PHOSPHORUS REDUCTION IN RUNOFF USING A
STEEL SLAG TRENCH FILTER SYSTEM

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PHOSPHORUS REDUCTION IN RUNOFF USING A
STEEL SLAG TRENCH FILTER SYSTEM

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Abstract: Excessive concentrations of phosphorus (P) can lead to the deterioration of surface waters by eutrophication. The objective of this study was to evaluate the performance of a steel slag trench filter system developed for P reduction in runoff under field conditions. The experimental design for the study was a 2 x 2 factorial with factors of filter material (6 mm steel slag or 13 mm washed river gravel) and triple superphosphate fertilizer (P applied or no P applied) replicated within irrigation zones covered with 'Astro' bermudagrass [Cynodon dactylon L. (Pers.)] mowed at 38 mm. Each irrigation block consisted of four plots that were 6.1 m wide with a uniform 5% slope that measured 24.4 m long. Four plastic containers (volume = 178 L each) were placed in a 5.2 m $\times$ 1.2 m trench dug in the middle of each plot perpendicular to the slope to accommodate filter materials. Runoff caused by either natural rainfall or irrigation was collected for comparison of P concentrations before and after filtration. Flow rates were determined using ultrasonic depth detection devices as runoff flowed through calibrated Parshall flumes. From March through September 2012 a total of 14 runoff events were studied. Runoff filtered by steel slag contained from 17% to 43% less dissolved P than runoff filtered through an inert gravel control. The P concentrations in runoff from the fertilized treatment were always greater than the unfertilized treatment. The difference between P concentrations from the fertilized and unfertilized treatments declined with each runoff event from 9.48 mg L^{-1} in the initial event after fertilization to 0.20 mg L^{-1}, 120 d and nine runoff events later. A previous P removal model developed by Penn and McGrath (2011) overestimated the maximum P loading potential of the slag filter structures (460 mg kg^{-1} vs. 269 mg kg^{-1} calculated from actual data), as well as the maximum P removal before the filters were spent (35.7 mg kg^{-1} vs 8.3 mg kg^{-1}). The overestimation of the performance of the P removal structure probably occurred because the slag used in this study had "inferior" P sorption qualities than that used for model development.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

LITERATURE REVIEW

According to a survey from the 2000 National Water Quality Inventory from the United States Environmental Protection Agency (USEPA), 39% of the rivers, 45% of the lakes and 51% of the estuaries in the United States are polluted. Eutrophication is the major factor that leads to widespread and significant water body problems. A myriad of consequences following eutrophication include blooms of undesirable algae, oxygen shortage, low quality drinking water and fish kills. Eutrophication is caused by an accelerated growth of algae and higher forms of plant life caused by the enrichment of nutrients in water (Correll, 1998). When these algae and plants die, they are degraded by aerobic bacteria. The degradation of this massive amount of dead biological material depletes oxygen in the water resulting in eutrophication. Even though nitrogen (N) and carbon (C) also contribute to the growth of aquatic biota, phosphorus (P) is often the limiting element, especially in fresh water (Daniel et al., 1998). Nitrogen is often the limiting element in marine water (USEPA, 1993). Phosphorus is an essential element for plant growth, and its presence is necessary to increase the biological productivity of surface waters (Daniel et al., 1998). However, it is clear from many sources of scientific literature that high concentrations of P can lead to eutrophication of surface waters. Phosphorus plays a key role (Sims et al., 1998) and may be the primary cause of the eutrophication of surface waters (Carpenter, 2005; Correll 1998). According to Sharpley et al. (2000), the best way to minimize eutrophication is to control the P concentration in drainage water. Phosphorus is believed to contribute to the eutrophication of surface water bodies at concentrations as low as 0.025 mg L^{-1} (Walker and Branham, 1992)

and total P concentrations exceeding 0.1 mg L^{-1} total P are unacceptably high for most lakes, streams, reservoirs, and estuaries (Daniel et al., 1998).

Agriculture and urban runoff

Pollutants from storm sewers are among the leading causes and sources of impairment of water bodies (USEPA, 2002). This is mainly due to the high input of phosphorus fertilizer and eutrophication caused by it. Eutrophication is hard to reverse because high concentrations of sediments keep releasing phosphorus to maintain a stable eutrophic situation (Carpenter, 2005). The P in runoff exists in either particulate or dissolved forms. Sharply et al. (1992) found that 60-90% of the P transported from most cultivated land is particulate P combined with soil particles and organic matter. When runoff occurs from grassland or turfgrass, P loss is mostly associated with dissolved P because grassland soils are not as erosive as cultivated land. This dissolved P is immediately biologically available. Sediment P is not immediately biologically available but can be a long slow release source of P whose bioavailability varies from 10% to 90% depending on soil types and nature of the receiving water bodies (Daniel et al, 1998).

The loss of P can be transported by either surface or subsurface flow. Generally speaking, P transport occurs in surface runoff and P loss from leaching and subsurface flow is small due to its low mobility in soils (Sims et al., 1998). However, P leaching can be an important factor in deep sandy soils and locations with artificial drainage systems. Allleoni et al. (2008) pointed out that phosphorus leaching can be extreme and represents a great concern in many Florida and other coastal plains soils with low P-sorption capacities. For instance, He et al. (2006) investigated the transportation of P from sandy soil used for agricultural production in South Florida. They found half of the sampled concentrations were higher than 1 mg L^{-1}, which is much higher than P critical levels. In a water quality study established in Illinois, Algoazany et al. (2007) found

subsurface drainage removed 16.1% of rainfall and runoff removed 2.6% of rainfall that occurred on four plots with artificial drainage systems typically used for agriculture. In this case, subsurface flow had greater soluble P loads than surface runoff due to greater flow volume. Phosphorus in subsurface flow is also a problem for artificial terrains dominated by sand such as golf course greens and athletic fields because of the high infiltration rates and low P sorption characteristics of sand (Soldat and Petrovic, 2008).

Phosphorus transport in runoff and subsurface drainage can be influenced by many factors such as rainfall intensity and timing, P application rate and method, soil properties and vegetative cover. Various best management practices (BMPs) can be applied to minimize P loss. For example, Shuman (2004) found that "watering in" the fertilizer with 0.64 cm of irrigation and waiting 3 d before applying precipitation to simulate a runoff event substantially decreased the amount of N and P in the runoff collected compared with events on the site where the fertilizer was not "watered in" and the period between application and precipitation to runoff was only 4 h. In addition to other environmentally sound management practices, grass buffer strips and vegetated waterways are two commonly employed BMPs for minimizing sediment loss from agricultural areas (Sims and Kleinman, 2005). Moss et al. (2006) found that graduated buffers of increasing height resulted in 17% less N, 11% less P, and 19% less runoff volume during 60 min of natural rainfall runoff and 18% less N and 14% less P during 60 min of irrigation runoff. The reduction in P loss by buffer strips was achieved mainly by reduced runoff volume rather than by reducing the concentration of dissolved reactive phosphorus (DRP). Fiener and Auerswald (2009) monitored watersheds with and without grassed waterways for five years and both types of watershed showed very similar dissolved P concentrations. They concluded that rough grassed waterways only had a small influence on DRP concentration.

Application of P sorbing materials (PSMs) is the most commonly applied method to reduce dissolved reactive phosphorus (DRP) concentrations from runoff waters. The main sorbing components in most PSMs are aluminum (Al), iron (Fe), calcium (Ca), and/or magnesium (Mg). Calcium and Mg remove P by precipitation reactions and Fe and Al sorb by adsorption and ligand exchange (Penn et al., 2010). Traditional PSMs include products such as alum (aluminum sulfate) and gypsum (calcium sulfate). A wide range of industrial byproducts also can be used as PSMs such as steel slag and water treatment residuals.

Amending soil with PSMs

Incorporation of PSMs into soil with excessive P, blending PSMs with nutrient sources, and surface application of PSMs are three of the most traditionally employed methods to reduce P loss from agricultural land (Wagner et al., 2008). The effectiveness of PSMs for reducing dissolved P from runoff on various surface types has been widely studied. For example, according to Vietor et al (2010) during early turf establishment, both surface spray of Alum or incorporation of Alum into soil effectively reduced dissolved P and total P from runoff. Chimney et al. (2007) broadcasted $CaSiO_3$ slag as a soil amendment to an organic soil after flooding, and the flux of topsoil P was reduced by 84% compared to the unamended soil control. However, little effect in reducing P concentration was observed by incorporating the same material into the soil. Gallimore et al. (1999) tested the effectiveness of water treatment residuals as a PSM. From bermudagrass pasture plots receiving poultry litter, the surface broadcast of water treatment residuals (WTRs) at 44.8 mg ha^{-1} combined with buffer strips reduced dissolved P concentrations significantly from 15.0 mg L^{-1} to 8.1 mg L^{-1} from runoff waters produced by simulated rainfall for 75 min. However, in a similar study conducted by Wagner et al. (2008), top dressed WTR (20 mg ha^{-1}) on buffer strips failed to provide statistically significant lower total P and dissolved P

compared to plots with non-treated buffers. The authors concluded that this was due to insufficient runoff contact and residence time with the WTR. Penn and Bryant (2006) conducted a study to assess the ability of several PSMs for reducing P loss from streamside cattle loafing areas. Four kinds of PSMs (alum, water treatment residuals, and fly-ash) were incorporated into soil, and runoff was produced by simulated rainfall 7 days and 28 days after incorporation. At three study sites, all of the PSMs reduced dissolved P concentrations in runoff compared to the untreated control after 7 days but these results were only statistically significant for two of the three sites. At 28 days after application, the significant differences between PSM treated plots and control plots disappeared. The authors concluded that the application of PSMs provides only temporary effects on dissolved P concentrations in runoff. In addition, the direct alum application (100 mg ha^{-1}) onto one of the grassed plots resulted in damage to the grass stand due to increases in acidity and Al toxicity. From an effectiveness perspective, the authors presumed that applying PSMs into runoff may be more effective than direct application to soils because the high P soils saturated the PSMs too quickly (Penn and Bryant, 2006).

