus flush was observed in Dougherty sand column, but no phosphorus flush in D+2.5%F, D+5%F, and shale columns. In the BTC of the Dougherty sand column, the phosphorus flush only occurred during the approximately first 10 pore volumes, and then the phosphorus effluent concentration dropped back close to the influent concentration. Therefore, the amount of this additional phosphorus was negligible. The initial phosphorus flush may be an artifact of the test procedure. When packing the column, the material was wetted with 9% by weight deionized water to achieve a better packing. Because Dougherty sand contains 14 mg/kg extractable P (Table 2), the extractable P could be released into the pore water and eluted to form the initial peak. The phosphorus sorption capacity of D+2.5%F, D+5%F, and M-shale are high, thus phosphorus was bound tightly with sorbing sites, and not released into the pore water. From the observed P BTCs, Dougherty sand was broken through immediately. D+2.5% and D+5% columns were not exhausted after 300 pore volumes, and the final C_e/C_i was 0.76, and 0.24, respectively. The expanded shale column was not exhausted after 150 PV, and the final C_e/C_i was 0.74. It was also noted that the actual BTCs leveled off for D+2.5%, D+5%, and expanded shale near the end of the experiments. These leveled-off BTCs may imply a long-term phosphorus sorption. Phosphorus sorption is generally characterized with a rapid short-term sorption followed by a slower long-term sorption (Barrow, 1985). Cheung and Venkitachalam (2001) found that fly ash can exert a steady phosphorus removal over a longer period. Forbes et al. (2004) reported that shale has a sustained ability of phosphorus retention. Thus, the long-term phosphorus sorption may prevent the Dougherty sand/fly ash mixtures and expanded shale from exhibiting a normal breakthrough. In short, it is apparent that D+5% removed phosphorus more efficiently than any other materials.

The transport model CXTFIT 2.1 could not fit the BTC in the Dougherty sand column. Judging from the actual BTC, there was no retardation of phosphorus in Dougherty sand. Thus, phosphorus retardation factor of Dougherty sand was assumed to be 1. The transport model fitted the BTCs of D+2.5%, D+5% and shale columns very well with a highest mean square error (*MSE*) of 0.005592 (Table 4). With the addition of 2.5% and 5% fly ash in Dougherty sand, retardation factors (*R*) were increased to 199 and 470, respectively. And the retardation factor of shale was 15.7.

A comparison was made between distribution coefficients from column experiments and those from batch sorption experiments (Table 4). The batch sorption resulted in much higher K_d. The discrepancy may be explained by the difference in hydrological condition (batch reactor versus continuous flow), and solid/water contact time. Sorption is mainly dependent on solid/water ratio and solid/water contact time. Although the solid/water ratio was increased in the column experiments, the solid/water contact time was decreased greatly. The residence time of water in the columns ranged from 1.5 hours to 3.2 hours (Table 4), far below 24 hours. The lower K_d in the column experiments indicated that the adverse effect of reducing contact time overweighed the positive effect of increasing solid/water ratio. The difference for expanded shale appeared more significant than others, which may be the result of dual porosity factors.

Estimation of Treatment Capacity and Lifetime

Dougherty sand amended with fly ash appeared to be a better filter media. Dougherty sand with 5% fly ash exhibited both high phosphorus retention and adequate hydraulic conductivity. Using the phosphorus sorption and transport information determined from the batch and column experiments, estimates of treatment capacity of filter media can be made. Two approaches were used to estimate the treatment capacity of filter media based on the dynamic transport modeling or the equilibrium batch sorption.

With the estimated transport parameters, the treatment capacity of any depth of filter media in bioretention cells for various runoff and phosphorus loadings can be determined by simulating BTCs in the transport model. The pore volumes when an arbitrary point, usually the treatment goal, is broken through can be read from the simulated BTCs. Then the treatment capacity in terms of treated runoff volume per unit bioretention area is:

$$D_B = N \cdot L \cdot \theta \tag{5}$$

where D_B (m) is the depth of runoff which can be treated by filter media with L (m) deep, L (m) is the depth of filter media, N is the number of pore volumes at the breakthrough point, and θ is the porosity of filter media.

The treatment capacity of 1 meter deep D+5%F infiltration layer receiving runoff with 1 mg/L P and 3 cm/hr loading rate was estimated (Table 5). The breakthrough point was selected as 0.037 mg/L, the water quality criteria for scenic rivers in Oklahoma (OWRB, 2004). This procedure is conservative because of assuming a reversible sorption process in the transport modeling. However, phosphorus sorption is more likely to be irreversible. An irreversible process retains more phosphorus. Moreover, the actual flow in the field is not continuous but intermittent with the intervals of dry period without rainfall. During the dry period, the Dougherty sand/fly ash mixture may continue to take up phosphorus from the pore water. The phosphorus adsorbed on the surface may transfuse into the interior of the particle. And the phosphate precipitates could be transformed to the more stable crystalline precipitates (Forbes et al., 2004). These possible phenomena could probably further reduce the actual effluent concentration. Thus, the procedure based on a reversible sorption process underestimated the treatment capacity of D+5%F.

The treatment capacity of filter media can also be estimated if assuming a batch sorption occurred in bioretention cells. As mentioned early in the isotherm section, Freundlich isotherm fitted the sorption of D+5%F better. Assuming a batch sorption in equilibrium and using Freundlich equation to predict the sorbed phosphorus at the equilibrium concentration (C), the treatment capacity of filter media can be determined as:

$$D_B = \frac{K_f C^n \rho L}{C_0 - C} \qquad (6)$$

where ρ (g/cm^3) is bulk density of filter media.

Again the treatment capacity of 1 meter deep D+5%F was estimated for runoff with 1 mg/L initial concentration (C_0) and 0.037 mg/L equilibrium concentration (C). The result is listed in Table 5. This procedure considered the irreversible sorption, but might overestimate the treatment capacity due to increased solid/water contact time.

Bioretention cells are designed to capture the first 12.7 mm (0.5 inch) runoff and the runoff beyond the first 0.5 inch is bypassed. Based on the rational formula (Davis et al., 2001) and the historical daily precipitation data, the annual runoff depth (D_R) loaded to bioretention cells is estimated as:

$$D_R = \frac{\sum Min(c \cdot R, 12.7)}{1000mf} \qquad (7)$$

where D_R (m) is runoff volume per unit bioretention area, c is a runoff coefficient for different land uses, R (mm) is daily rainfall depth, m is the number of years of daily precipitation record, f is ratio of bioretention area to drainage area, and 1000 is an unit conversion factor.

Fifty years of daily precipitation data (1/1/1950-12/31/1999) for Grove, OK (Storm et al., 2001) from the Cooperative Observer Network of the National Oceanic & Atmospheric Administration (NOAA) were used. Pavements and lawns were taken as two extreme urban land uses. The filter media will bear the severest or lowest runoff loading when receiving runoff from pavements or lawns, respectively. Assuming f is 0.05, and c is 0.82 or 0.20 for pavements or lawns (Haan et al., 1994), the annual runoff loading depth from pavements and lawns is 11.8 m and 4.3 m, respectively. The lifetime of D+5%F was then computed as D_B/D_R (Table 5). For bioretention cells receiving runoff from pavements, the effluent phosphorus concentration will be below 0.037 mg/L from 4 to 12 years. For bioretention cells receiving runoff from lawns, the effluent concentration will be below 0.037 mg/L from 11 to 34 years. Moreover, the filter media could still remove phosphorus over a much longer period after the effluent phosphorus concentration exceeds 0.037 mg/L.

Conclusions

The phosphorus removal of bioretention cells has been highly variable due to the diverse properties of soils. Soil amendments with fly ash improved the phosphorus sorption of soils. However, the addition of fly ash decreased the hydraulic conductivity of Dougherty sand exponentially. Dougherty sand with 5% fly ash exhibited high phosphorus sorption and adequate hydraulic conductivity. Column flow-through experiments and phosphorus transport modeling indicated that the mixture of Dougherty sand and fly ash was more efficient to remove phosphorus than Dougherty sand and expanded shale. In a hypothetical scenario, the sand/fly ash infiltration layer provides a satisfactory phosphorus removal over a long period. The incorporation of sand/fly ash infiltration layer in bioretention cells is expected to enhance the phosphorus retention. However, pilot and field studies are still needed to evaluate the performance of this kind of bioretention cells.

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Table 1. Chemical compositions of fly ash.

Composition	Content, %
SiO_2	38.1
Al_2O_3	18.4
Fe_2O_3	5.93
MnO	0.02
MgO	5.43
CaO	22.9
Na_2O	1.82
K_2O	0.56
Ti_2O	1.39
P_2O_5	1.37
BaO	0.69
Cr_2O_3	0.01
SrO	0.30
LOI [A]	0.69
Total	97.6

[A] LOI: Loss of ignition

Table 2. Relevant properties of soils and other materials.

Materials	pH [A]	CEC [B], meq/100g	Exchangeable Ca [C], mg/kg	Extractable P [D], mg/kg	K_d, mL/g
Teller loam	6.2	~ 9	1140	71	0.41
Dougherty sand	6.3	~ 1	148	14	2.08
Fly ash	11.5	~ 78	14300	13	2180
Limestone	9.0	~ 4	457	6.7	12.1
Peat moss	2.9	~ 7	821	23	-5.79 [E]
M-shale	6.4	~ 10	1180	32	280
N-shale	8.6	~ 1	192	18	1.21

[A] pH was measured in batch sorption experiments

[B] CEC was determined by summing the amount of exchangeable Ca, Mg, K, Na, and Al displaced by ammonium acetate (SSSA and ASA, 1996)

[C] Exchangeable Ca was displaced by ammonium acetate and determined by ICP-AES (Spectro CIROS^{CCD})

[D] Extractable Mehlich3 P was determined by the ascorbic acid method (LACHAT, Qiuckchem 8000)

[E] Negative K_d indicated the phosphorus production

Table 3. Estimated isotherm parameters for Dougherty sand, D+5%F, and expanded shale.

	Langmuir			Freundlich		
	S_m, mg/kg	b, L/mg	r^2	K_f, L/kg	n	r^2
Dougherty sand	23.8	0.278	0.948	4.93	0.622	0.914
D+5%F	385	2.89	0.998	203	0.295	0.985
M-shale	82.0	3.30	0.997	52.9	0.254	0.986

Table 4. Parameters and results of phosphorus column experiments and transport modeling for Dougherty sand, D+2.5%F, D+5%F, and M-shale.

	Dougherty sand	D+2.5%F	D+5%F	M-shale
Influent pH	6.7	6.7	6.7	6.7
Effluent pH	6.5	9.8	10.3	6.7
P input from the influent, mg	141	240	236	249
P output in the effluent, mg	138	82.4	35.2	149
Mass removal, %	2	66	85	40
Bulk density (ρ), g/cm^3	1.55	1.76	1.82	0.92
Porosity (θ)	0.415	0.336	0.312	0.653
Pore-water velocity (v), cm/hr	7.14	8.70	9.41	4.53
Residence time ^{A}, hr	2.0	1.6	1.5	3.2
Solid/water ratio ^{B}	3.7	5.2	5.8	1.4
Hydraulic dispersion coefficient (D), cm^2/hr	--	43.4	249	404
Retardation factor (R)	1 ^{C}	199	470	15.7
MSE	--	0.001273	0.005592	0.001356
K_d ^{D} from column experiments	0	37.8	80.4	10.4
K_d from batch sorption	2.08	307	398	280

^{A} Calculated by dividing the length of column by pore-water velocity

^{B} Estimated from the relationship of $2.65(1-\theta)/\theta$

^{C} Estimated from the actual BCT assuming negligible retardation indicates a retardation factor of 1

^{D} Calculated based on the relationship of retardation factor and distribution coefficient for a linear equilibrium transport model ($R = 1 + K_d \cdot \rho/\theta$)

Table 5. Estimation of treatment capacity and lifetime for Dougherty sand with 5% fly ash (filter media depth: 1 m; runoff loading rate: 3 cm/hr; inflow phosphorus concentration: 1 mg/L; effluent concentration: 0.037 mg/L).