The effectiveness of long-term direct application of PSMs to soil has been questioned by many other researchers. According to Watts and Torbert (2009), four different rates of gypsum were surface applied to the buffer strips of a tall fescue pasture. During 30 min of simulated runoff immediately following the gypsum application, gypsum reduced soluble P concentration by 32 - 40%. While in second simulated runoff events four weeks after the initial runoff event, the effectiveness of gypsum disappeared. Thus, they concluded gypsum only provides a short-term solution for reducing soluble P.

The Performance of PSMs used in P removal structures under field trials

Many studies have been conducted to evaluate the performance of PSMs applied directly to water bodies. For instance, Leytem and Bjorneberg (2005) evaluated the effect of alum on soluble P concentrations in return flow water. In the field, following application of 40 mg L^{-1} alum to return flow water produced by agricultural irrigation, soluble P concentrations were reduced by up to 98%. However, the researchers also pointed out the expense of routine applications of alum. Penn et al. (2007) discussed the importance of removing P from drainage ditch water. Based on their previous research, the application of PSMs to hydrologically active areas could provide temporary targeted control of excessive P. The researchers suggested that PSM filled structures located in drainage pathways could provide the ultimate removal of dissolved P because the sorbed P would remain within the ditch filter structure. Many P removal structures have been built and their P-sorption performances evaluated.

Penn et al. (2007) developed a phosphorus removal structure installed in a ditch where the annual soluble P load was approximately 13 kg by flow from local agricultural farms. The removal structure was filled with approximately 200 kg of acid mine drainage residuals as the PSMs and was expected to sorb more than half (~7 kg) of the annual P load. During one storm event, 99% of the dissolved P was removed from water that flowed through the structure. However, the goal for removal of 50% of the annual P load was not achieved because during some extreme events, the flow produced in the ditch exceeded the flow parameters of the structure.

Shilton et al. (2006) conducted a full scale application of steel slag, a byproduct of steel manufacture, as a P filter media in filter beds at a wastewater treatment plant in New Zealand. High P concentration wastewater effluent was distributed at one end of the filter beds through perforated pipes at the filter surface and then flowed through filter media to be collected by a

buried pipe at the downstream end. The filter was used for a period of 11 years (1993-2004). The plant achieved 77% total P removal efficiency during the initial five years. Although the efficiency decreased significantly after the sixth year, the result was still impressive considering the relatively high inflow P concentration (8.2 mg L^{-1}).

A P removal structure designed by Penn et al. (2012) was constructed in a drainage ditch and filled with steel slag at the outlet of a watershed consisting of residential, undeveloped, and golf course property. The treated water consisted of a minor amount of drainage water from nearby irrigated golf greens and runoff produced by rainfall. During a five-month period, the structure captured 25.9 mg P kg^{-1} which accounted for 25.2% of the total dissolved P that flowed through the ditch.

Agrawal et al. (2011) installed a filter structure filled with media mixed of blast furnace slag, zeolite, coconut-activated carbon and a cement kiln dust/sand mixture at a golf course in Waco, TX. The filter was expected to remove phosphate (PO_4^{3-}) and pesticides. A P fertilizer and pesticides were applied 30 min before a simulated rainfall of six hours produced by sprinkler irrigation. The results indicated that the filter captured 22% $\pm$ 4.5% of the PO_4^{3-} in drainage when the inflow rate was below 0.037 L s^{-1}. This accounted for 0.19% reduction in the total incoming P load. However, when the inflow rate was higher than 0.037 L s^{-1}, the mixed filter media added in excess of 146% of the incoming PO_4^{3-} to the outflow (inflow of 3086.10 mg vs outflow of 7605.29 mg).

Chan et al. (2008) assessed the wastewater treatment ability of a pilot scale "vegetated sequencing batch slag bed" which is a system consisting of coal slag as a substrate and biofilm formed by vegetation on the coal slag. Pollutant removal efficiencies were calculated by treatments with different wastewater contact time from 0 h minimum to 18 h maximum. The

system removed 40% of the total P input during a ten month period. A smaller scale test was also completed under lab conditions in which tanks filled with vegetative biofilm coated slag were used to filter municipal water using a contact time of 18 h. Approximately 42% of the total P input was removed by the system mainly by adsorption (at least 69.1% of the total P removed) and microbial processing (26.2% of the total P removed).

Volha et al. (2007) studied the performance of a P filter bed filled with oil-shale ash as filter material constructed near a wetland system whose outflow entered the filter bed. The filter bed size was 4.75 x 2.5 x 0.4 m and contained about 1400 kg of ash. The ash was isolated from the ditch bed with a polyethylene membrane at the bottom and sides. The filter structure removed 71% of the total P input during the operation of the first four months at retention times of 1.3 – 2 d. However, the performance of the ash decreased after four months due to an increase in annual water discharge and increasing P concentrations up to 3.5 to 6.0 mg L^{-1} P.

McDowell et al. (2008) conducted a field trial to assess the P sorbing ability of several industrial byproducts. In the field trials, two slag treatments and a control treatment were backfilled at tile drain outputs to filter P from drainage. For 12 drainage events during a period of two years, the mean dissolved P and total P concentration from slag treatments were significantly ($P<0.05$) lower than those of a control treatment.

The Performance of PSMs in Laboratory Trials

Batch isotherm experiments have been widely used at the laboratory scale to assess the P sorption ability of soils or materials that attract phosphate ions. The results of these trials may be used as criteria for selecting the most suitable materials (Cucarella and Renman, 2009). For example, as early as 1986, Yamada et al. (1986) utilized steel slag as a filter material to remove P from wastewater. In a batch isotherms study, the amount of P adsorbed increased rapidly and the

percentage of phosphate adsorbed decreased gradually at P concentrations from 0 - 400 mg L^{-1}. The slag adsorbed most P at a pH range of 7 - 8 and the adsorption decreased rapidly below pH 6 and above pH 8. In addition, under the same conditions, slag with larger porosity adsorbed much more P than slag with smaller porosity. Kaasik et al. (2008) studied the P removal ability of oil-shale ash, which is a byproduct of oil-shale with a high content of reactive Ca materials. Its sorption mechanism is mainly by precipitation. In a batch experiment 67 - 85% of dissolved P was removed and maximum sorption was 65 mg P g^{-1} at a contact time of 48 h. Sakadevan and Bavor (1998) compared the P sorption ability of soils and steel slags in a batch isotherm study. At higher P concentrations (>200 mg L^{-1} P), blast furnace slag and steel slag could still adsorb more than 50% of the applied P. Cucarella and Renman (2009) summarized several batch studies that had been conducted prior to 2008 and suggested that the P sorbing capacity determined by batch studies was relative because it was estimated under different conditions. The data strongly depend on the experimental procedure itself and on parameters like the amount of the material, the material to solution ratio, the pH of the solution, the initial concentration of the P solution, the contact time, the amount of agitation, and the temperature of the reaction. Since most of the batch experiments reviewed had been studied under different parameters, the results were difficult to compare. In addition, a batch experiment does not necessarily simulate true field conditions where flows through the system vary constantly. The batch experiment is a "closed" system in which all of the substances are consistent and contained. Also, in a batch experiment, the whole surface of the material is exposed to the P solution while in field conditions the total surface exposed to P is limited by the packing or compaction of the materials. Consequently, the P removal ability of the materials could be overestimated by batch experiment results (Cucarella and Renman, 2009). An alternative to a batch isotherm experiment is a column study in which a P

containing solution flows continuously through a column filled with PSMs. A column study is more representative of field conditions where water flows through the filter system rather than residing within it. Sometimes column studies are combined with batch studies to assess the P removal ability of certain materials. For instance, Sibrell et al. (2009) conducted a series of lab tests on the P sorption ability of six acid mine drainage sludges with different composition and physical properties. The batch method results showed that the sludge containing both Al and Fe performed best and could adsorb 20,000 mg P kg^{-1} at a concentration of 1 mg L^{-1} P. In column tests, by alternating flow between a pair of adsorption columns on a 12-h basis, the P adsorption ability of the sludge increased dramatically. Over 160 days, 60% of the P from a continuous waste stream with a P concentration of 0.13 mg L^{-1} was removed at a relatively fast wastewater flux rate (169 L min^{-1} m^{-2}). Wei et al. (2008) tested the P removal ability of acid mine drainage sludge which was composed mainly of iron and aluminum hydroxides using batch adsorption and column studies that included a parameter of hydraulic retention time. In the batch study, 1 g L^{-1} acid mine drainage sludge removed 95% of the dissolved P (from 20 mg L^{-1} to 1.08 mg L^{-1} P solutions) during a mixing time of 1 h. Approximately 89% of the P was removed during the first 5 min. The authors also determined that high pH inhibited P adsorption by AMD sludge and its adsorption ability favored a neutral or slightly acidic pH. Ferrihydrite was responsible for most of the P adsorption. Dissolved metal concentrations were examined at a pH range of 6 to 8 and no appreciable metal leaching was detected. In the continuous adsorption study under retention times of 1 h, 1 g L^{-1} acid mine drainage sludge removed 91% of the dissolved P (outflow 1.80 mg L^{-1} vs. 20 mg L^{-1} inflow) Bowden et al. (2009) examined the P removal ability of basic steel slag in both batch and column experiments. For the batch experiment, the highest P removal was observed at pH 12 and precipitation was the dominant removal mechanism when pH > 8. For the column

experiments which were performed continuously for 406 days, basic steel slag removed up to 62% P at retention times between 8 h and 22 h. Penn and McGrath (2012) suggested that retention times > 1 h are more suitable to wetland treatment systems where the flow rates are much lower than those of P removal structures installed in ditches that receive convergent flows. Stoner et al. (2012) developed a flow-through procedure to determine how retention time and P concentration affect P removal for several industrial by-products capable of P sorption. A small amount of slag was placed in a flow-through cell and the bottom of the cell was connected to a single channel pump using plastic tubing. The desired retention time was achieved by adjusting the pump flow rate. By using a reasonable retention time for runoff water to pass through a P removal structure this procedure was deemed suitable to simulate the performance of a landscape-scale filter structure in which contact between flow and sorption materials is limited. The research indicated that under the flow-through settings, increased P removal among materials was most likely to occur via precipitation, whereas retention time had little effect on materials that remove P via ligand exchange. Penn and McGrath (2012) also used this model to compare the predicted P sorption ability of a pond filter from a flow-through model and a Langmuir model developed from batch isotherms. During 22 days, the pond filter removed 88 mg P kg^{-1}, which was quite similar to the prediction of 59 mg kg^{-1} using a flow-through model. The batch isotherm model, however, overestimated the P removal predicting removal of 329 mg kg^{-1}.

The N removal performance of PSMs

Some researchers reported that PSMs are also capable of N removal. For instance, Renman et al. (2008) conducted a column study to test the N removal ability of several slags. Wastewater was pumped and sprinkled over the surface area of a 0.5 m long column containing slag at 0.5 L h^{-1} for 67 weeks at a daily hydraulic loading rate of approximately 85 L m^{-2} d^{-1}. The influent

concentrations of NH_4-N and NO_3-N were 26.6 ± 5.5 and 26.9 ± 12.6 mg L^{-1} respectively. After about one week, the concentration of NH_4-N leaving the column was < 1 mg L^{-1} and overall 90% of the NH_4-N was removed at the end of experiments regardless of the filter material. The decreased effluent concentration of NH_4-N was due to microbial immobilization and nitrification for some columns while for columns with effluent pH above 9.3, the decreased NH_4-N concentration was caused by volatilization as NH_4^+ was converted to NH_3. Despite the apparent removal of NH_4-N, the removal of NO_3-N was not observed and NO_3-N leached from most of the columns. During the operation of "the vegetated sequencing batch slag bed" (Chan et al., 2008), under laboratory conditions, 37% of dissolved N entering the system was removed. However, rather than chemical removal, the removal of N was mainly achieved by microbial processing which accounted for 69% of the total N removal. Adsorption was responsible for approximately 20% of the total N removed. Under pilot scales, the "vegetated sequencing batch slag bed" removed 50% of the ammonium nitrogen. In addition, in a study conducted by Volha et al. (2007), a filter bed filled with oil-shale ash was reported to remove 20% of the total N input.

Main factors that influence the P removal efficiency of PSMs

Flow rates and retention time

Hydraulic flow plays a vital role in the effectiveness of a filter. Rapid flow rates lead to shorter retention times and less surface contact area, therefore lower removal efficiency. Agrawal et al. (2011) speculated that the high flow rate and very short retention time (< 1 min) in their study caused limited contact among filter materials and hydraulic flow. In Penn et al. (2012) the filter removed dissolved P from irrigation runoff (62%) more efficiently than that from rainfall (21%). Since 75% of the runoff transported into the structure was from the six largest rainfall events that occurred during the study, it is quite possible that the difference in efficiency among irrigation

and rainfall events was due to the high P concentrations and rapid flow rates produced by the intense rainfall events. In addition, large rainfall events resulted in shorter retention time (8.9 min) compared with irrigation events (50 min) which was negatively correlated with P removal efficiency. In an experiment conducted by McDowell et al. (2008), who simulated drain flow using a continuous flow of P solution, P uptake with PSMs performed better at low flow rates, and poorer at higher flow rates. Therefore, the 77% total P removal efficiency obtained over the initial 5 years at the wastewater treatment plant in New Zealand (Shelton et al., 2006) is not likely to be achieved by a ditch filter with faster flow rates and less retention time (Penn et al., 2012).

pH and redox potential

Solution pH is an important factor affecting P removal efficiency. Different PSM's have individual optimal pH ranges for maximum P sorption. For example, generally speaking, steel slag reaches its highest P removal efficiency at alkaline conditions, while acid mine drainage sludge prefers a neutral to acid pH range for maximum P sorption. Pratt et al. (2007) examined the influence of pH and Eh (redox potential) on the P sorption efficiency of melter slag. Exhausted melter slag samples were obtained from filter beds and were examined in a lab at various pH and Eh combinations. The research indicated that P release from melter slag filters was significantly influenced by changes in both pH and Eh. The P removal efficiency of melter slag filters was optimal at oxidizing Eh and neutral pH. Reducing Eh and acid pH were favorable for P release. In the lab test, 95% of total P was released from exhausted slag samples at the lowest Eh (400 mv) and lowest pH (4.9) levels. In practice, low-oxygen water usually diminishes the capacity of slag to adsorb P because low-oxygen is generally characterized by reducing Eh levels. In addition, in high P concentrated water containing algal blooms the use of CO_2 during

algae metabolism may increase the pH of the water to a point where a P desorption reaction could occur.

Estimation of PSMs lifespan

The lifespan of a filter structure is also an important parameter to assess its utility. Some researchers attempt to predict the effective lifespan of the PSMs in their filter structures. The most common way to make this prediction is to multiply the filter structure volume by its P removal capacity per unit of filter material. For example, Chan et al. (2008) estimated the effective lifetime of their system was 8 years by presuming that the maximum adsorption ability would remain the same. McDowell et al. (2008) estimated the lifetime of backfilled slag using the mean P uptake (80% of per ha loss) estimating that it would take about 60 years for P retention to cease. However, this is not the case. Many articles have indicated that the P removal ability of filter materials decreases with cumulative P treated. For instance, according to the research of Volha et al., (2007), the design capacity for the filter material studied was 4 g P kg^{-1} and it was estimated to sorb P effectively for 1.5 years. In reality, the filter was saturated after 4 months of use. Its sorption ability was 1.2 g P kg^{-1} during fall 2002 while in 2003 and 2004 its sorption ability dropped to 0.8 g kg^{-1} and 0.5 g kg^{-1}, respectively. A more accurate way to predict the longevity of the filter material in a structure is to base its effective lifetime on models developed from previously related research. Specifically, for a ditch flow filter structure with a rapid flow rate, a flow-through model (Stoner et al., 2012) can be useful for predicting discrete and cumulative P removal and the longevity of the PSM. Models can be helpful to screen for materials that have potential for use as PSMs and to predict total P removal for a landscape P filter structure with a known P loading. Penn et al. (2012) predicted the lifetime and performance of a filter structure using a model developed by Stoner et al., (2012). The results suggested that

the potential lifetime of the structure was 16.8 months which was quite close to its actual lifetime of 15.4 months. However, the flow-through equations overestimated the actual P removal (79 vs. 26 mg P kg^{-1}) by the P removal structure. The differences between the prediction and field measurements were due to the variability in slag chemical properties between the slag used in the P removal structure and that used for development of the flow-through equations. Therefore, the equation may be limited to predicting the performance of filter materials with the same chemical properties and a universal model that considers chemical properties in addition to retention time and P concentrations is needed.