	Treatment capacity (D_B), m^3/m^2	Lifetime [C], yr	
		Pavements	Lawns
Transport Approach [A]	50	4	11
Batch Approach [B]	145	12	34

[A] Estimation was conservative and based on the reversible sorption process

[B] Estimation was liberal and based on the Freundlich batch sorption isotherm

[C] Based on the 50-year historical daily precipitation data in Grove, OK, where bioretention cells are located in the hypothetical scenario

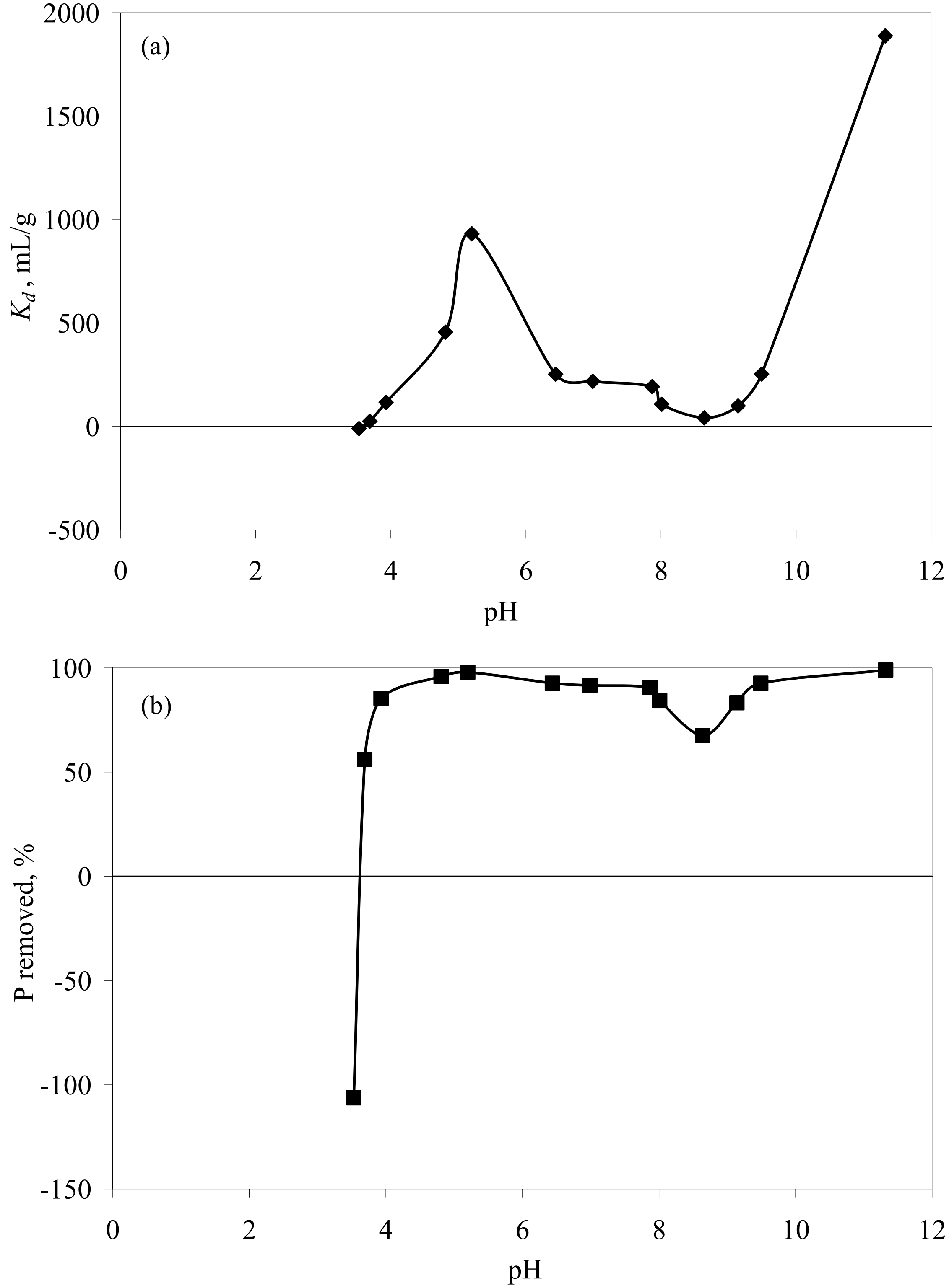

Figure 1. Effect of pH on phosphorus sorption of fly ash in terms of (a) distribution coefficient (mL/g) and (b) Removal efficiency (%).

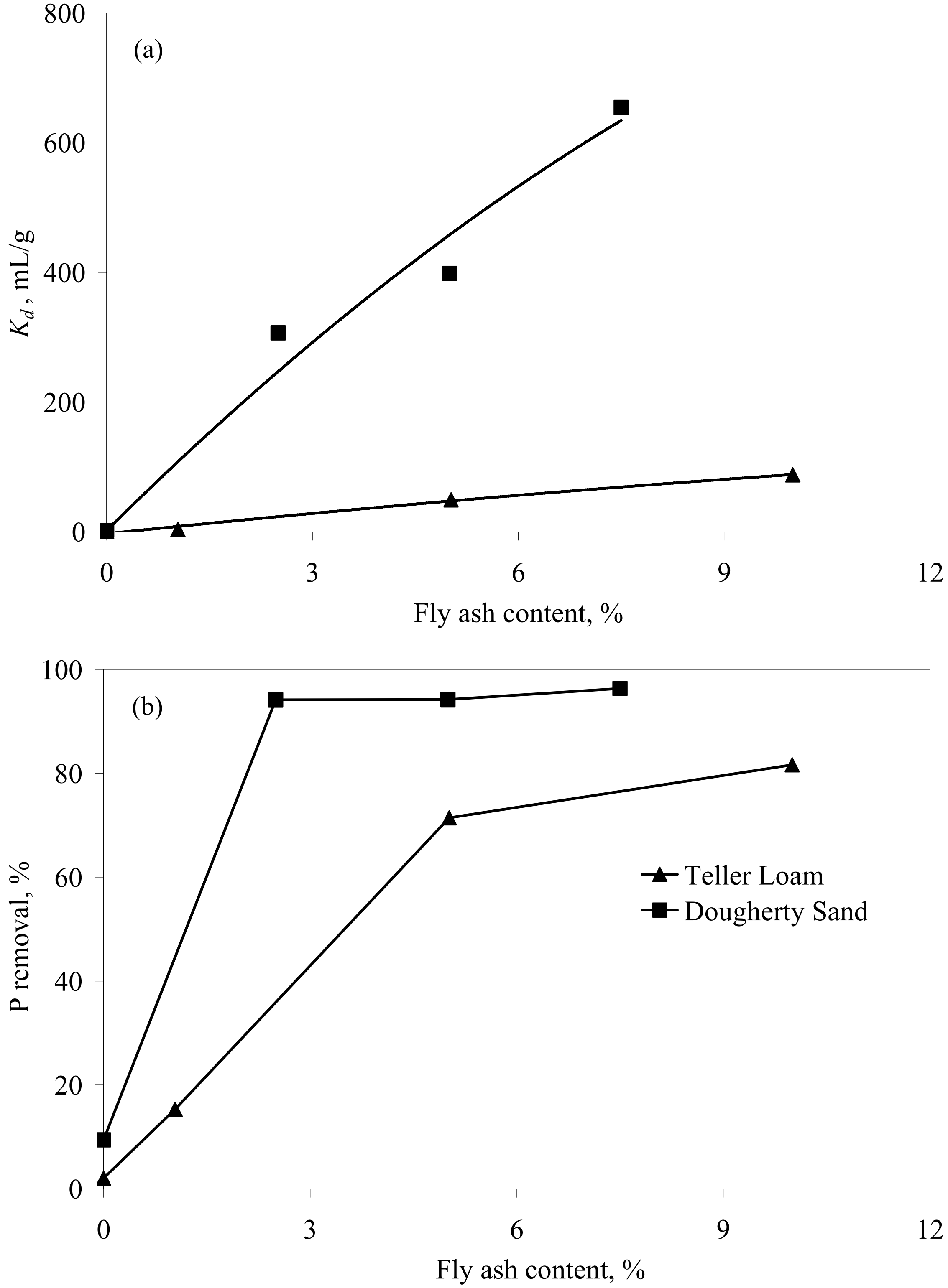

Figure 2. Effect of the fly ash addition on phosphorus sorption of soils in terms of (a) distribution coefficient (mL/g) and (b) Removal efficiency (%).

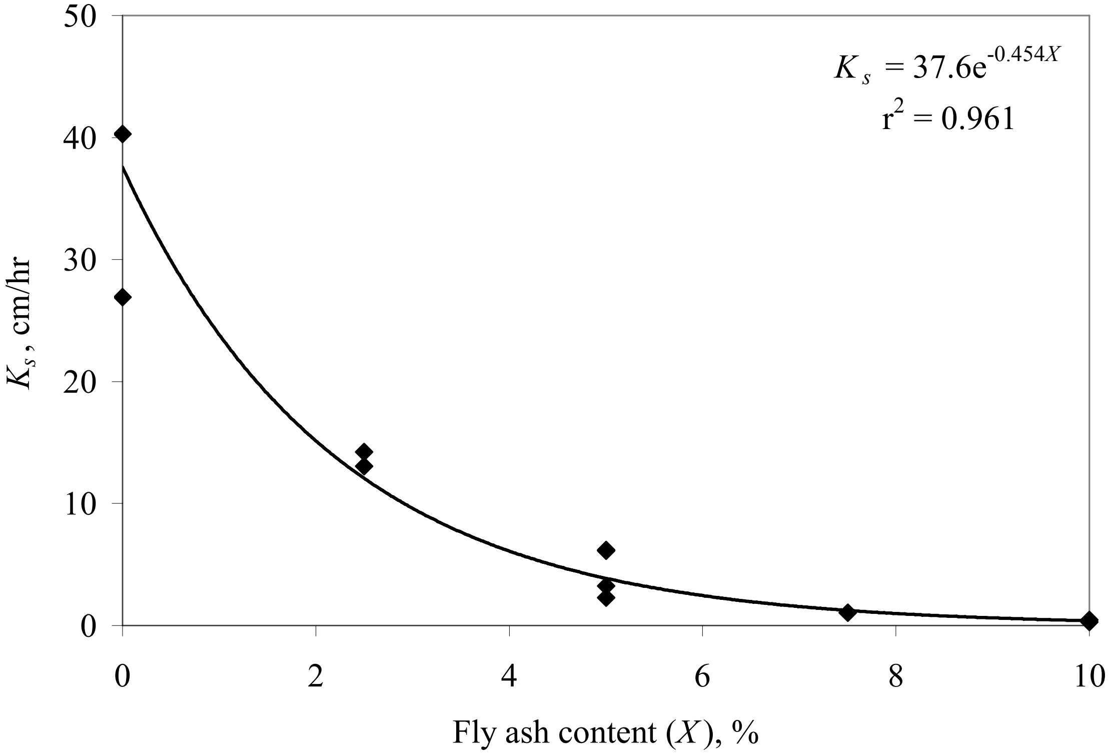

Figure 3. Effect of the fly ash addition on saturated hydraulic conductivity of Dougherty sand.

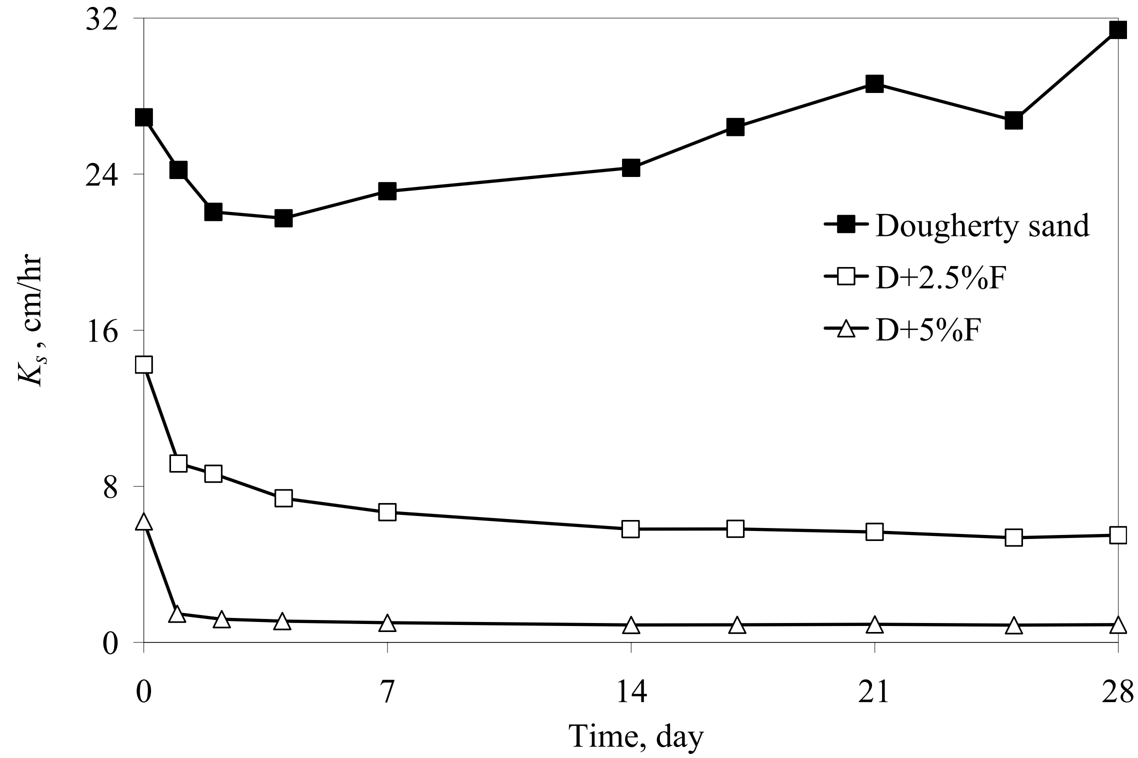

Figure 4. Effect of extended saturation period on saturated hydraulic conductivity of Dougherty sand, D+2.5%F, and D+5%F.