Spent PSMs rejuvenation and treatment

Penn et al. (2011) treated P-saturated slag with aluminum sulfate solution in an effort to extend its useful life. Different chemical properties such as lower pH were observed from the rejuvenated slag compared with normal slag. After two weeks, normal slag and rejuvenated slag in a pond filter removed 38% and 36% of dissolved P, respectively. Pratt et al. (2009) investigated several physical techniques to rejuvenate exhausted melter slag but none of the methods were successful for long-term rejuvenation. In the study, exhausted slag was dried, agitated, crushed and placed in a column that was continuously fed with pond water at a retention time of 12 h. Results indicated that the treated exhausted slag achieved higher P removal efficiency than untreated saturated slag but the long term difference was small (7%). The treated slag had over 40% P removal efficiency in the first two months but its efficiency fell rapidly to approximately 7%. Hylander and Siman (2001) investigated the prospective usage of saturated P sorbing materials as P fertilizers. The researchers compared the plant available P from P fertilizer applied as K_2HPO_4 with P from eight different saturated PSMs. These PSMs were soaked in a P solution, rinsed and dried and then incorporated into a P-depleted agricultural soil maintained at 60%-80% of water holding capacity

at the same P quantities comparative to K_2HPO_4. The results showed most of the PSMs increased the dry matter of treated plants compared with a no P check and the application of crystalline slag at 0.2 μmol P g $^{-1}$ led to higher yields than the application of fertilizer P. One thing worth noting was that the materials used in the experiment were finer (< 4 mm) than most PSMs. Coarse materials that have a high hydraulic conductivity have less surface contact area with soil and may reduce the efficiency of P sorbed by plants. However, if the PSMs can sorb other pollutants such as trace metals, its usage as a P fertilizer in agriculture after P saturation must be considered (Westholm, 2006).

Summary

The use of industrial byproducts as PSMs has been studied extensively under both lab and field conditions. Compared to traditional methods of applying PSMs directly to soils or water bodies, ditch filters are an innovative means of controlling the amount of P that enters surface water. Phosphorus filter structures built in hydraulically active ditches have demonstrated promise for reducing P runoff or drainage losses permanently. However, traditional batch and column studies may not be entirely suitable for screening the PSMs used in ditch filters. Up to now, large scale field studies of ditch filter systems are rare and data for model development is limited. Therefore, a more complete flow-through model suitable for predicting the P sorption ability and lifetime of ditch filters is needed and larger scale field studies are required to determine the actual efficiency of filter structures.

CHAPTER II

MATERIALS AND METHODS

Site description

This research was conducted on the Oklahoma State University Turfgrass Runoff Research Site, Stillwater, OK. The soil at the site was a Norge silt loam (fine-silty, mixed, active, thermic Udic Paleustolls) with a pH of 6.9 and an infiltration rate of 13 mm h^{-1}. Soil texture was 43% sand, 37% silt, and 20% clay with organic matter of 2.6%. Prior to the study the soil contained 69 mg kg^{-1} P according to Bray 1 method. The experimental design for the study was a 2 x 2 factorial with factors of filter material (6 mm steel slag or 13 mm washed river gravel) and triple superphosphate fertilizer (P applied or no P applied) replicated within irrigation zones. For this study, half the experimental units were filled with river gravel (control) and half with electric arc furnace slag (steel slag). The river gravel was sieved to approximately 13 mm and the steel slag was sieved to 6 mm or larger. Although most of the runoff collected was caused by natural rainfall events, it was sometimes necessary to simulate rainfall using the onsite sprinkler irrigation system. Consequently, the runoff site was divided into three large blocks by irrigation zone.

Each irrigation block consisted of four plots that were 6.1m wide with a uniform 5% slope that measured 24.4 m long. Earthen mounds that confined runoff to the area under investigation separated experimental units and blocks. An in-ground sprinkler-type irrigation system that delivered a precipitation event of 28.5 mm h^{-1} was located along the edges of every two plots. The site was sodded with 'Astro' bermudagrass [Cynodon dactylon L. (Pers.)] in 1998. The site was mowed at 38 mm to simulate a home lawn or golf course rough. Each plot was divided equally

17

into an upper experimental unit and a lower experimental unit by a 5.2 m × 1.2 m trench that was dug perpendicular to and in the middle of the slope. These trenches were covered continuously to prevent rainfall from entering the trenches directly during a rainfall event. The slopes on the earthen mounds on each side of the plots accounted for approximately 0.6 m on each side of the plot so the trench did not have to be quite as wide (5.2 m) as the plot to collect all of the runoff that flowed from the plot. Four plastic containers (Volume = 178 L each: Doerr 178 L stock tanks, Ace Roto-Mold, Hospers, IA.) were placed in each plot trench in a line perpendicular to the slope to accommodate filter materials. These containers were used to allow reasonably rapid replacement of PSM material during or between studies but were not changed during this study. The plastic containers in half the plots were filled with steel slag to a height of 5.1 cm below the top of the containers. Based on the bulk density (1.8 g cm^3) of the slag, approximately 252 kg slag was filled into each tub and a total of 6048 kg of slag in the six slag treatment plots. The total pore space of slag (1276 L) was calculated based on the total mass (6048kg), bulk density (1.8 g cm^3), and porosity (38%). The containers in the six remaining plots were filled with river gravel to a height of 5.1 cm from the top of the containers for use as an experimental control. Prior to container placement rubber pond liners (EPDM Pond Liner, Firestone Building Products, Indianapolis, IN) were used to cover the bottom of the trench to prevent runoff from leaching into the soil. A 10-cm diameter polyvinyl chloride (PVC) perforated drain pipe was placed in the trench over the liner and surrounded by concrete sand (Stillwater Sand and Gravel, Stillwater, OK) to support the weight of the plastic containers above it. Before filling the plastic containers with filter material, the bottom of each container was drilled with 13 holes with a diameter of 2.5 cm. A piece of 170 g geotextile fabric (Firestone) surrounded the perforated drain pipes to keep the sand from infiltrating into the pipe. The holes in the bottom of the tub, the concrete sand surrounding the drain pipe, and the number and size of perforations in the drain pipe forced runoff to drain slower than it would normally drain through the steel slag prolonging its contact time with the slag but allowing for rapid enough drainage to prevent water from running over the

18

trench. In a field situation where plastic containers were not used, retention times could be controlled by the number and size of perforations in the drain pipe. Non-perforated subsurface 10 cm diameter PVC pipe was connected perpendicular to the perforated pipe under the plastic containers and buried under the lower plots to carry filtered water downslope to the bottom of the plots and offsite.

Galvanized sheet metal plates and shingles at the upslope edge of the trench were used to channel runoff from the turf into the plastic containers by gravity flow. The galvanized sheet metal plates had a 7.5 cm right angle bend and were placed over the soil with the right angle bend driven into the soil on the upslope side to prevent runoff from going under the plate. Aluminum angle was placed under the plate near the lower side and long bolts extending upward through the angle and the plate were used to suspend galvanized sheet metal rain covers that prevented rainfall from falling directly into the trenches. The same galvanized material was used to form a shingle-type attachment that slid under the downslope side of the metal plate and extended to the plastic containers to channel runoff from the plate into the containers.

During a runoff event, unfiltered runoff, "raw runoff", was collected by a small plastic trough made of 3.8 cm diameter PVC pipe cut in half lengthwise and placed beneath the shingle to capture runoff before it entered the plastic containers. The trough was connected to a 1.3 cm diameter PVC pipe that was buried along with the non-perforated subsurface pipe. During a runoff event raw runoff was continuously conducted through this pipe into a plastic bucket buried at the bottom of the plot for sampling. A ball valve in the trench was used to adjust the flow so that the collection bucket did not overflow during long runoff events.

Polyvinyl chloride pipes (1.3 cm diameter) attached to tee shaped fittings were inserted through 2.2 cm holes drilled in the side of each plastic container at the bottom of the filter materials to collect filtered runoff continuously during a runoff event. The four tee fittings in the trench were connected to a 1.3 cm flexible polyethylene pipe that conducted filtered runoff collected from each of the plastic containers to a collection bucket buried at the bottom of the slope next to the

raw runoff collection bucket for sampling. The other end of the system was attached to a pipe that extended above the trench to the open air and acted as a vent. Since this system was added after the downslope piping was buried, the flexible pipe was fished through the existing 10 cm drain pipe from the trench to the bottom of the slope. A ball valve located in the trench was used to adjust the incoming volume of filtered runoff so the collection bucket would not overflow during long events.

Because accurate collection of runoff samples and flow rates was not deemed possible through the drainage system, the lower experimental units described earlier as exactly the same as the upper experimental units were used to determine the rate of runoff flow from each experimental unit during each event. This procedure was based on the assumption that the upper experimental units and lower experimental units experienced the same amount of runoff and was used to estimate the P mass loss during events.

Christiansen's Coefficient of Uniformity (ASAE, 1993) was used to determine irrigation uniformity and rate in each irrigation block. At the bottom of the lower experimental units covered troughs collected runoff water and channeled it through calibrated Parshall flumes by gravity flow (Moss et al., 2006). As with the filtration trenches, a galvanized sheet metal plate with a 7.6 mm right angle bend was placed over the soil with the right angle bend driven into the soil to prevent runoff from going under the plate. The plate channeled runoff water into the collection troughs. An aluminum angle was attached under and near the downslope side of the plate with long screws extending upward through the angle and the plate to suspend the upslope edge of the rain covers made of the same galvanized material.