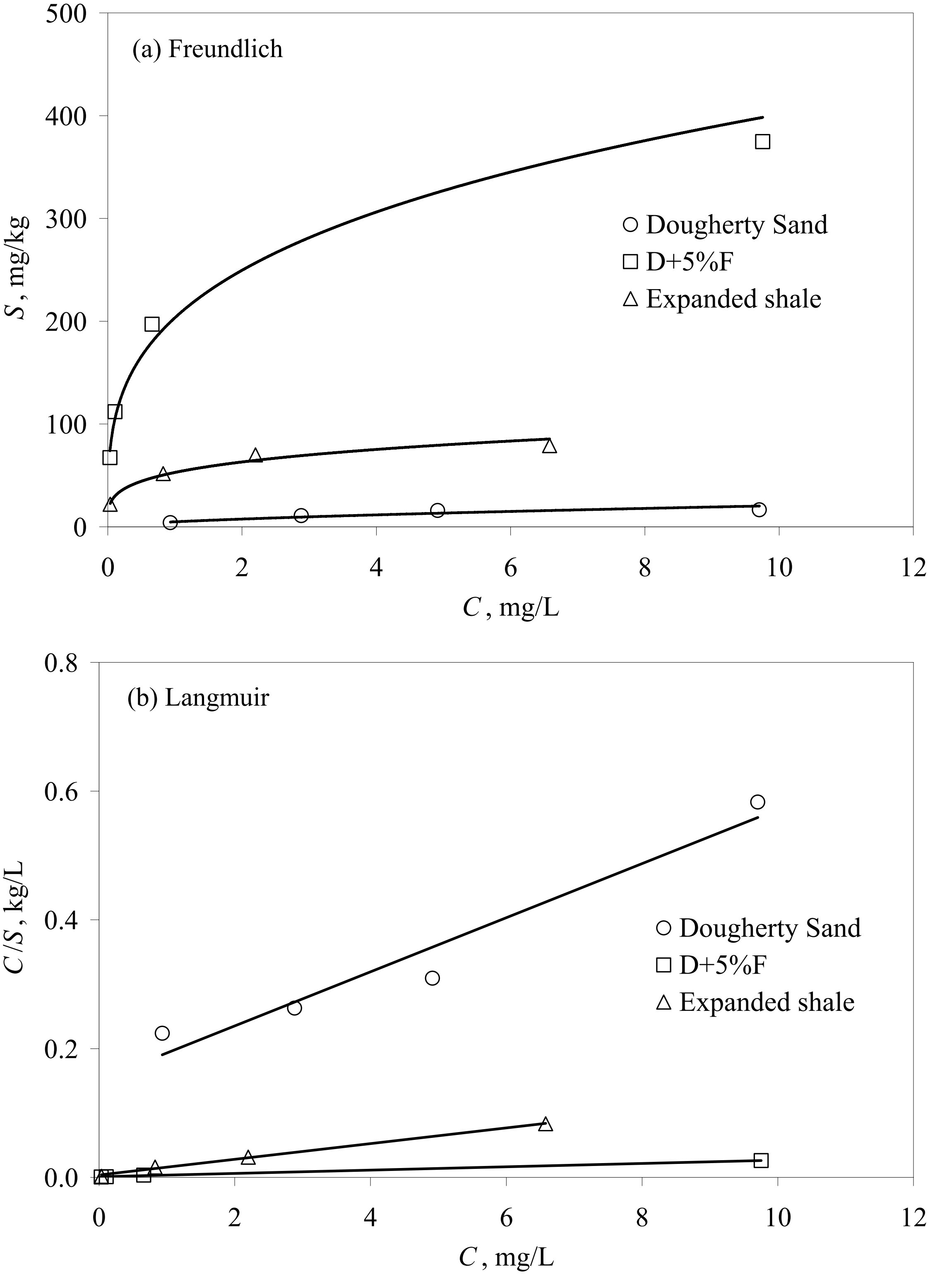

Figure 5. Sorption isotherms of Dougherty sand, D+5%F and expanded shale from KS (M-shale) (a) Freundlich and (b) Langmuir.

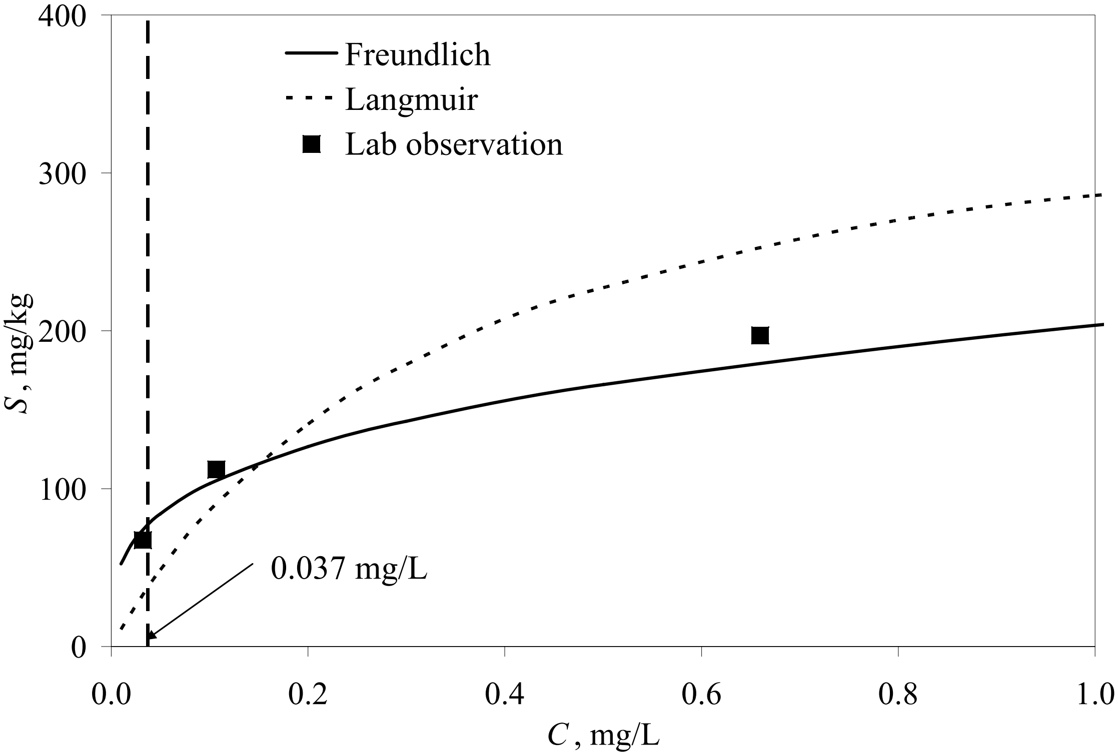

Figure 6. Observed and predicted phosphorus sorption of D+5%F for equilibrium phosphorus concentrations (*C*) under 1 mg/L.

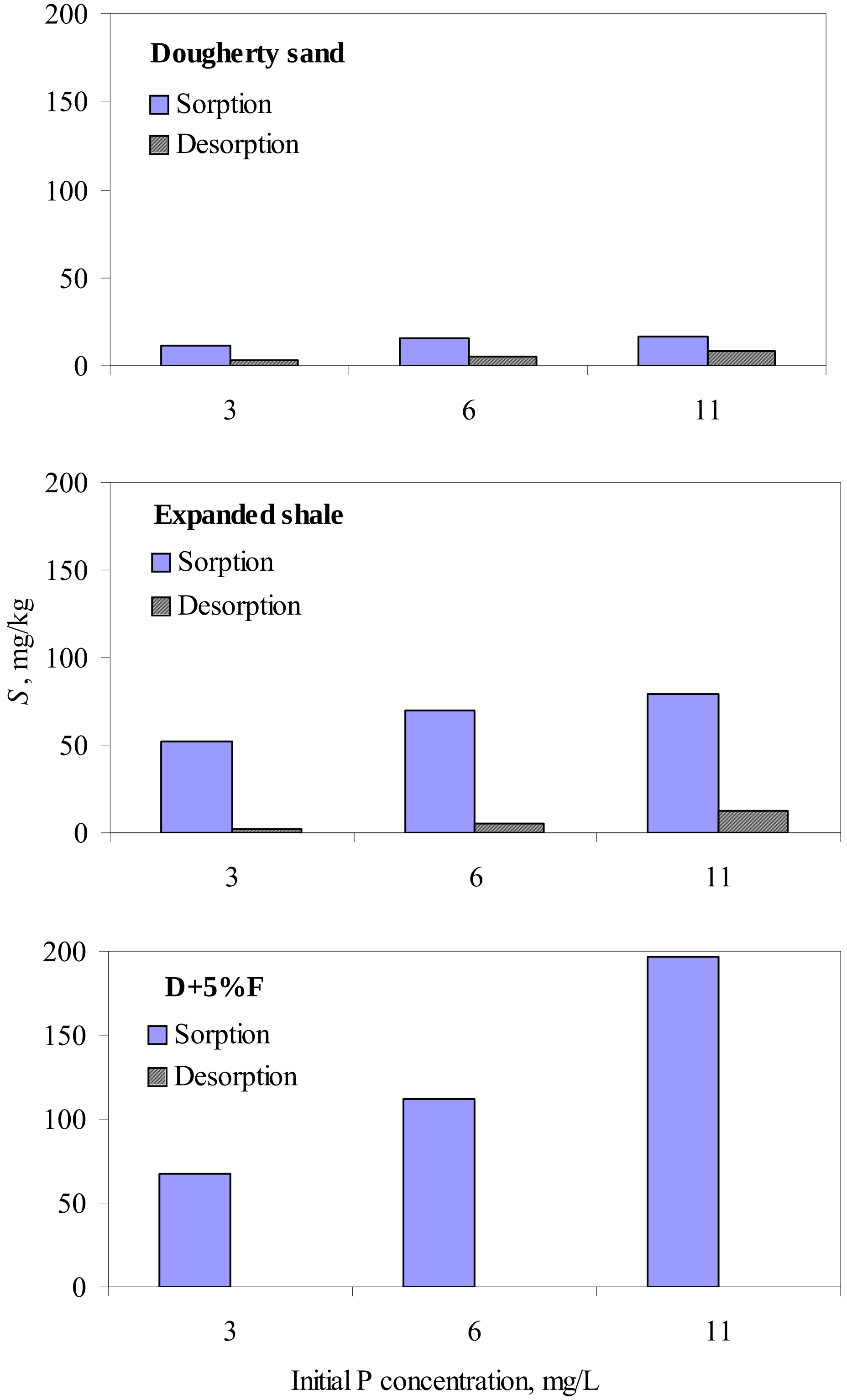

Figure 7. Initial sorption with phosphorus concentration ranging from 3 to 11 mg/L, followed by desorption.

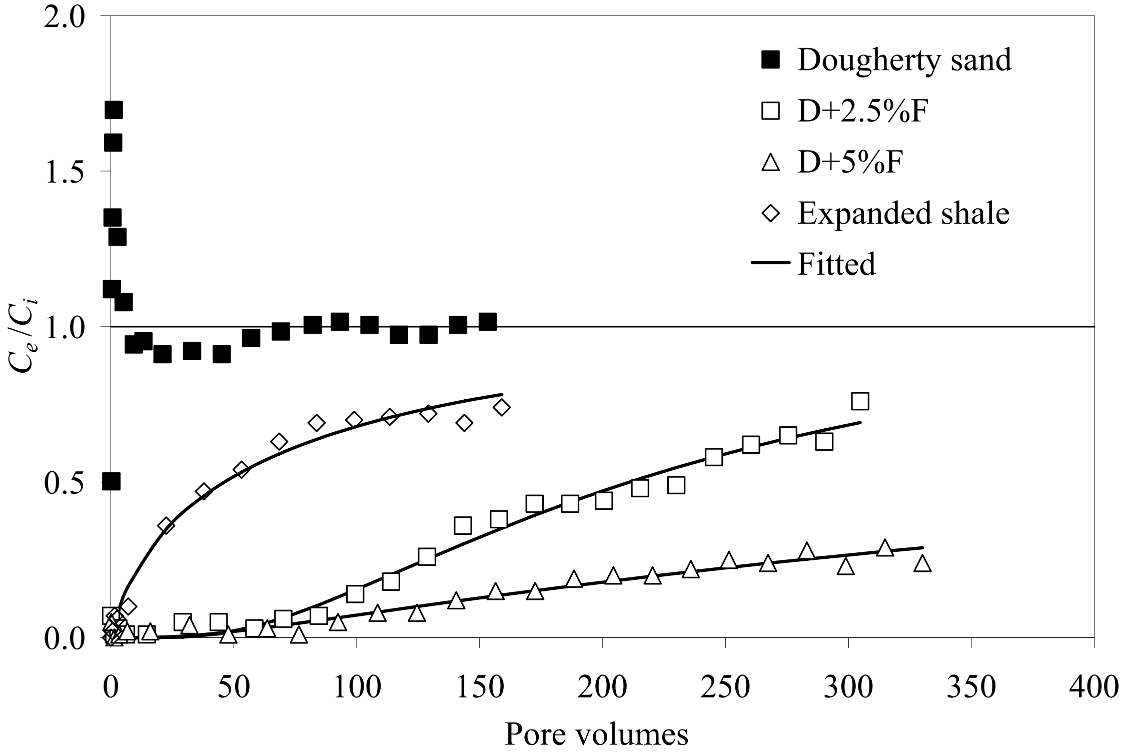

Figure 8. Observed and fitted phosphorus BTCs for Dougherty sand, D+2.5%F, D+5.0%F, and expanded shale from KS (M-shale).