A total of 12 automatic samplers, six Isco 6700 and six Isco 6712 portable samplers (Isco, Lincoln, NE) were secured to concrete platforms located at the bottom of each plot. When the runoff was channeled from the covered troughs to Parshall flumes, Ultrasonic Modules (Isco 710) mounted over each Parshall flume used ultrasonic reflection to measure water depth in the flume each minute after runoff began. A Rapid Transfer Device (Isco 581) enabled information transfer

from samplers to a computer. Runoff flow rate was calculated from the depth measures based on a predetermined calibration of Parshall flumes: Flow rate $= 151.7 \times$ waterdepth$^{1.55}$.

To test the impact of P fertilizer on P runoff, 49 kg ha^{-1} P was applied as super triplephosphate (0-46-0) granules on half the plots on September 22, 2011, March 29, 2012 and August 14, 2012. The other half plots were not fertilized with P. Nirogen as urea (46-0-0) granules was applied at 49 kg ha^{-1} N on all runoff plots monthly to maintain a uniform turfgrass cover. The fertilizers were "watered-in" for 7 min immediately after fertilizer application. The site had not been fertilized for four years previous to this study. Runoff was initiated by either natural rainfall or simulated precipitation delivered by the irrigation sprinklers. From March to September 2012, eight natural rainfall runoff events and six simulated runoff events were collected.

Runoff sampling Analytical Procedure

Runoff samples were collected from both the "raw" and "filtered" collection buckets respectively from each plot within 12 h of a runoff event for comparison of P concentrations before and after filtration. Each "raw" or "filtered" sample was collected in triplicate and stored at room temperature (20 °C). Samples were analyzed within 3 d from being collected. Runoff samples were analyzed for dissolved P using the Murphy-Riley molybate blue method (Murphy and Riley, 1962) and NO_3-N and NH_4-N using colorimetric methods by automated flow injection analysis. The concentration of NO3-N, NH4-N, and dissolved P in the precipitation was measured after each runoff event and subtracted from the measured concentrations before statistical analyses were performed. Copper (Cu), zinc (Zn), and manganese (Mn) were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The pH of the samples was measured using a pH probe.

Statistical analyses were performed using SAS version 9.3. PROC MIXED procedures were used to determine the inflow P concentration as a function of P fertilizer applied and the P removal as a function of P filter materials for a factorial design with three blocks. There was no filter materials $\times$ P application interaction ($P<0.05$).

Laboratory Flow-Through Experiment

A Flow-through setting specified in Penn and McGrath (2011) and Stoner et al. (2012) was constructed to test the slag P removal performance under different inflow P concentrations. The four different P concentration gradients used in the flow-through test were 1, 2, 4, and 8 mg L^{-1}. The inflow P concentrations of 1 and 2 mg L^{-1} represent the typical inflow P concentration from unfertilized plots in the field study. P concentrations of 4 and 8 mg L^{-1} are similar to the inflow P concentration from P fertilized plots a short time after fertilization in the field study. Slag (2 g) was mixed with 3 g acid-washed, lab-grade sand (pure Si sand, 14808-60-7; Acros Organics, Morris Pains, NJ) and placed in flow-through cells in P concentrations of 1 and 2 mg L^{-1}. Slag (5 g) was placed in flow-through cells in P concentrations of 4 and 8 mg L^{-1} and no sand was added. In order to better estimate the P removal curve, the slag should not be spent (0 % P removal) for the duration of the entire experiment. A 0.45-µm filter was inserted between the materials, and the bottom of the cell and the cell was connected to a single channel pump (VWR variable rate "ultra low flow," 54856-070) using plastic tubing. The designed retention time in this experiment was 10 min which corresponds to an averaged 10.2 min retention time of the slag filter structures used in field. The solution volume in the flow-through cell was kept constant via a constant head Mariotte bottle apparatus. The P solution flowed into the cells for 5 h. The outflow solution was sampled at 0, 30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 min. Solutions were analyzed by the Murphy-Riley molybate blue method (Murphy and Riley, 1962). Each concentration treatment was duplicated as a set resulting in a total of eight experimental units.

Prediction of Field results using an Empirical Model

The model used to predict P removal was based on the flow-through equations specified by Penn and McGrath (2011) and specified by Penn et al (2012).

Discrete P removal $= be^{mx}$ [1]

Parameters b and m:

log-m=(0.08506RT)- (0.07416C_{in})- 2.53493   [2]

log b= (0.06541RT)-(0.00864C_{in}) + 1.60631   [3]

Maximum P added= $\dfrac{\ln b}{-m}$ [4]

Cumulative P removed= $\int_0^x (be^{mx})dx$....................[5]

CHAPTER III

RESULTS AND DISCUSSIONS

Runoff volume and P losses

From March through September 2012 a total of 14 runoff events were studied, including eight natural rainfall events and six simulated precipitation events caused by the in-ground sprinkler irrigation system. Precipitation rate, runoff volume, and runoff duration were highly variable among natural rainfall events. The largest rainfall event was 7 cm on April 14. Runoff volume delivered by rainfall events ranged from 2.46 m^3 to 54.5 m^3. The two major runoff events resulting from storms on 14 Apr 2012 and 25 Aug 2012 accounted for more than 50% of the total runoff collected during the research period (Table 1). The average (1-12 plots) runoff duration for natural rainfall events ranged from 28 min to 96 min. Compared to natural rainfall events, simulated events were more controlled and less variable. During simulations the irrigation system was stopped after 20-30 minutes of runoff had occurred on all plots in each block. The Christiansen's coefficient of uniformity for irrigation applied using the in-ground sprinkler irrigation system at 28.5 mm h^{-1} ranged from 73% to 91% among plots. Approximately 523 g of dissolved P entered the filter trenches in runoff from the upper plots over a 7-month period in 2012. The two storms on 14 Apr 2012 and 25 Aug 2012 that created the greatest runoff caused 362 g of dissolved P to enter the trench filters and accounted for 69% of the total dissolved P lost to runoff over the research period. Although the rainfall event on 11 Apr 2012 caused runoff with a volume of 8.9 m^3 and accounted for only 6.2% of the total runoff volume lost, this event caused the loss of 60 g of dissolved P which accounting for 11.5% of the total dissolved P lost during the

period. This event caused more dissolved P loss than other events with similar runoff volumes. For example, the irrigation event on 23 Apr 2012 produced a runoff volume of 7.8 m^3 with a dissolved P loss of 19.6 g (5.53% of total volume lost and 3.7% of total dissolved P lost). The rainfall event on 15 Jun 2012 produced a runoff volume of 10.92 m^3 with a dissolved P loss of 16.3 g (7.7% of total volume lost and. 3.1% of total dissolved P lost). The high dissolved P loss during the 11 Apr 2012 event was due to higher dissolved P concentrations that were caused by a recent (29 Mar 2012) P fertilizer application on the plots selected for the P fertilizer treatment. Since dissolved P loss was determined by runoff volume multiplied by dissolved P concentration, high P concentrations or large runoff volumes or both could result in large amounts of dissolved P lost. The two storm events with the largest runoff volumes (14 Apr 2012 and 25 Aug 2012) also had relatively high P concentrations in the runoff due to recent fertilizer applications (l5 days and 16 days after fertilization, respectively). Therefore these two storm events became the major contributors of dissolved P lost over the period of the study. Precipitation events with small runoff volumes followed shortly after fertilization could also contribute to relatively large amounts of dissolved P loss.

Table 1. Runoff volume and dissolved phosphorus (P) loss produced by natural rainfall and simulated runoff events in 2012. Fourteen runoff events were collected during the research period. Runoff volume is displayed in m^3 by event and runoff volume from each event as the percentage of the total runoff volume that occurred over the research period. Phosphorus loss per event is displayed in g and also as % of the total P lost in runoff during the study.