CHAPTER III

ENHANCEMENT OF HEAVY METALS RETENTION BY SOIL AMENDMENT

Abstract

Stormwater runoff from heavily polluted urban areas can transport a significant load of heavy metals. Thus, the metals retention capacity of filter media in stormwater infiltration systems, such as bioretention cells, is important. Batch sorption experiments were conducted to determine the distribution coefficients of copper, lead, and zinc in three Oklahoma soils, Dougherty sand, Teller loam, and Slaughterville loam, and fly ash. Dougherty sand had the lowest heavy metals distribution coefficients while fly ash had the highest. The addition of fly ash to Dougherty sand increased its heavy metals retention. Column leaching experiments were conducted on Dougherty sand and its mixtures with 2.5% and 5% by weight fly ash. Heavy metals transport in these three media was examined in detail using a linear equilibrium, convection-dispersion transport model. The resultant retardation factors indicated that the addition of fly ash to Dougherty sand improved its heavy metals retention dramatically.

Keywords: Stormwater, Runoff, Infiltration, Heavy metals, Transport, Retardation, Fly ash

Introduction

Urban stormwater runoff is the second largest impairment source for estuaries and the third largest pollution source for lakes in the United States, according to the National Water Quality Inventory 2000 Report (USEPA, 2002). Urbanization increases the area of impervious surfaces such as parking lots, rooftops, and road pavements. Rain falling on these impervious surfaces runs off, mobilizes deposited pollutants along the flow path, and transports a wide range of pollutants into receiving water bodies. The Nationwide Urban Runoff Program (NURP) study conducted by the EPA revealed that heavy metals such as copper (Cu), lead (Pb), and zinc (Zn) are the prevalent pollutants in stormwater runoff (USEPA, 1983). A number of local studies have found a range of heavy metals in stormwater runoff (Drapper et al., 2000; Sansalone and Buchberger, 1997; Wu et al., 1998; Zhang et al., 2003; Zobrist et al., 2000). Runoff from heavily traveled roads frequently has a heavy metals concentration exceeding water quality standards. For example, in an urban highway runoff in Cincinnati, Ohio, the event mean concentration of total Zn ranged from 459 to 15,244 μg/L, total Cu from 43 to 325 μg/L, and total Pb from 31 to 97 μg/L (Sansalone and Buchberger, 1997). In a study in Queensland, Australia, the median first flush concentration in the runoff from 21 road sites had levels of total Zn from 160 to 1,850 μg/L, total Cu from 30 to 305 μg/L, total Pb from 50 to 575 μg/L (Drapper et al., 2000).

The major sources of heavy metals in stormwater runoff are vehicular activity, roadway abrasion and degradation, building materials weathering, and atmospheric deposition (Davis and Burns, 1999; Davis et al., 2001; Mason et al., 1999; Turer et al., 2001; Zobrist et al., 2000). Painted structures contribute a significant load of Pb to stormwater runoff (Davis and Burns, 1999). Engine exhaust was a major Pb source until leaded gasoline was banned in the United States, and is still the case where leaded gasoline is not prohibited (Turer et al., 2001). Building sidings are an important source for Cu, Cd, Pb, and Zn, vehicle brake emission for Cu, and tire abrasion and oil leakage for Zn (Davis et al., 2001).

The reduction of heavy metals in stormwater runoff is important because of their toxicity, persistence, and bioaccumulation. Structural stormwater best management practices (BMPs) such as infiltration ponds, bioretention cells, and other engineered devices have been developed to remove heavy metals from stormwater runoff (Davis et al., 2003; Mason et al., 1999; Norrström and Jacks, 1998; Sansalone and Buchberger, 1995; Sonstrom et al., 2002). Soils are commonly used as filter media. However, sandy soils may have low heavy metals retention (Liu et al., 2005; Zhang et al., 2003). The downward transport of heavy metals has occurred in some stormwater infiltration systems due to limited retention of heavy metals in the filter media, exposure to high NaCl concentration from de-icing salts, or preferential flow (Mason et al., 1999; Norrström and Jacks, 1998). Also stormwater infiltration may pose a threat of groundwater contamination in some vulnerable areas where acidic rain occurs (Gong and Donahoe, 1997). Norrström and Jacks (1998) found that the groundwater 4.5 meters below the surface of an infiltration pond was polluted by Pb. Therefore, the heavy metals sorption capacity of the filter media in stormwater infiltration systems should be given serious attention.

Retention of heavy metals in soils is often associated with the content of Fe, Al, and Mn oxides and hydroxides, clay, and organic matter and pH (Barbosa and Hvitved-

Jacobsen, 1999; Davis, 1984; Farrah and Pickering, 1976; Gadde and Laitinen, 1974; Gong and Donahoe, 1997; McKenzie, 1980; Norrström and Jacks, 1998). Research has been undertaken to find more effective filter media for heavy metals removal (Liu et al., 2005). Also cost-effective filter media is needed to reduce the expense of stormwater BMPs. Fly ash, a waste product of burning coal, is abundant and inexpensive. Previous research has shown that fly ash is effective at removing heavy metals including Cu, Cd, Zn, Cr, Hg, Pb, and Ni (Ayala et al., 1998; Banerjee et al., 2003, 2004; Bayat, 2002; Erol et al., 2005).

This study investigated improving heavy metals retention by amending soil with fly ash. Batch sorption experiments with Cu, Pb, and Zn were conducted on three Oklahoma soils, Dougherty sand, Teller loam, and Slaughterville loam, fly ash, and Dougherty sand with 2.5% and 5% by weight fly ash. Column leaching experiments were performed to obtain the breakthrough curves (BTCs), and the columns were sectioned to determine the spatial distribution of any non-eluted heavy metals. Transport of the heavy metals was modeled by a linear adsorption equilibrium transport model to estimate retardation factors.

Materials

Dougherty sand (Thermic Arenic Haplustalf), Teller loam (Thermic Udic Argiustoll), and Slaughertville loam (Thermic Udic Haplustolls) were obtained from field locations in Payne County, Oklahoma. Soil samples were air dried and passed through a 2 mm sieve before use. Precipitator fly ash was collected from the Sooner power plant in Red Rock, Oklahoma. The fuel source was a sub-bituminous coal from the Power River Basin, Wyoming. Fly ashes from power plants burning the different types of fuels could have different chemical compositions. Chemical compositions of the fly ash were analyzed by X-ray fluorescence (XRF) analyzer (Philips PW-2400) at Activation Laboratories Ltd., Ontario, Canada and are showed in Table1. The fly ash used in this study is class C fly ash with quicklime more than 10%. The characteristics of materials were determined by the procedures of ASA and SSSA (ASA and SSSA, 1986; SSSA and ASA, 1996) and are also presented in Table 1.

Methods

Batch Sorption Experiments

Two grams of sorbent were placed in 50 mL polypropylene centrifuge tubes with 40 mL solution containing 10 mg/L of Cu, Pb, and Zn (0.05 solid/water ratio). Solution ionic strength was fixed with 0.01 mol/L potassium chloride (KCl). The tubes were shaken on a rotary agitator at 30 RPM and 23±2 ^{o}C for 24 hrs. Then the suspensions were centrifuged, and the pH was measured. The supernatants were filtered through a 0.45 μm Glass/Nylon filter. The filtrates were acidified and then analyzed by ICP-AES (Spectro CIROS^{CCD}) in the Soil, Water and Forage Analytical Laboratory (SWFAL) of the Department of Plant and Soil Sciences, Oklahoma State University. The instrumental detection limit was 0.01 mg/L for Cu and Zn, and 0.02 mg/L for Pb (Kress, 2005). The distribution coefficient (K_d) of heavy metals (ASTM, 2004) was calculated as:

$$K_d = \frac{(C_0 - C)V}{M_s C} \qquad (1)$$

where K_d (mL/g) is distribution coefficient, C_0 (mg/L) is the initial concentration in the blank, C (mg/L) is the final concentration of heavy metals remaining in the solution, V (mL) is the volume of solution, and M_s (g) is the mass of sample.

Dougherty sand was amended with 2.5% (D+2.5%F) and 5% (D+5%F) fly ash. To better simulate the actual metals concentration in the stormwater runoff, a lower initial concentration of 1 mg/L was used to measure distribution coefficients for Dougherty sand and these mixtures.

Column Leaching Experiments

Dougherty sand, D+2.5%F, and D+5%F were packed into acrylic columns with 14.4 cm inner diameter and 14.3 long. Column characteristics are presented in Table 2. Influent containing 1 mg/L Cu, Zn, and Pb passed upward through the columns with a loading rate of 3 cm/hr. Influent and effluent samples were collected periodically, and their pH was measured. Effluent samples were turbid in the early period of the Dougherty sand experiment. Those samples were centrifuged to remove suspended solids. Experiments lasted about three weeks, and produced approximately 240 L of effluent. All samples were acidified and analyzed for Cu, Pb, and Zn by ICP-AES in SWFAL. Breakthrough curves (BTCs) were established by plotting normalized concentration versus pore volume.

A concern over the high pH effluent from alkaline materials was addressed by a final column experiment repeated for D+5%F. Four one-liter effluent samples were collected during the three-week experiment. pH was measured upon sample collection. These samples then were stored from 4 to 25 days before analyzing pH, alkalinity, and hardness by SWFAL.

Distribution of Non-eluted Metals

Column cores were removed intact from the columns and dried in a vacuum oven at 80 °C with the ends covered to minimize water transport along the core axis. Then the outside of the cores was trimmed to eliminate any cross contamination using clean knives. Cores were sectioned into seven two cm long slices. Each slice was placed in a clean plastic bag and mixed thoroughly. The soil slice samples and uncontaminated soil samples were acid-digested (USEPA, 1996), and the digestates were analyzed by ICP-AES for total available Cu, Pb, and Zn. By subtracting soil background concentrations, metals concentration retained in the soils were obtained, which included metals in the pore water.

Transport Modeling

A linear equilibrium, convection-dispersion transport model in CXTFIT 2.1 in the STANMOD software package (Simunek et al., 1999, Riverside, California) was used to simulate transport of Zn, Cu, and Pb in Dougherty sand, D+2.5%F, and D+5%F. The STANMOD software package was developed to evaluate solute transport in porous media using analytical solutions of the convection-dispersion equation by the U.S. Salinity Laboratory. The third-type inlet boundary and step input conditions were applied. It was assumed that there was no production or decay of heavy metals. Three approaches were used in the transport modeling. The first approach was to fit BTCs directly using the transport model to estimate the retardation factor (R) and hydrodynamic dispersion coefficient (D) if the metals were detected in the effluent. This approach was applied to the transport modeling of Zn in Dougherty sand. For the heavy metals whose effluent concentrations were below the detection limit, two alternative approaches were used. Hydrodynamic dispersion coefficients must be fixed before implementing these two approaches. Hydrodynamic dispersion is the sum of mechanical dispersion and molecule diffusion. Ignoring molecule diffusion, hydrodynamic dispersion was assumed to be the same for transport of phosphorus, Cu, Pb, and Zn. Therefore, hydrodynamic dispersion coefficients were estimated from the transport modeling of Zn in Dougherty sand, and phosphorus in D+2.5%F and D+5%F in the previous study (Chapter II). Modeling parameters are presented in Table 2.

The second modeling approach estimated the minimum retardation factor from the BTCs. The value of retardation factor was changed until the transport model gave metals concentration in the last sampling point equal to the detection limit. This approach produces the minimum retardation factor that could have occurred.

The third approach estimated retardation factors from the non-eluted heavy metals spatial distribution. Metals retained in soils included metals in both the solid phase and the liquid phase. Thus,

$$S_T = \frac{C_r\theta + S\rho}{\rho} \tag{2}$$

where S_T (mg/kg) is the total concentration, S (mg/kg) is the concentration in the solid phase, C_r is the concentration in the liquid phase, θ is the porosity, and ρ (g/cm^3) is the dry bulk density of soils.

Sorption was assumed to be linear and in equilibrium. Therefore,

$$S = K_d C_r \tag{3}$$

Incorporate Eq. (3) into Eq. (2), and rearranging yields,

$$C_r = \frac{S_T}{(\frac{\theta}{\rho} + K_d)} \tag{4}$$

For a linear equilibrium adsorption transport model, the relationship between retardation factor (R) and distribution coefficient (K_d) is:

$$R = 1 + \frac{K_d\rho}{\theta} \tag{6}$$

Using a trial and error process, retardation factors were estimated by minimizing the mean square error (MSE) between the simulated and observed concentrations in the liquid phase:

$$MSE = \frac{1}{n}\sum_{i=1}^{n}(C_{roi} - C_{rsi})^2 \qquad (7)$$

where MSE(mg^2/L^2) is the mean square error, n is the number of slices, C_{roi} (mg/L) is the observed C_r in the i slice from the metals distribution, C_{rsi} (mg/L) is the simulated C_r in the i slice from the model simulation.

Results and Discussion

Batch Sorption Experiments

Distribution coefficients (K_d) of heavy metals in soils and fly ash are presented in Table 3. Dougherty sand had much lower distribution coefficients compared to Teller loam and Slaughterville loam. The low metals sorption of Dougherty sand may be attributed to its low soil CEC, clay and organic matter content (Table 1). Soil CEC, clay content, and organic matter content are positively correlated with heavy metals retention (Barbosa and Hvitved-Jacobsen, 1999; Davis, 1984; Farrah and Pickering, 1976; Gong and Donahoe, 1997). It was noted that Dougherty sand had an insufficient sorption for Zn, with K_d only 7.91 mL/g and 20.6 mL/g for initial concentrations of 10 mg/L and 1 mg/L, respectively. Fly ash had the highest distribution coefficients for all three metals (Table 3). The alkaline nature and high content of Al, Fe, and Ca oxides may explain the high metals retention of fly ash (Table 1) (Bayat, 2002; Erol et al., 2005; Gadde and Laitinen, 1974; Gong and Donahoe, 1997; McKenzie, 1980). pH is an important factor for the sorption of heavy metals. A number of studies indicated that the sorption of heavy metals increases with increasing pH and decreases with lowering pH (Ayala et al., 1998; Banerjee et al., 2003; Erol et al., 2005; Farrah and Pickering, 1976; Gadde and Laitinen, 1974). The primary mechanisms of the removal of heavy metals by fly ash are ion exchange, surface and solution precipitation, and adsorption, which are usually lumped as sorption process. Erol et al. (2005) found that Cu^{2+} and Pb^{2+} were precipitated as metal hydroxides. Bayat (2002) asserted that adsorption by oxides such as Al_2O_3 and Fe_2O_3 came into play when pH was less than 8.0. However, the precipitates of heavy metals were still observed at the pH above 2.0 (Ayala et al., 1998). Nevertheless, the high pH and oxides content together explain the high heavy metals sorption capacity of fly ash.

After being amended with fly ash, Dougherty sand showed a significant improvement of heavy metals retention (Table 3), especially for Zn. Adding 5% fly ash to Dougherty sand increased K_d of Zn from 20.6 mL/g to 843 mL/g. The trend for Pb cannot be seen clearly because the final concentration of Pb was below the detection limit.

Column Leaching Experiments and Transport Modeling

The mass balance of heavy metals in the column tests are summarized in Table 4. The mass balance for Dougherty sand and D+2.5%F were from 56% to 99%. Sample was believed lost in the end of the first slices adjacent to the column inlet during the sectioning. Because of the mobility of Zn in Dougherty sand, the first slice was saturated with Zn, and most of Zn has already migrated into the deeper layer, producing a near perfect recovering. However, with the improved Zn retention in D+2.5%F, its recovery was lowered due to the sample loss. Cu and Pb have higher affinity to Dougherty sand and D+2.5%F than Zn. Therefore, the sample loss lowered their recovery in Dougherty sand, and degraded it further in D+2.5%F. With the precaution in the experiment of

D+5%F, all three metals exhibited a satisfactory recovery. Because metals were usually enriched in the first slices, the correction of metals concentration in the first slices was made based on the recovery of 100%.

In the leaching experiments, only Zn was detected in the effluent from the Dougherty sand column. By the first approach, the retardation factor of Zn in Dougherty sand was estimated and presented in Table 5. The observed and fitted BTCs are shown in Figure 1.

There were no detectable metals in the effluents from the other experiments, thus the second and third modeling approaches were used. One example of the second approach is shown in Figure 2 and the estimated minimum retardation factors are presented in Table 5. Obviously, the minimum retardation factors increased with the addition of fly ash to Dougherty sand. Because of the higher detection limit of Pb, its minimum retardation factor of Pb is smaller compared to Cu and Zn.

Approach 3rd fitted the experimental data well with a small *MSE* (Table 5). The observed and simulated spatial distribution of C_r and S_T are plotted in Figure 3 and Figure 4, respectively. C_r and S_T decreased with the distance from the inlet. For D+5%F, almost all metals were retained in the first 2 cm layer as shown in Figure 4. The worst fit was for Zn in Dougherty sand with a *MSE* of 0.0179 mg^2/L^2 (Table 5). The reason wasn't understood clearly. However, Approach 3rd was still able to give retardation factor of 490, which is very close to the value of 513 obtained by directly fitting the BTC (Table 5). The retardation factors from Approach 3rd indicated that the addition of fly ash to Dougherty sand improved the retardation of heavy metals dramatically. The retardation factors of Dougherty sand amended with 5% fly ash were three orders of magnitude greater than Dougherty sand.

A comparison was made between the distribution coefficients from column leaching experiments and those from batch sorption. The distribution coefficients calculated from retardation factors were much higher than those from batch sorption. Solid/water ratio and solid/water contact time are two important factors to affect sorption. Column leaching experiments had residence time ranged from 1.5 hr to 1.9 hr, which is lower than 24 hr in batch sorption experiments. Also, the solid/water ratio varied from 4.2 to 6.0, which is much larger than 0.05 in the batch sorption. Sorption of heavy metals usually has a fast initial sorption reaction, which takes approximately 1 hour to reach the equilibrium state in fly ash (Ayala et al., 1998; Banerjee et al., 2003). The residence time might be adequate to obtain the equilibrium state for heavy metals. Apparently, the difference of distribution coefficients indicated that the positive effect of increasing solid/water ratio overweighed the adverse effect of reducing solid/water contact time.

The mean influent pH was 5.9, and the mean effluent pH for Dougherty sand, D+2.5%F, and D+5%F were 5.9, 10.2, and 10.3, respectively. Dougherty sand did not change the influent pH statistically (two tail *t*-test, $P>0.98$). D+2.5%F and D+5%F did raise the influent pH (one tail *t*-test, $P<0.0001$).

There was a concern with the high effluent pH of alkaline media that may violate the pH criteria for water quality (Liu et al., 2005). To address this issue, the alkalinity of effluents was examined. Effluent alkalinity of D+5%F was high at the beginning and dropped rapidly to only 28 mg/L as $CaCO_3$ at the end of experiment as listed in Table 6. Effluent hardness also followed the same trend (Table 6). This was probably caused by the first flush of ions at the beginning of the experiment. Because of low alkalinity, the effluent pH can be easily neutralized, including the dissolution of carbon dioxide from the environment. The weak buffering is also demonstrated by the fact that after storage, the pH of the effluents always decreased as shown in Table 6. The pH of the last effluent sample was 8.4, which meets the pH criteria.

Conclusions

Urban stormwater runoff may transport high levels of heavy metals. Stormwater infiltration practices are commonly used to mitigate the non-point source pollution from stormwater runoff. However, insufficient heavy metals retention capacity of filter media in the infiltration systems may pose a risk of contaminating recipient water bodies. Thus, filter media in stormwater infiltration systems must have adequate sorption capacity for heavy metals. Batch sorption experiments indicated that Dougherty sand had the lowest heavy metals distribution coefficients, while fly ash had the highest. The addition of fly ash to Dougherty sand improved its heavy metals sorption. Column leaching experiments and transport modeling proved that adding fly ash to Dougherty sand increased its heavy metals retardation dramatically. Especially, the retention of Zn was improved markedly. Thus, the application of the sand/fly ash mixture could improve the heavy metals retention in stormwater infiltration systems.

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Table 1. Characteristics of soils and fly ash.

	Sand, %	Silt, %	Clay, %	USDA classification	CEC [A]	OC [B], %	pH
Dougherty	98	2 [C]		Sand	~ 1	0.1	6.8
Teller	52	31	17	Loam	~ 9	1.2	6.9
Slaughterville	47	35	18	Loam	~ 10	0.5	8.0
Fly ash	Major chemical composition, %				~ 78	--	11.3
	SiO_2	Al_2O_3	Fe_2O_3	CaO			
	38.0	18.4	5.93	22.9			

[A] CEC: cation exchange capacity

[B] OC: organic carbon content

[C] Silt plus clay content

Table 2. Column characteristics and transport modeling parameters for Dougherty sand, D+2.5%F, and D+5%F.

	Dougherty sand	D+2.5%F	D+5%F
Dry bulk density (ρ), g/cm^3	1.62	1.74	1.84
Porosity (θ)	0.389	0.343	0.305
Retardation factor (R)	*variable*	*variable*	*variable*
Hydraulic dispersion coefficient (D), cm^2/hr	15.7 [A]	43.4 [B]	249 [B]
Pore-water velocity (v), cm/hr	7.60	8.69	9.64
Total pore volumes	269	307	341
Residence time [C], hr	1.9	1.6	1.5
Solid/water ratio [D]	4.2	5.1	6.0

[A] From Zn transport modeling in Dougherty sand

[B] from phosphorus transport modeling in Chapter II

[C] Calculated by dividing the length of columns by the pore-water velocity

[D] Estimated by the relationship of $2.65(1-\theta)/\theta$

Table 3. Heavy metals distribution coefficients of soils, fly ash, and the mixtures of Dougherty sand with fly ash.

Materials	Cu		Pb		Zn	
	pH	K_d, mL/g	pH	K_d, mL/g	pH	K_d, mL/g
Dougherty sand [A]	5.5	11.6	5.9	335	6.1	7.91
Teller loam [A]	6.3	1650	6.0	557	6.2	351
Slaughertville loam [A]	6.3	4680	7.9	646	6.7	113
Fly ash [A]	11.4	8410	11.4	3050	11.6	4010
Dougherty sand [B]	6.9	155	7.6	>1220[C]	7.2	20.6
D+2.5%F [B]	11.1	226	11.0	>1230[C]	11.0	618
D+5%F [B]	11.3	239	11.1	>1240[C]	11.3	843

[A] Initial concentration of heavy metals was 10 mg/L

[B] Initial concentration of heavy metals was 1 mg/L

[C] Final concentration of Pb was below the detection limit

Table 4. Mass balance of heavy metals in column experiments of Dougherty sand, D+2.5%F, and D+5%F.

	Dougherty sand			D+2.5%F			D+5%F		
	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn
Input from the influent, mg	246	236	240	248	236	246	238	231	233
Output in the effluent, mg	0.1	0.3	4.4	0	0	0.5	0	0	0
Non-eluted metals, mg	220	182	232	149	132	209	287	246	263
Recovery, %	89	77	99	60	56	85	121	106	113

Table 5. Estimated retardation factors (*R*) from transport modeling for Dougherty sand, D+2.5%F, and D+5%F.

Medium	Heavy metals	Approach 1st		Approach 2nd		Approach 3rd		
		R	*MSE*	Min. *R*	Min. K_d, mL/g[B]	*R*	*MSE*, $(\mathrm{mg/L})^2$	K_d[B], mL/g
Dougherty sand	Cu	*BTC not usable for fitting*[A]		730	175	1100	7.50×10^{-4}	264
	Pb			635	152	2350	1.20×10^{-4}	564
	Zn	513	9.34×10^{-6}	--	--	490	1.72×10^{-2}	117
D+2.5%	Cu	*BTC not usable for fitting*[A]		1310	257	6700	1.19×10^{-5}	1320
	Pb			1080	213	7100	1.97×10^{-5}	1400
	Zn			1310	257	2000	6.14×10^{-4}	394
D+5%	Cu	*BTC not usable for fitting*[A]		4050	671	175000	9.08×10^{-7}	29000
	Pb			3050	505	>295000	1.17×10^{-6}	>48900
	Zn			4050	671	145000	6.86×10^{-7}	24000

[A] Solute not detected in effluents

[B] Calculated from retardation factors

Table 6. pH, alkalinity, and hardness of leaching effluent from D+5%F.