Event	Precipitation	Runoff		P loss	
		$-$ m^3 $-$	$-$ % $-$	$-$ g $-$	$-$% $-$
10 Mar 12	natural	2.46	1.73	4.42	0.85
19 Mar 12	naturall	3.46	2.44	6.03	1.15
23 Mar 12	simulated	6.64	4.69	6.12	1.17
11 Apr 12	natural	8.85	6.24	60.53	11.55
14 Apr 12	natural	54.52	38.43	268.26	51.30
23 Apr 12	simulated	7.84	5.53	19.59	3.75
29 Apr 12	natural	3.28	2.31	11.76	2.25
15 May 12	simulated	3.46	2.44	6.59	1.26
28 May 12	natural	5.52	3.90	8.41	1.61
15 Jun 12	natural	10.92	7.70	16.27	3.11
26 Jun 12	simulated	4.73	3.34	5.62	1.08
9 Aug 12	simulated	2.90	2.05	3.81	0.73
25 Aug 12	natural	20.39	14.37	94.07	17.99
30 Sep 12	simulated	6.85	4.83	11.44	2.19

Fertilizer application impact on raw runoff concentrations

The P concentrations in raw runoff (runoff inflow prior to filtering) from the fertilized treatment were always significantly greater ($P < 0.05$) than the unfertilized treatment except for the 23 Mar 2012 event that occurred 214 days after the initial fertilizer was applied on 22 Sep 2011 (Table 2). The difference between P concentrations from the fertilized and unfertilized treatments declined with succeeding events for the first three runoff events (10 Mar 2012, 19 Mar 2012 and 23 Mar 2012), and dissolved P concentrations declined with each subsequent runoff event. After fertilizer was applied on 29 Mar 2012, the dissolved P concentration in runoff for the fertilized treatment increased rapidly, from 1.01 mg L^{-1}, 23 March 2012, to 13.11 mg L^{-1}, 11 April 2012, 13 days after the second fertilizer treatment. Similar to the first three runoff events, runoff following the

fertilizer treatment on 29 Mar 2012, with one exception, 29 Apr 2012, differed in P concentrations from the fertilized and unfertilized treatments. The difference between the fertilized and unfertilized treatments declined with each runoff event from 12.19 mg L^{-1} in the initial event on 11 Apr 2012 to 0.43 mg L^{-1}, 133 d and nine runoff events after fertilization. Phosphorus concentrations declined with each subsequent runoff event following fertilization except for 29 Apr 2012 and 9 Aug 2012 (Fig. 1). This decline occurred because the later runoff events dissipated the P fertilizer residue left in the soil from the previous runoff events following fertilization and because of plant and microbial uptake. Compared to the P fertilized treatment, the dissolved P concentrations in the unfertilized treatment was more consistent among events. For the unfertilized treatment, dissolved P concentrations differed by no more than 1.2 mg L^{-1} among events, a difference likely caused by the variance in flow rate among runoff events. Even though the unfertilized plots had not received P fertilizer applications for the last four years, in eight runoff events the average dissolved P concentration in runoff from for the unfertilized treatment exceeded 1 mg L^{-1} a relatively high concentration for runoff from turfgrass covered areas. Penn et al. (2012) reported an average 0.5 mg L^{-1} dissolved inflow P concentration from a ditch filter structure built at a golf course in Stillwater, OK. A golf course in Texas produced an average dissolved P concentration of 0.13 mg L^{-1} over five years (King et al., 2007). The high dissolved P concentration from the unfertilized plots in this study was probably due to cumulative P fertilizer applications to the plots from previous nutrient runoff studies. Even though there was sufficient soil P (69 kg ha^{-1}) on the runoff site, P fertilizer was still applied to the plots that received P fertilizer treatments for research purposes. Therefore, the excessively high P concentration in runoff produced from fertilized plots during the study does not represent the typical average inflow P concentration in runoff that is likely to be transported from golf courses or residential areas to water bodies under typical management conditions.

Table 2. Phosphorus (P) concentrations in runoff from P fertilized and unfertilized treatments and proportion of P removed by the gravel and slag treatments. Fertilizer was applied at 49 kg ha^{-1} P on plots receiving fertilizer treatments on 22 Sep 2011, 29 Mar 2012 and 9 Aug 2012.

Event	Precipitation	P concentration		P removed	
		Fertilized	Unfertilized	Slag	Gravel
		——— mg L^{-1} ———		——— (%) ———	
10 Mar 12	natural	2.24*	1.55	42.83*	1.50
19 Mar 12	natural	1.91*	1.58	35.65*	0.60
23 Mar 12	simulated	1.01	0.94	30.40*	0.10
11 Apr 12	natural	13.11*	0.92	25.38*	-0.12
14 Apr 12	natural	8.63*	1.19	22.80*	0.35
23 Apr 12	simulated	4.60*	0.56	24.57*	-0.20
29 Apr 12	natural	6.68*	0.69	25.42*	1.13
15 May 12	simulated	3.29*	0.80	23.63*	0.65
28 May 12	natural	2.53*	0.76	31.33*	1.63
15 Jun 12	natural	2.00*	1.02	29.05*	-0.03
26 Jun 12	simulated	1.43*	1.05	18.53*	0.10
9 Aug 12	simulated	1.59*	1.16	22.40*	0.48
25 Aug 12	natural	7.36*	1.76	17.87*	1.13
30 Sep 12	simulated	2.11*	1.18	17.32*	-1.95

*Fertilized treatment is significantly ($P < 0.05$) different than the unfertilized treatment or the slag treatment is significantly ($P < 0.05$) different than the gravel control.
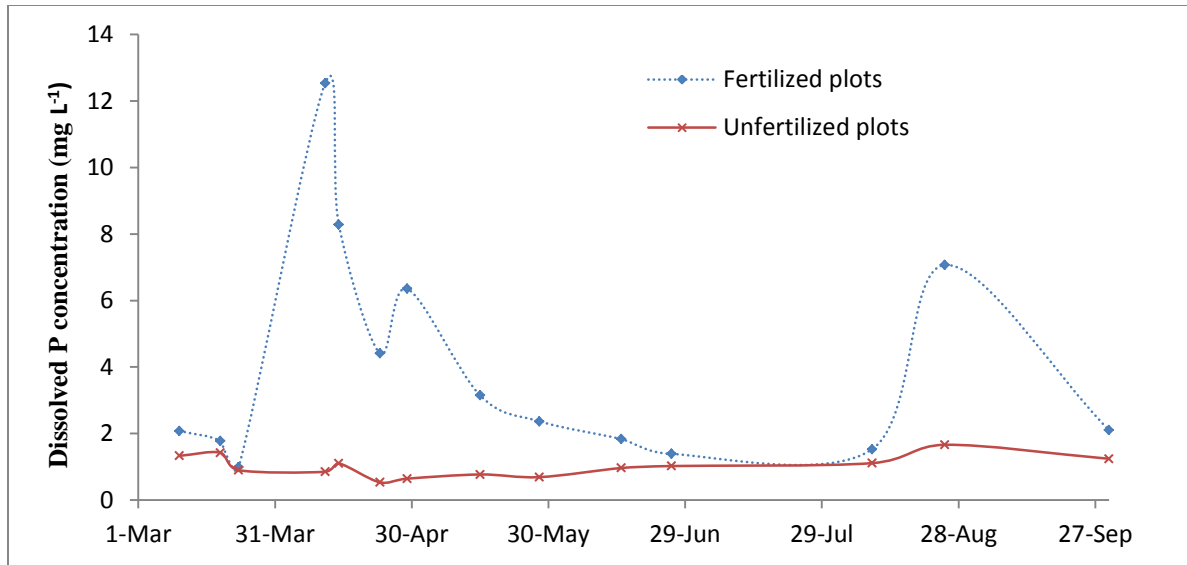
Figure 1. Dynamics of dissolved phosphorus (P) concentrations in natural and simulated rainfall runoff between P fertilized and unfertilized plots on dates from 11 Mar through 30 Sep 2012. Fertilizer applications of 49 kg ha^{-1} P were applied on plots receiving fertilizer treatments on 22 Sep 2011, 29 Mar 2012 and 9 Aug 2012

Filter materials effectiveness compared by event

Because the dissolved P concentrations in the raw and filtered runoff differed significantly between gravel and slag treatments (Table 2), data were analyzed by percent dissolved P removed by treatment [(dissolved P concentration in runoff that entered the slag filters − dissolved P concentration that exited the slag filters) x 100 / (dissolved P concentration in runoff that entered the slag filters)]. Statistical comparisons (ANOVA; $P < 0.05$) of each runoff event indicated that the P concentrations in runoff filtered through steel slag were significantly lower than the P concentrations in runoff filtered through gravel in all 14 events (Table 2). Runoff filtered by steel slag contained from 17% to 43% less dissolved P than runoff filtered through the inert gravel control. Gravel served as a good control as predicted. The gravel treatment's P removal percentage varied from -1.95% to 1.63%. For the slag treatment, the first runoff event on 10 Mar 2012 removed the greatest percentage of dissolved P by concentration (43%), followed by the

second runoff event on 19 Mar 2012 (36%). Following the first two events the P removal percentage varied among events from 30% to 17%. The last two events removed the least P, about 17%, which suggested that the P removal efficiency of the slag decreased as cumulative P loading increased.

Filter material effectiveness and fertilizer application impact on raw runoff concentrations

Because there was significant interaction between precipitation types and P concentrations and precipitation types and P removal percentage, data were analyzed separately for natural rainfall and simulated events. There was no significant interaction between P fertilizer treatments and filter materials; therefore, only main effects are discussed.

The average P concentration in runoff (5.56 mg L^{-1}) from natural rainfall events was significantly higher ($P<0.05$) than the unfertilized control (1.18 mg L^{-1}) over the research period (Table 3). Similarly, for simulated events, the average P concentration in runoff (2.34 mg L^{-1}) was significantly higher ($P<0.05$) than the unfertilized treatment (0.95 mg L^{-1}) over the research period (Table 4). Slag significantly ($P<0.05$) removed more dissolved P than gravel for both natural rainfall and simulated events (28.79% vs. 0.78% for rainfall events and 22.81% vs. -0.78% for simulated events) over the research period.

Table 3. The influence of P fertilizer application on the dissolved P concentrations in raw runoff from natural rainfall events. Data are pooled over the two filter material treatments.

P Fertilizer treatment	Concentration	
	$-$ mg L^{-1} $-$	
None	1.18	*
P	5.56	

*Fertilized treatment is significantly ($P < 0.05$) different than the unfertilized treatment

Table 4. The influence of P fertilizer application on the dissolved P concentrations in raw runoff from simulated events. Data are pooled over the two filter material treatments.

P Fertilizer treatment	Concentration
	$- \text{mg L}^{-1} -$
None	0.95 *
P	2.34

*Fertilized treatment is significantly ($P < 0.05$) different than the unfertilized treatment

Table 5. The dissolved P removal percentage by filter materials from runoff caused by natural rainfall events. Data are pooled over fertilizer treatments.

Filter material	P removed
	$- \% -$
Slag	28.79 *
Gravel	0.78

*The slag treatment is significantly ($P < 0.05$) different than the gravel control.

Table 6. The dissolved P removal percentage by filter materials from runoff caused by simulated events. Data are pooled over fertilizer treatments.

Filter material treatment	P removed
	$- \% -$
Slag	22.81 *
Gravel	-0.14

*Fertilized treatment is significantly ($P < 0.05$) different than the unfertilized treatment

The P removal performance of the steel slag filled structure

Approximately 269 g of dissolved P (44.5 mg P kg^{-1} slag) or 6.33 kg dissolved P ha^{-1} entered the steel slag filter systems (six plots) and 19% of all the dissolved P that entered was removed. The three largest runoff events accounted for 81% of the dissolved P that entered the steel slag filter systems and 74% of the dissolved P removed by the systems.

The lifetime of the filter structure was estimated by the predicted P removal curve produced by flow-through equations developed in Penn and McGrath (2011) for electric arc furnace steel slag and the actual P removal curve that was fit to measured field data (Fig. 2). The discrete P removal (%) was set as the Y axis and P loading of the structures was set as the X axis. For the measured field data, the discrete (meaning the results of a single event) P removal was calculated as a percent of the P that entered all six slag filters in that particular event [(P in runoff that entered the slag filters –P that exited the slag filters) x 100 / (P that entered)]. The predicted curve has two parameters: Y intercept (b) and slope coefficient (m) which were calculated by Eq. 2 and 3, respectively. Inflow P concentration and retention time (RT) are the two inputs used in Eq. 2 and 3. The RT estimated was 10.2 min (total structure pore space/ average flow rate), which was the averaged retention time for all 14 runoff events. The average flow–weighted P inflow concentration was 4.3 mg L^{-1}. The calculated slope coefficient (m) was -0.01, and the calculated Y intercept (b) was 172.1%. Because the Y intercept is discrete P removed by percent when P added equals zero, the value cannot exceed 100%. Therefore, the Y intercept (b) was adjusted from 172.1% to 100%. The potential maximum P loading of the slag filters (mg P kg^{-1} slag) can be estimated when discrete P removal (%) approaches zero. At this point, the inflow P concentration will be equal to the outflow P concentration, which means the slag is P saturated or spent and it needs to be replaced with new slag. By using the Y intercept (b) and slope coefficient (m) as input in Eq. [4], a maximum P loading of 460 mg kg^{-1} was calculated. The measured P removal curve that was produced by fitting discrete P removal (%) and cumulative P that entered the slag filters is displayed in Fig. 3. The maximum P loading estimated by the measured P

removal curve was 249 mg kg^{-1}. The predicted P removal curve overestimated the maximum P loading by 211 mg kg^{-1}. In practice the average P loading of the three major storm events during the research period was 12 mg kg^{-1} per event. At that loading rate, according to the predicted curve, the slag would be spent after about 38 such storms events. According to the measured curve calculated using the actual data accumulated, the slag would be spent after only 20 such storm events. The difference between the measured and predicted curves could have been foreseen because the equations that were used to produce the predicted curve were based on the specific chemical properties of the steel slag tested by Penn and McGrath (2011) and the chemical properties of the slag used in the trench filter system were not the same as those used to develop the earlier models. Penn et al (2012) also reported that the predicted curve of Penn et al (2012) overestimated the actual maximum P loading of the slag used in a field filter structure because of the variability in chemical properties between the slag used for the filter and the slag used for model development.
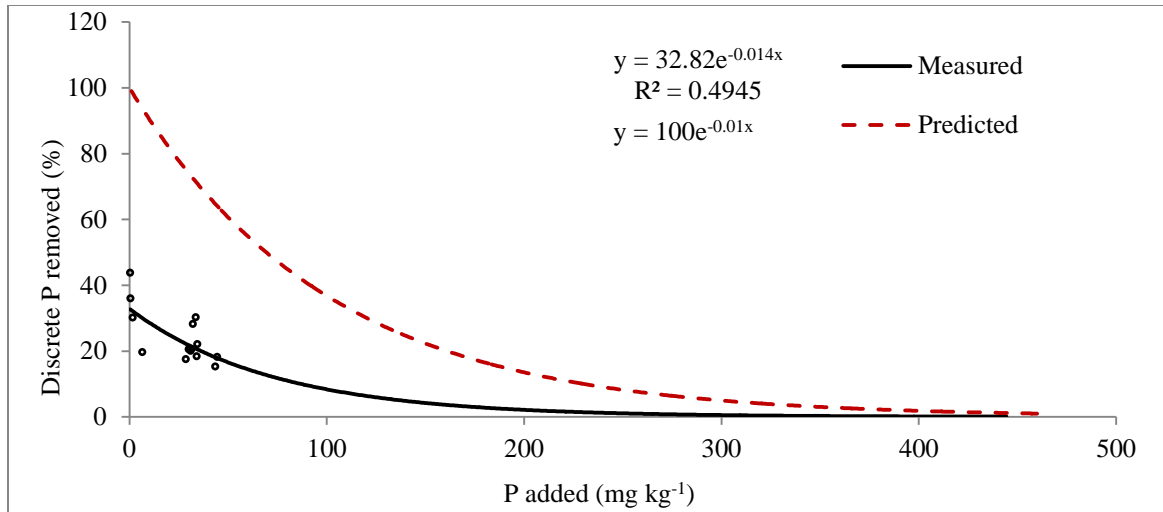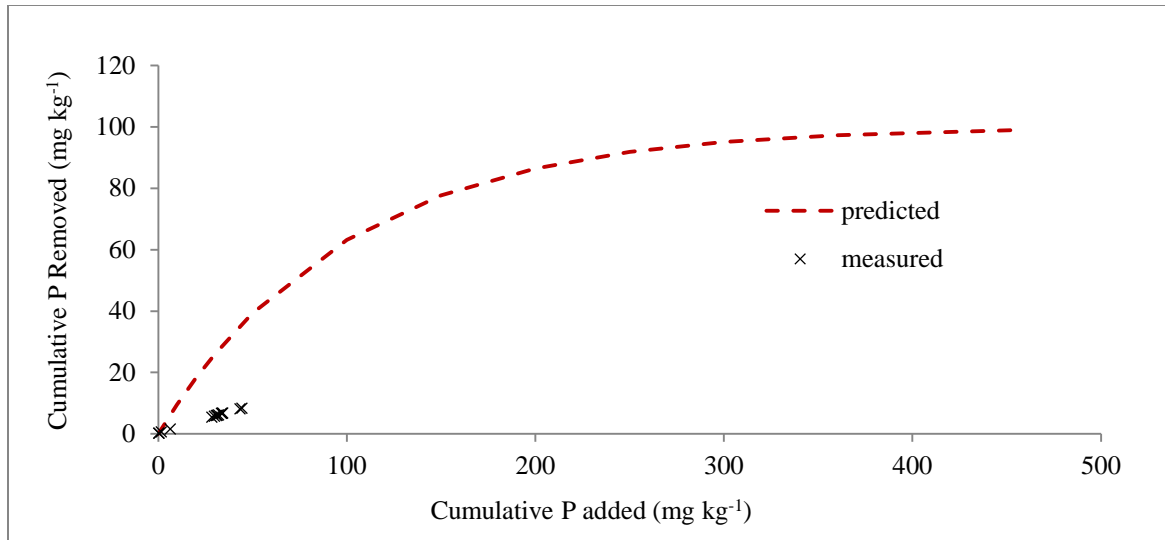
Figure 2. Discrete phosphorus (P) removal as a function of cumulative P added to the slag filters. Predicted P removal (dashed line) was estimated based on the average retention time (10.2 min) and inflow P concentration (4.3 mg L^{-1}) of the total 12 runoff events collected over the research period using Eq. 1-3. Measured discrete P removal (open circles and solid line) was calculated on a per event basis.