Pore volumes	Tested after sample storage				pH tested when collecting samples	pH difference
	pH	Alkalinity, mg/L as $CaCO_3$	Hardness, mg/L as $CaCO_3$	Storage duration, days		
1	11.5	544	436	25	12.1	0.6
116	10.0	40	45	18	11.2	1.2
240	9.1	20	33	10	10.9	1.8
336	8.4	28	28	4	10.8	2.4

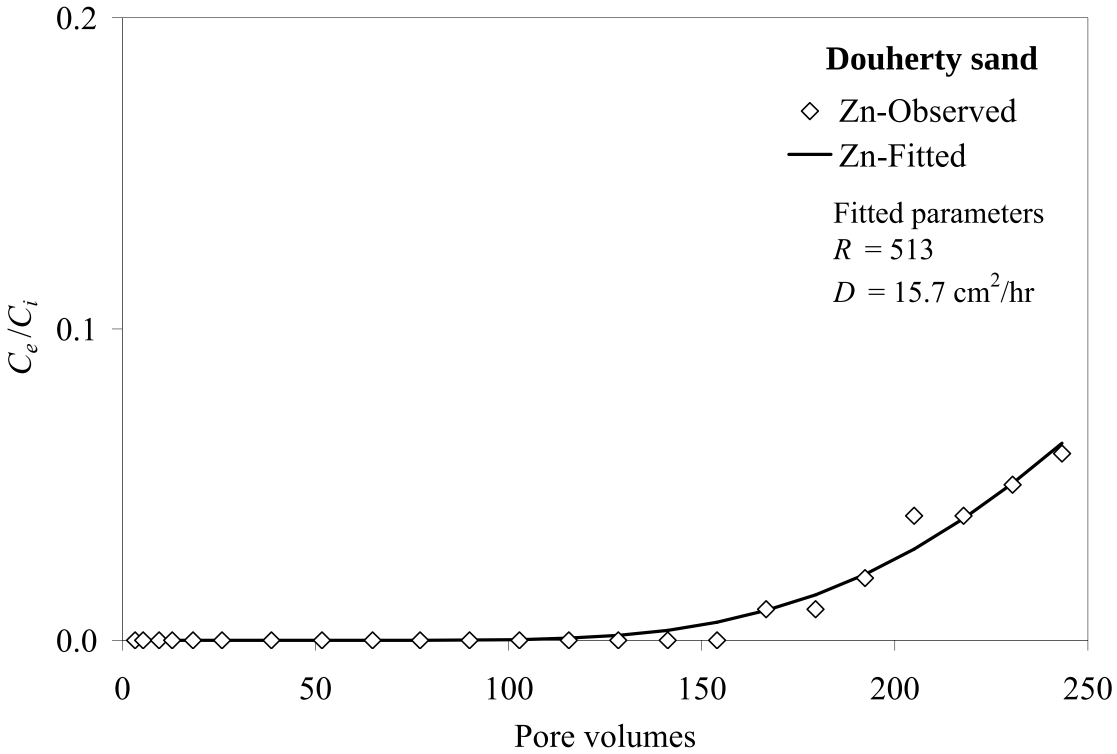

Figure 1. Observed and simulated Zn breakthrough curve in Dougherty sand, by Approach 1st.

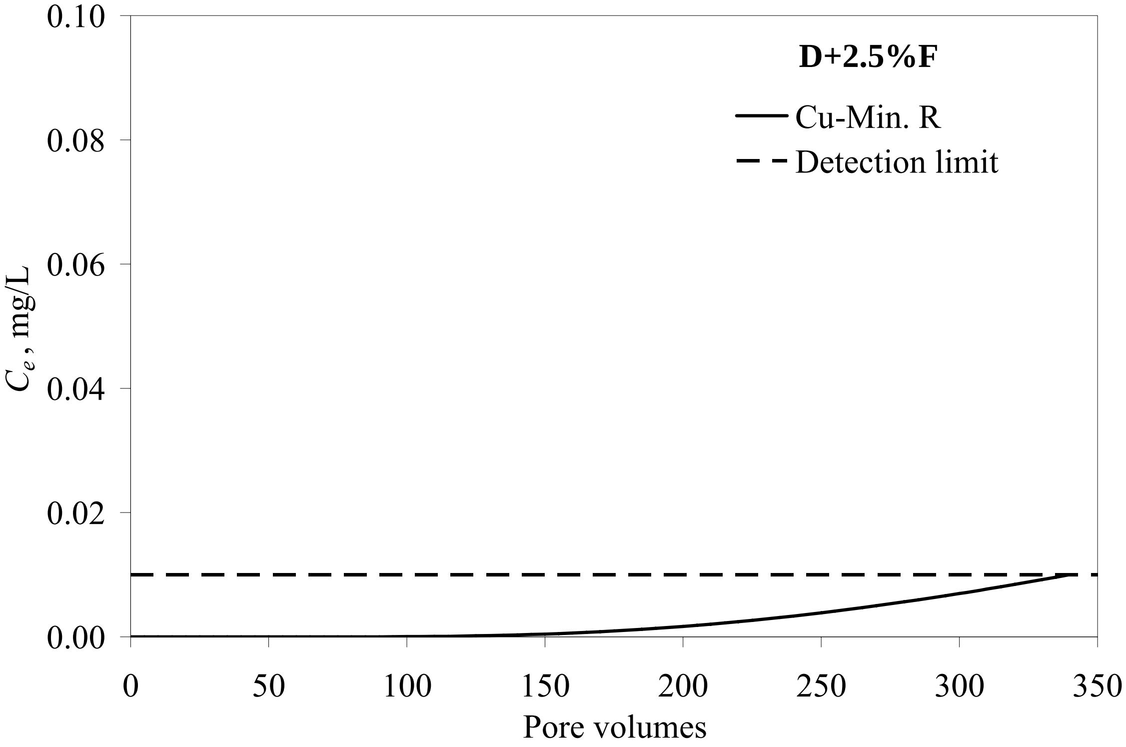

Figure 2. Example of estimation of minimum retardation factor (*R*) by Approach 2nd.

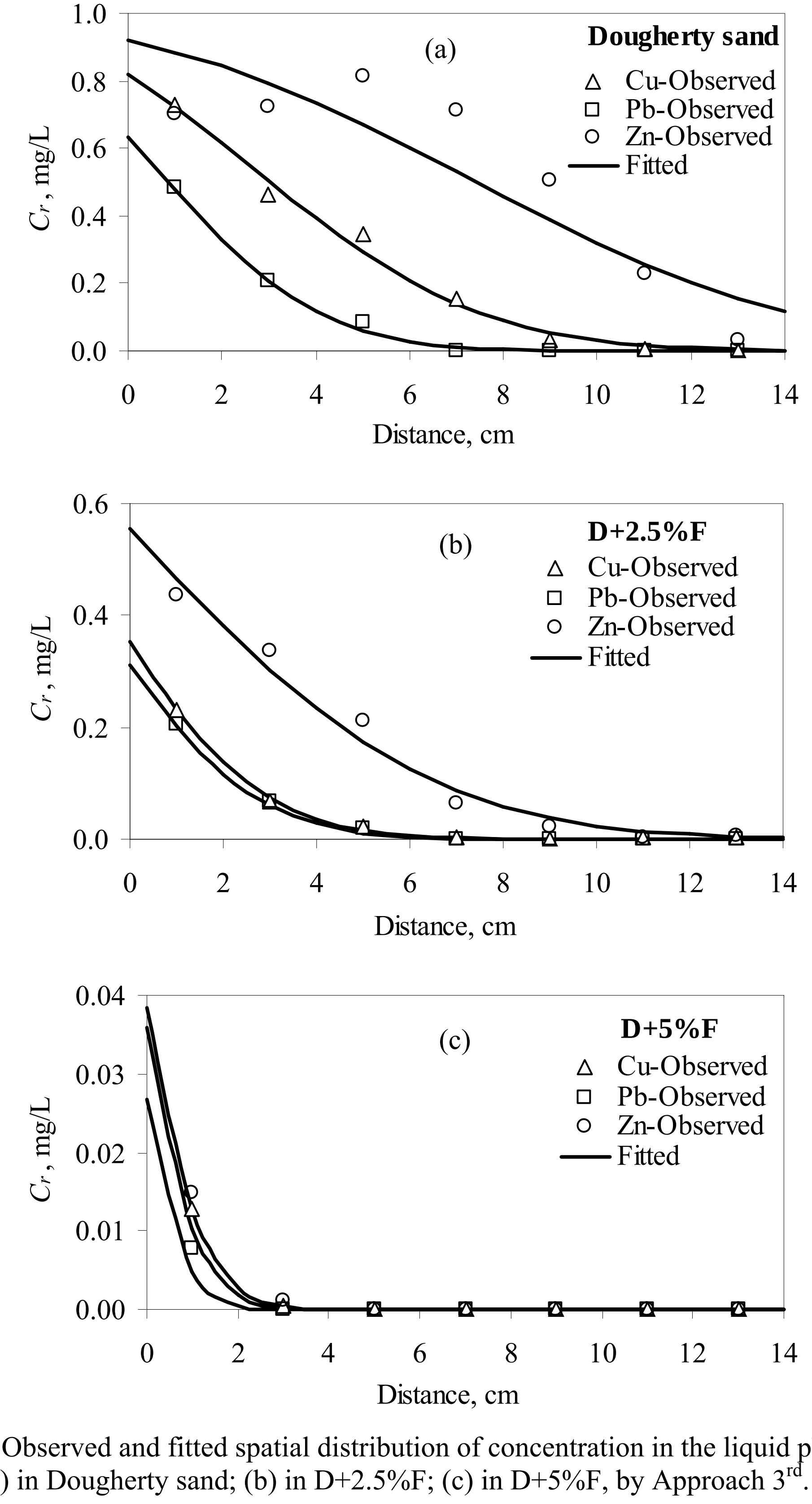

Figure 3. Observed and fitted spatial distribution of concentration in the liquid phase (C_r, mg/L): (a) in Dougherty sand; (b) in D+2.5%F; (c) in D+5%F, by Approach 3rd.

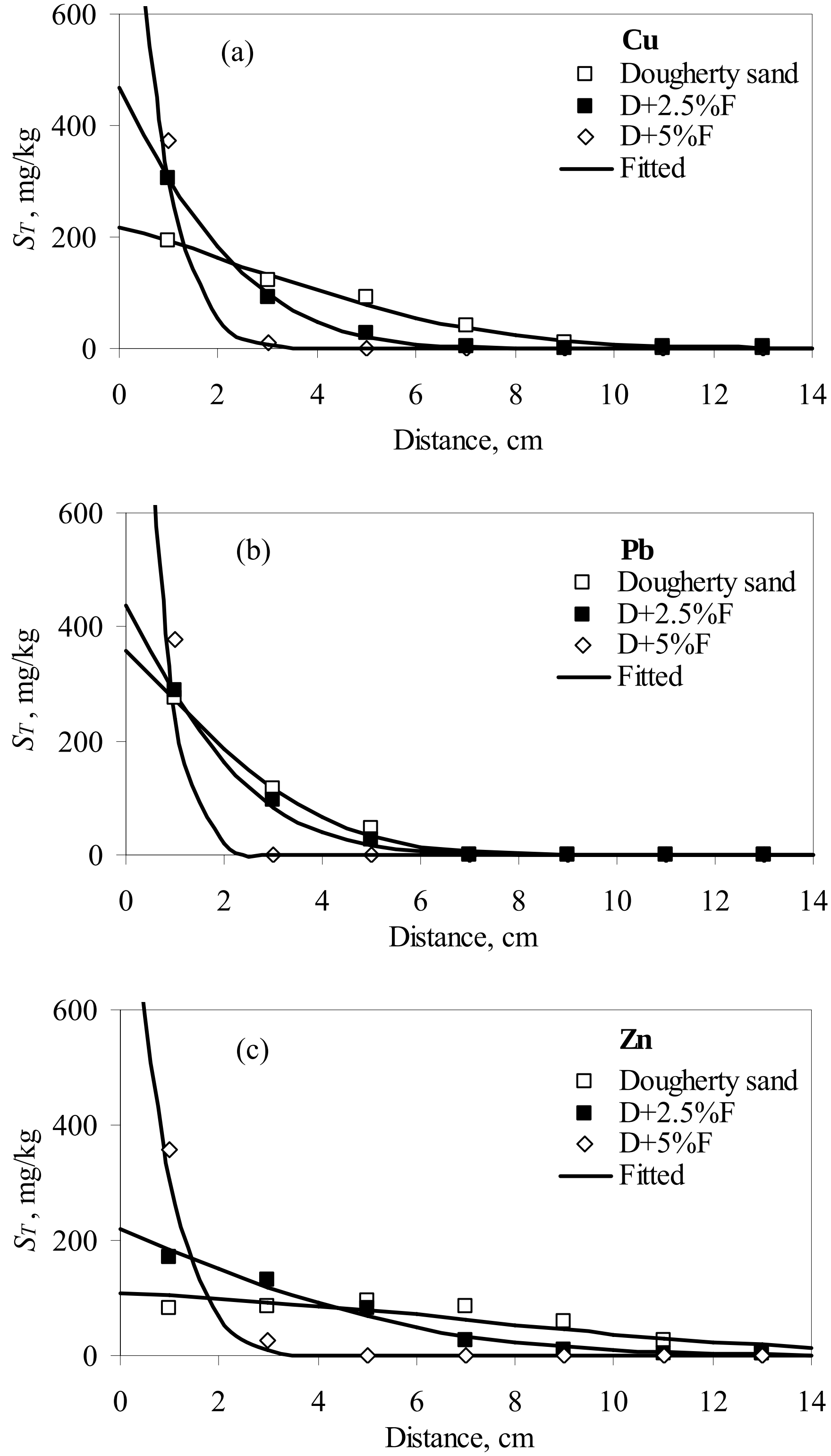

Figure 4. Observed and fitted spatial distribution of non-eluted metals concentration (S_T, mg/kg): (a) Cu distribution; (b) Pb distribution; (c) Zn distribution, by Approach 3^{rd}.

Appendix

Experimental Data

Table A1. Distribution coefficients (K_d) of various materials.

Materials	P		NO_3-N [C]		NH_4-N [C]		Cu		Pb		Zn	
	pH	K_d, mL/g	pH	K_d, mL/g	pH	K_d, mL/g	pH	K_d, mL/g	pH	K_d, mL/g	pH	K_d, mL/g
Dougherty sand [A]	6.3	2.08	6.5	-0.40	6.4	-3.01	5.5	11.6	5.9	335	6.1	7.91
Teller loam [A]	6.2	0.41	6.3	-1.19	6.3	-2.30	6.3	1649	6.0	557	6.2	351
Slaughterville loam [A]	8.0	3.98	8.0	-0.73	8.0	-1.18	6.3	4680	7.9	646	6.7	113
Fly ash [A]	11.5	2176	11.4	-0.30	11.4	-0.65	11.4	8410	11.4	3046	11.6	4012
Limestone [A]	9.0	12.1	9.0	-0.13	9.0	-2.07	8.9	9606	9.2	3372	8.9	>20796
Peat moss [A]	2.9	-5.65	--	--	--	--	--	--	--	--	--	--
Shale (Marquette, KS) [A]	6.4	280	7.0	0.58	7.0	0.39	6.2	173	6.9	5494	6.6	17.5
Shale (New Market, MO) [A]	8.6	1.21	7.3	0.05	8.3	0.28	6.3	106	7.4	3061	6.7	20.2
Dougherty sand [B]	--	--	--	--	--	--	6.9	155	7.6	>1219 [D]	7.2	20.6
Dougherty+2.5% fly ash [B]	10.9	307	--	--	--	--	11.1	226	11.0	>1234 [D]	11.0	618
Dougherty+5% fly ash [B]	11.1	398	--	--	--	--	11.3	239	11.1	>1236 [D]	11.3	843

[A] Initial concentration was 1 mg/L for P, 2 mg/L for NO_3-N and NH_4-N, and 10 mg/L for heavy metals

[B] Initial concentration was 1 mg/L for P and heavy metals

[C] Negative sign indicated production of solute

[D] Final concentration of Pb was below the detection limit.

Table A2. Data from phosphorus batch sorption experiments for fly ash and the mixtures of soils with fly ash.

Materials	pH	K_d, mg/L	P removal, %
Teller loam	6.2	0.41	2.0
Teller + 1%fly ash	7.4	3.57	15.3
Teller + 5%fly ash	9.9	49.3	71.4
Teller + 10%fly ash	10.8	88.0	81.6
Dougherty sand	6.3	2.08	9.42
Dougherty + 2.5% fly ash	10.9	307	94.2
Dougherty + 5% fly ash	11.1	398	94.2
Dougherty + 7.5% fly ash	11.3	654	96.3
Fly ash [A]	11.3	1888	99.0
	9.5	253	92.7
	9.2	99.1	83.2
	8.6	42.0	67.5
	8.0	107	84.3
	7.9	192	90.6
	7.0	218	91.6
	6.4	252	92.7
	5.2	931	97.9
	4.8	455	95.8
	3.9	116	85.3
	3.7	25	56.0
	3.5	-10 [B]	-106 [B]

[A] Experiments were conducted to investigate the effect of pH on the phosphorus sorption of fly ash

[B] Negative sign indicated the production of phosphorus

Table A3. Data from phosphorus batch sorption isotherms experiments.

Materials	C_0, mg/L	C, mg/L	Sorption amount (S), mg/kg	C/S, kg/L
Dougherty sand	1.14	0.93	4.16	0.22
	3.43	2.88	11.0	0.26
	5.71	4.91	15.9	0.31
	10.5	9.71	16.7	0.58
Dougherty + 5% fly ash	3.43	0.03	67.3	0.0005
	5.71	0.11	112	0.0010
	10.5	0.66	197	0.0033
	28.6	9.76	375	0.0260
Expanded shale (Marquette, KS)	1.14	0.04	22.0	0.0016
	3.43	0.83	51.8	0.0159
	5.71	2.20	70.0	0.0314
	10.54	6.58	79.0	0.0833

Table A4. Data from phosphorus desorption experiments.

Materials	C_0, mg/L	Sorption amount (*S*), mg/kg	Desorption amount (*DS*), mg/kg	*DS*/*S*, %	Average *DS*/*S*, %
Dougherty sand	1.14	4.16	2.28	54.7	41.9
	3.43	11.0	3.47	31.7	
	5.71	15.9	4.96	31.2	
	10.5	16.6	8.29	49.8	
Dougherty + 5% fly ash	3.43	67.5	0.289	0.43	0.12
	5.71	112	0.307	0.27	
	10.5	197	0.000	0.00	
	28.6	375	0.052	0.01	
	57.1	346	0.076	0.02	
	114	408	0.060	0.01	
Expanded shale (Marquette, KS)	1.14	22.0	0.000	0.00	6.69
	3.43	51.8	1.62	3.14	
	5.71	70.0	5.70	8.15	
	10.5	79.0	12.2	15.5	

Table A5. Data from column flow-through experiment of phosphorus for Dougherty sand.

Column characteristics	Inner diameter, cm	Length, cm	Bulk density (ρ), g/cm^3	Porosity (θ)
	14.4	14.3	1.55	0.415
	Pore volume, cm^3	Flow rate, mL/hr	Darcy velocity (q), cm/hr	Pore-water velocity (v), cm/hr
	963	482	2.96	7.14
	Average influent concentration (C_i), mg/L		Average influent pH	Average effluent pH
	0.96		6.7	6.5

Time, hr	Effluent volume, mL	Pore volumes	Effluent concentration (C_e), mg/L	Experimental	Fitted
				C_e/C_i	C_e/C_i
0.5	241	0.3	0.48	0.50	*unable to fit*
1.0	482	0.5	1.07	1.12	
1.5	724	0.8	1.29	1.35	
2.0	965	1.0	1.52	1.59	
2.5	1206	1.3	1.62	1.70	
5.5	2654	2.8	1.23	1.29	
10.5	5066	5.3	1.03	1.08	
18.7	9008	9.4	0.9	0.94	
26.5	12785	13.3	0.91	0.95	
42.0	20263	21.1	0.87	0.91	
66.0	31842	33.1	0.88	0.92	
90.0	43421	45.1	0.87	0.91	
114.0	55000	57.1	0.92	0.96	
138.0	66579	69.2	0.94	0.98	
163.9	79083	82.2	0.96	1.01	
185.9	89698	93.2	0.97	1.02	
209.9	101277	105.2	0.96	1.01	
233.9	112856	117.2	0.93	0.97	
257.9	124435	129.3	0.93	0.97	
281.9	136014	141.3	0.96	1.01	
305.9	147593	153.3	0.97	1.02	

Table A6. Data from column flow-through experiment and transport modeling of phosphorus for Dougherty sand with 2.5% fly ash (D+2.5%F).

	Inner diameter, cm	Length, cm	Bulk density (ρ), g/cm^3	Porosity (θ)
Column characteristics	14.4	14.3	1.76	0.336
	Pore volume, cm^3	Flow rate, mL/hr	Darcy velocity (q), cm/hr	Pore-water velocity (v), cm/hr
	780	476	2.92	8.70
	Average influent concentration (C_i), mg/L		Average influent pH	Average effluent pH
	1.01		6.7	9.8

Time, hr	Effluent volume, mL	Pore volumes	Effluent concentration (C_e), mg/L	Experimental	Fitted
				C_e/C_i	C_e/C_i
0.1	60	0.1	0.07	0.07	0.000
2.1	1007	1.3	0.01	0.01	0.000
5.1	2420	3.1	0.03	0.03	0.000
10.1	4799	6.2	0.01	0.01	0.000
24.1	11488	14.7	0.01	0.01	0.000
48.0	22835	29.3	0.05	0.05	0.0025
71.9	34196	43.9	0.05	0.05	0.012
95.7	45507	58.4	0.03	0.03	0.036
115.1	54748	70.2	0.06	0.06	0.064
138.7	65975	84.6	0.07	0.07	0.105
162.8	77450	99.4	0.14	0.14	0.153
186.8	88871	114.0	0.18	0.18	0.202
210.8	100268	128.6	0.26	0.26	0.252
234.7	111649	143.2	0.36	0.36	0.301
258.8	123116	157.9	0.38	0.38	0.348
282.5	134373	172.4	0.44	0.43	0.393
306.1	145640	186.8	0.44	0.43	0.435
328.7	156351	200.6	0.45	0.44	0.473
352.8	167826	215.3	0.49	0.48	0.511
376.9	179323	230.0	0.50	0.49	0.547
402.0	191234	245.3	0.59	0.58	0.581
426.7	202995	260.4	0.63	0.62	0.612
451.4	214748	275.5	0.66	0.65	0.641
475.5	226229	290.2	0.64	0.63	0.668
499.4	237574	304.8	0.77	0.76	0.692

Retardation factors (R)		Hydrodynamic dispersion coefficient (D), cm^2/hr		MSE
Mean	95% confidence interval	Mean	95% confidence interval	
199.4	(191.3, 207.5)	43.45	(31.52, 55.38)	0.001273

Table A7. Data from column flow-through experiment and transport modeling of phosphorus for Dougherty sand with 5% fly ash (D+5%F).

Column characteristics	Inner diameter, cm	Length, cm	Bulk density (ρ), g/cm^3	Porosity (θ)
	14.4	14.3	1.82	0.312
	Pore volume, cm^3	Flow rate, mL/hr	Darcy velocity (q), cm/hr	Pore-water velocity (v), cm/hr
	724	478	2.94	9.41
	Average influent concentration (C_i), mg/L		Average influent pH	Average effluent pH
	0.99		6.7	10.3

Time, hr	Effluent volume, mL	Pore volumes	Effluent concentration (C_e), mg/L	Experimental	Fitted
				C_e/C_i	C_e/C_i
0.2	114	0.2	0.05	0.05	0.000
2.3	1077	1.5	0.00	0.00	0.000
5.3	2516	3.5	0.01	0.01	0.000
10.1	4815	6.7	0.02	0.02	0.000
24.4	11672	16.1	0.02	0.02	0.000
48.4	23139	32.0	0.04	0.04	0.006
72.4	34584	47.8	0.01	0.01	0.018
96.3	46045	63.6	0.03	0.03	0.033
115.9	55382	76.5	0.01	0.01	0.046
139.9	66863	92.4	0.05	0.05	0.064
164.2	78490	108.5	0.08	0.08	0.082
188.4	90067	124.5	0.08	0.08	0.100
212.7	101646	140.5	0.12	0.12	0.117
236.8	113199	156.5	0.15	0.15	0.134
261.2	124864	172.6	0.15	0.15	0.151
285.2	136327	188.4	0.19	0.19	0.167
309.4	147872	204.4	0.20	0.20	0.182
333.5	159431	220.4	0.20	0.20	0.198
357.1	170700	235.9	0.22	0.22	0.212
380.5	181863	251.4	0.25	0.25	0.226
404.6	193404	267.3	0.24	0.24	0.239
428.5	204805	283.1	0.28	0.28	0.252
452.3	216220	298.9	0.23	0.23	0.265
476.6	227829	314.9	0.29	0.29	0.278
499.7	238834	330.1	0.24	0.24	0.289

Retardation factors (R)		Hydrodynamic dispersion coefficient (D), cm^2/hr		*MSE*
Mean	95% confidence interval	Mean	95% confidence interval	
469.8	(440.1, 499.4)	249.1	(124.8, 373.4)	0.005592

Table A8. Data from column flow-through experiment and transport modeling of phosphorus in expanded shale.

	Inner diameter, cm	Length, cm	Bulk density (ρ), g/cm^3	Porosity (θ)
Column characteristics	14.4	14.3	0.92	0.653
	Pore volume, cm^3	Flow rate, mL/hr	Darcy velocity (q), cm/hr	Pore-water velocity (v), cm/hr
	1515	481	2.96	4.53
	Average influent concentration (C_i), mg/L		Average influent pH	Average effluent pH
	1.03		6.7	6.7

Time, hr	Effluent volume, mL	Pore volumes	Effluent concentration (C_e), mg/L	Experimental	Fitted
				C_e/C_i	C_e/C_i
0.2	86	0.1	0.00	0.00	0.000
2.1	1001	0.7	0.02	0.02	0.010
5.0	2426	1.6	0.07	0.07	0.038
8.1	3915	2.6	0.06	0.06	0.068
22.2	10694	7.1	0.10	0.10	0.165
70.9	34103	22.5	0.37	0.36	0.348
119.5	57460	37.9	0.49	0.47	0.456
167.7	80599	53.2	0.56	0.54	0.532
215.8	103728	68.5	0.65	0.63	0.590
263.8	126787	83.7	0.71	0.69	0.637
312.1	150032	99.0	0.72	0.70	0.676
357.8	172016	113.5	0.73	0.71	0.708
406.7	195507	129.1	0.74	0.72	0.737
453.2	217829	143.8	0.71	0.69	0.760
501.1	240896	159.0	0.76	0.74	0.782

Retardation factors (R)		Hydrodynamic dispersion coefficient (D), cm^2/hr		*MSE*
Mean	95% confidence interval	Mean	95% confidence interval	
15.72	(7.179, 24.27)	404.2	(112.5, 695.9)	0.001356

Table A9. Data from column leaching experiment and transport modeling of Cu, Pb, and Zn in Dougherty sand.

<table>
<tr><td rowspan="6">Column characteristics</td><td colspan="2">Inner diameter, cm</td><td>Length, cm</td><td>Bulk density (ρ), g/cm^3</td><td colspan="2">Porosity (θ)</td></tr>
<tr><td colspan="2">14.4</td><td>14.3</td><td>1.62</td><td colspan="2">0.389</td></tr>
<tr><td colspan="2">Pore volume, cm^3</td><td>Flow rate, mL/hr</td><td>Darcy velocity (q), cm/hr</td><td colspan="2">Pore-water velocity (v), cm/hr</td></tr>
<tr><td colspan="2">903</td><td>482</td><td>2.96</td><td colspan="2">7.60</td></tr>
<tr><td colspan="3">Average influent concentration (C_i), mg/L</td><td rowspan="2">Average influent pH</td><td rowspan="2">Average effluent pH</td><td rowspan="2">Total pore volumes</td></tr>
<tr><td>Cu</td><td>Pb</td><td>Zn</td></tr>
<tr><td></td><td>1.00</td><td>0.94</td><td>0.98</td><td>5.9</td><td>5.9</td><td>268.7</td></tr>
</table>

Time, hr	Effluent volume, mL	Pore volumes	Effluent concentration (C_e), mg/L			Experimental C_e/C_i			Fitted (Zn) [A]
			Cu	Pb	Zn	Cu	Pb	Zn	C_e/C_i
6.1	2958	3.3	*nd* [B]	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
10.2	4907	5.4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
17.7	8533	9.5	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
24.2	11655	12.9	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
34.3	16532	18.3	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
48.4	23290	25.8	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
72.4	34840	38.6	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
96.9	46650	51.7	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
121.5	58478	64.8	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
144.5	69586	77.1	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
168.6	81166	89.9	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.000
192.7	92770	102.8	0.01	*nd*	*nd*	0.01	*nd*	*nd*	0.000
216.7	104340	115.6	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.001
240.6	115866	128.4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.002
264.8	127490	141.2	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.003
288.7	139008	154.0	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	0.006
312.5	150448	166.7	*nd*	*nd*	0.01	*nd*	*nd*	0.01	0.010
336.6	162050	179.5	*nd*	*nd*	0.01	*nd*	*nd*	0.01	0.015
360.6	173614	192.3	*nd*	*nd*	0.02	*nd*	*nd*	0.02	0.021
384.4	185068	205.0	*nd*	*nd*	0.04	*nd*	*nd*	0.04	0.029
408.3	196612	217.8	*nd*	*nd*	0.04	*nd*	*nd*	0.04	0.039
432.2	208078	230.5	*nd*	*nd*	0.05	*nd*	*nd*	0.05	0.050
456.2	219633	243.3	*nd*	*nd*	0.06	*nd*	*nd*	0.06	0.063

Retardation factors (R)		Hydrodynamic dispersion coefficient (D), cm^2/hr		*MSE*
Mean	95% confidence interval	Mean	95% confidence interval	
512.9	(452.2, 573.5)	15.72	(10.53, 20.91)	9.34×10^{-6}

[A] Only BTC of Zn was fitted by transport model

[B] *nd*: not detected in the effluent

Table A10. Data from column leaching experiment of Cu, Pb, and Zn in Dougherty sand with 2.5% fly ash (D+2.5%F).

<table>
<tr><td rowspan="8">Column characteristics</td><td colspan="2">Inner diameter, cm</td><td>Length, cm</td><td>Bulk density (ρ), g/cm^3</td><td colspan="2">Porosity (θ)</td></tr>
<tr><td colspan="2">14.4</td><td>14.3</td><td>1.74</td><td colspan="2">0.343</td></tr>
<tr><td colspan="2">Pore volume, cm^3</td><td>Flow rate, mL/hr</td><td>Darcy velocity (q), cm/hr</td><td colspan="2">Pore-water velocity (v), cm/hr</td></tr>
<tr><td colspan="2">797</td><td>485</td><td>2.98</td><td colspan="2">8.69</td></tr>
<tr><td colspan="3">Average influent concentration (C_i), mg/L</td><td rowspan="2">Average influent pH</td><td rowspan="2">Average effluent pH</td><td rowspan="2">Total pore volumes</td></tr>
<tr><td>Cu</td><td>Pb</td><td>Zn</td></tr>
<tr><td>1.02</td><td>0.92</td><td>1.00</td><td>5.9</td><td>10.2</td><td>306.6</td></tr>
</table>

Time, hr	Effluent volume, mL	Pore volumes	Effluent concentration (C_e), mg/L			Experimental C_e/C_i			Fitted
			Cu	Pb	Zn	Cu	Pb	Zn	C_e/C_i
6.4	3102	3.9	*nd*[A]	*nd*	*nd*	*nd*	*nd*	*nd*	*unable to fit*
10.5	5069.0	6.4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
17.6	8516	10.7	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
24.5	11887	14.9	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
34.6	16802	21.1	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
48.7	23630	29.7	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
72.8	35302	44.3	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
97.3	47192	59.2	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
121.8	59064	74.1	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
144.8	70226	88.1	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
168.7	81846	102.7	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
192.8	93506	117.4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
216.7	105110	131.9	*nd*	*nd*	0.01	*nd*	*nd*	0.01	
240.5	116672	146.4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
264.6	128320	161.0	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
288.3	139844	175.5	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
312.0	151316	189.9	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
335.9	162914	204.5	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
359.9	174576	219.1	*nd*	*nd*	0.01	*nd*	*nd*	0.01	
383.8	186144	233.6	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
407.8	197798	248.2	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
431.7	209388	262.8	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
455.8	221068	277.4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	

[A] *nd*: not detectable in the effluent

Table A11. Data from column leaching experiment of Cu, Pb, and Zn in Dougherty sand with 5% fly ash (D+5%F).

<table>
<tr><td rowspan="8">Column characteristics</td><td colspan="3">Inner diameter, cm</td><td colspan="3">Length, cm</td><td colspan="3">Bulk density (ρ), g/cm^3</td><td colspan="3">Porosity (θ)</td></tr>
<tr><td colspan="3">14.4</td><td colspan="3">14.3</td><td colspan="3">1.84</td><td colspan="3">0.305</td></tr>
<tr><td colspan="3">Pore volume, cm^3</td><td colspan="3">Flow rate, mL/hr</td><td colspan="3">Darcy velocity (q), cm/hr</td><td colspan="3">Pore-water velocity (v), cm/hr</td></tr>
<tr><td colspan="3">708</td><td colspan="3">479</td><td colspan="3">2.94</td><td colspan="3">9.64</td></tr>
<tr><td colspan="6">Average influent concentration (C_i), mg/L</td><td colspan="2" rowspan="2">Average influent pH</td><td colspan="2" rowspan="2">Average effluent pH</td><td colspan="2" rowspan="2">Total pore volumes</td></tr>
<tr><td colspan="2">Cu</td><td colspan="2">Pb</td><td colspan="2">Zn</td></tr>
<tr><td colspan="2">0.98</td><td colspan="2">0.95</td><td colspan="2">0.96</td><td colspan="2">5.9</td><td colspan="2">10.3</td><td colspan="2">340.7</td></tr>
</table>

Time, hr	Effluent volume, mL	Pore volumes	Effluent concentration (C_e), mg/L			Experimental C_e/C_i			Fitted
			Cu	Pb	Zn	Cu	Pb	Zn	C_e/C_i
6.0	2885	4.1	*nd* [A]	*nd*	*nd*	*nd*	*nd*	*nd*	*unable to fit*
10.0	4790.0	6.8	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
18.7	8943	12.6	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
23.6	11316	16.0	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
33.5	16049	22.7	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
47.3	22650	32.0	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
71.1	34035	48.1	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
94.8	45396	64.1	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
118.8	56883	80.4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
142.7	68336	96.6	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
166.6	79761	112.7	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
190.5	91194	128.9	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
214.3	102619	145.0	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
238.2	114052	161.2	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
261.9	125401	177.2	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
286.2	137042	193.6	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
310.6	148715	210.1	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
334.8	160318	226.5	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
359.1	171951	243.0	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
383.4	183596	259.4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
407.7	195215	275.8	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
431.7	206726	292.1	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
455.5	218105	308.2	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
479.6	229648	324.5	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	
503.5	241089	340.7	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*	

[A] *nd*: not detectable in the effluent

Table A12. Spatial distribution of non-eluted heavy metals in soil columns (unit: mg/kg).

Distance, cm	Dougherty sand			D+2.5%F			D+5%F		
	Zn	Pb	Cu	Zn	Pb	Cu	Zn	Pb	Cu
After correction based on mass balance									
1	82.9	274	193	172	289	304	356	378	374
3	85.4	117	123	133	94.8	89.9	26.2	0.0	11.4
5	95.5	47.6	92	83.1	25.8	27.7	0.2	0.0	0.0
7	83.7	0.0	40.1	25.7	0.0	3.8	0.0	0.0	1.1
9	59.5	0.0	9.1	8.6	0.0	1.0	0.0	0.0	1.5
11	27.0	0.0	0.9	1.8	0.0	2.6	0.0	0.0	0.8
13	4.0	0.0	0.0	3.0	0.0	2.1	0.0	0.0	0.8
Before correction based on mass balance									
1	76.5	171	144	107	108	131	405	403	454
3	85.4	117	123	133	94.8	89.9	26.2	0.0	11.4
5	95.5	47.6	91.9	83.1	25.8	27.7	0.2	0.0	0.0
7	83.7	1.0	40.1	25.7	0.0	3.8	0.0	0.0	1.1
9	59.5	0.4	9.1	8.6	0.0	1.0	0.0	0.0	1.5
11	27.0	0.6	0.9	1.8	0.0	2.6	0.0	0.0	0.8
13	4.0	0.5	0.0	3.0	0.0	2.1	0.0	0.0	0.8

Table A13. Saturated hydraulic conductivity of Teller loam, expanded shales, Dougherty sand, and Dougherty sand amended with various levels of fly ash.

Materials	Bulk density (ρ), g/cm^3	Hydraulic conductivity (K_s), cm/hr
Teller loam	1.28	0.30
Expanded shale (Marquette, KS)	0.87	39.2
Expanded shale (New Market, MO)	0.81	54.0
	0.97	19.1
Dougherty sand	1.48	26.9
	1.52	40.3
Dougherty sand with 2.5% fly ash	1.60	13.1
	1.57	14.2
Dougherty sand with 5% fly ash	1.63	3.24
	1.73	2.30
	1.60	6.20
	1.52	6.13
Dougherty sand with 7.5% fly ash	1.69	1.07
Dougherty sand with 10% fly ash	1.74	0.31
	1.72	0.48

Table A14. Saturated hydraulic conductivity of Dougherty sand, D+2.5%F, and D+5%F in extended saturation time.

Time, day	Hydraulic conductivity (K_s), cm/hr		
	Dougherty sand	D+2.5%F	D+5%F
0	26.9	14.2	6.20
1	24.2	9.17	1.47
2	22.1	8.64	1.19
4	21.7	7.39	1.10
7	23.1	6.67	1.01
14	24.3	5.81	0.89
17	26.4	5.82	0.91
21	28.6	5.66	0.92
25	26.8	5.37	0.88
28	31.4	5.50	0.91

VITA

WEI ZHANG

Candidate for the Degree of

Master of Science

Thesis: IMPROVEMENT OF PHOSPHORUS AND HEAVY METALS RETENTION IN STORMWATER TREATMENT

Major Field: Biosystems Engineering

Biographical:

Personal Data: Born in Zhongxiang, Hubei, China, on September 27, 1977, the son of Shichuan Zhang and Yuqing Li.

Education: Graduate from Zhongxiang First High School, Hubei, China in 1996; received Bachelor of Science degree in Environmental Chemistry from Nanjing University, Nanjing, China in July 2000. Completed the requirements for the Master of Science degree with a major in Biosystems Engineering at Oklahoma State University in July 2006.

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Professional Memberships: American Society of Agricultural and Biological Engineers, American Society of Civil Engineers

Name: WEI ZHANG Date of Degree: July, 2006

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: IMPROVEMENT OF PHOSPHORUS AND HEAVY METALS RETENTION IN STORMWATER TREATMENT

Pages in Study: 91 Candidate for the Degree of Master of Science

Major Field: Biosystems Engineering

Scope and Method of Study: The objectives of this study were to find filter media with high phosphorus sorption and adequate hydraulic conductivity for use in bioretention cells, and to evaluate the improvement of heavy metals retention in sandy soil after amending with fly ash. The pollutant retention capacity of a filter media is an important consideration in stormwater infiltration systems. Batch sorption experiments were used to screen filter media. Column experiment and transport modeling allowed the evaluation of phosphorus and heavy metals sorption capacity of filter media in a dynamic condition.

Findings and Conclusions: Soils had a low phosphorus sorption. Fly ash had the highest phosphorus sorption. The addition of fly ash in soils increased the phosphorus sorption, but decreased the hydraulic conductivity. Sandy soil amended with fly ash exhibited a high phosphorus sorption while maintaining adequate hydraulic conductivity. Sandy soil had the lowest heavy metals sorption while fly ash the highest. The addition of fly ash in sandy soil increased the heavy metals sorption. These results will provide valuable information for the practical use of fly ash in amending soils to improve phosphorus and heavy metals retention in stormwater infiltration systems such as bioretention cells.

ADVISER'S APPROVAL: Glenn O. Brown