By integrating the discrete P removal curve shown in Fig 2. using Eq. [5], the predicted cumulative amount of P that the slag filters will remove was estimated as a function of cumulative P added (Fig 3). For comparison, the measured cumulative P removed by the P slag filters was also plotted on Fig 3 as a function of the cumulative P that entered the slag filters during the seven-month research period. The predicted curve produced by flow-through equations overestimated the cumulative P removed. Over the seven-month period, a total of 44.4 mg dissolved P kg^{-1} entered the slag filters. The actual measured cumulative P removal during the study was 8.3 mg kg^{-1}, while the predicted cumulative P removal curve estimated a cumulative P removal of 35.7 mg kg^{-1}. At the point where the slag reaches P saturation, the predicted cumulative P removal curve estimated the P removed by the slag filters at 98.9 mg kg^{-1}, which accounted for 21% of the total P that entered the filters. By integrating the measured P discrete removal curve, the estimated P removed by the slag filters is 22.7 mg kg^{-1}, which accounted for

34

9% of the total P that entered the filters. In the previous study, the slag filter structure built by Penn et al. (2012) was projected to have a maximum cumulative P removal of 65 mg kg^{-1}, which was determined by integrating the measured P removal curve in their study while the predicted curve developed by flow-through equations estimated a maximum cumulative P removal of 101 mg kg^{-1}. Penn et al. (2012) suggested that the overestimation of the P removal effectiveness by the predicted P removal curve was because the flow-through equations used for the prediction did not accurately estimate the Y intercept (b) of the discrete P removal curve. Because it is an industrial byproduct rather than a manufactured product, there is considerable variability in slag properties such as Ca and Fe content, alkalinity, and pH all of which are very important parameters that affect P removal efficiency (Bowden et al 2009). Even though the slag used in this study was from the same steel mill with the same size fraction as the slag used in the flow-through model and the slag used in the P filter structure on the golf course, the P removal efficiency of the different batches of slag were not consistent. For example, the average inflow and outflow pH from the slag filter structure built by Penn et al. (2012) was 7.7 and 9.2, respectively, while the average inflow and outflow pH from this study was 7.6 and 7.9, respectively. The higher outflow pH in the previous study occurred because the slag used in that study had a higher pH. High pH can promote the precipitation of calcium phosphate.

Figure 3. Cumulative phosphorus (P) removal as a function of cumulative P added to the slag filters over the seven month period. Predicted cumulative P removal (dashed line) estimated by integration of the curve presented in Fig. 2 using Eq. 5.
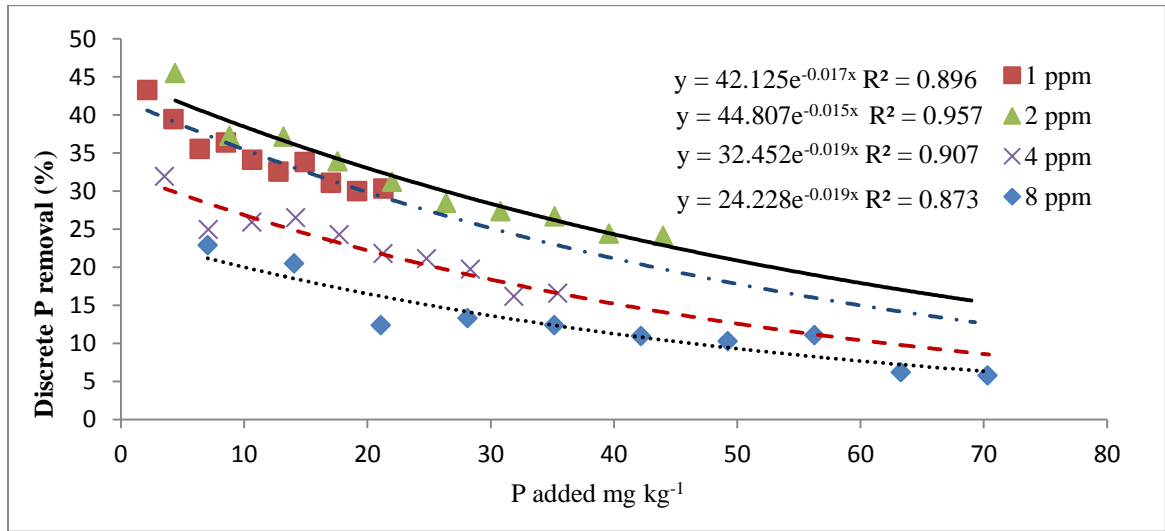
Flow-through results

The flow-through discrete phosphorus (P) removal (%) curves were constructed under four different concentrations (1, 2, 4 and 8 mg L^{-1}) at a retention time of 10 min (Fig 4). The curves produced by the flow-through studies had similar Y intercepts (b) and slope coefficients (m) as those of the measured discrete removal curve produced in the field (y =32.82e$^{-0.014x}$). The Y intercept estimated by the P removal curve for 4 mg L^{-1} was 32.45% and was very close to the Y intercept of 32.82% estimated by the field curve using a flow-weighted inflow P concentration of 4.3 mg L^{-1}. The similarity between the flow-through and field-based discrete P removal curves may indicate that the flow-through experiment provided a good simulation of the same slag applied in the field using similar parameters. Based on Eq.1, a discrete removal curve with a large Y intercept (b) and gentle slope (m) has a larger maximum P loading than a curve with a small Y intercept (b) or a steep slope (m). In general, except for the curve calculated for the 2 mg L^{-1} concentration, increasing the P inflow concentration decreased the Y intercept (b), the P removal

at zero P inflow, and also decreased the discrete P removal of each following sample collected. By inserting the Y intercept (b) and the slope coefficient (m) from each concentration shown in Fig 4 in Eq 4, the estimated maximum P loading of steel slag for the flow-through experiment under the four different concentrations appears in table 7. The results indicate that with lower inflow P concentrations (1 and 2 mg L^{-1}), the slag had a larger maximum P loading than slag tested with higher inflow P concentrations (4 and 8 mg L^{-1}). By integrating the discrete P removal curves shown in Fig 4 using Eq. 5, the cumulative maximum P removal (mg kg^{-1} and percentage) under the four different concentrations can be estimated and are also displayed in Table 7. The maximum P removal was decreased under higher inflow P concentrations of 4 or 8 mg L^{-1} compared with inflow P concentrations of 1 or 2 mg L^{-1}. Therefore, in general, increasing inflow P concentration has a negative effect on P removal effectiveness. The reason that maximum P loading and maximum P removal decreased as inflow P concentration increased in this study probably was due to a low amount of water soluble Ca in solution, which would quickly exhaust the pool of available Ca via precipitation with P when inflow concentration increased. The negative correlation between inflow P concentration and P removal could also be caused by the lower pH and the low buffer index of the slag used. Since acidity increased with precipitation of calcium phosphate (Lindsay .1979), when the pH was poorly buffered the Ca was unable to precipitate P effectively even though there was a higher P concentration in the inflow. In practice, the negative correlation between inflow P concentration and P removal indicates that the slag filters using the same slag in the field under P fertilizer treatments may have a shorter lifetime and lower P removal ability than those where P fertilizer is not applied.

Table 7. Maximum P loading and maximum cumulative P removal for slag under four phosphorus (P) concentrations at a retention time of 10 min in flow-through experiments. Maximum P loading was estimated using the experimentally determined flow-through P removal curves shown in Fig. 4.using Eq. 4. Maximum P removed was determined by the integration of the flow-through P removal curves shown in Fig. 4. using Eq. 5. Maximum P removed (%) was determined by maximum P removed as a percentage of maximum P loading.

P Concentration	Max P loading	Max P removed	Max P removed
$-$ mg L^{-1} $-$	$-$ mg kg^{-1} $-$	$-$ mg kg^{-1} $-$	$-$ % $-$
1	220	24.2	11.0
2	253	29.2	11.5
4	183	16.6	9.0
8	167	12.2	7.3

The chart shows:
- $y = 42.125e^{-0.017x}$ $R^2 = 0.896$ ■ 1 ppm
- $y = 44.807e^{-0.015x}$ $R^2 = 0.957$ ▲ 2 ppm
- $y = 32.452e^{-0.019x}$ $R^2 = 0.907$ ✕ 4 ppm
- $y = 24.228e^{-0.019x}$ $R^2 = 0.873$ ◆ 8 ppm

X-axis: P added mg kg^{-1}
Y-axis: Discrete P removal (%)

Figure 4. Experimentally Determined flow-through discrete phosphorus (P) removal curves for slag at four different inflow phosphorus (P) concentrations and a retention time of 10 min.

N removal

To test whether slag could be effective for removing dissolved nitrogen (N) from runoff, raw runoff and filtered runoff samples were collected from the runoff events on 11 Apr 2012, 15 May 2012 and Aug 9 2012 for analysis of total dissolved N (ammonium + nitrate) concentration. There was no significant difference ($P<0.05$) in N concentration between slag and gravel treatments in each of the three runoff events (Table 8). The negative removal percentage (outflow N concentration higher than inflow N concentration) was possibly caused by N release from the decay of mowed turfgrass clippings that entered the filter structures. This result is likely because N accumulation is mainly a result of biological processes. The microbial activity that is involved in the removal of ammonium and nitrogen requires a long reaction time to maximize its efficiency (Chan et al, 2007). However, in the case of the slag filters, the retention time was short (10 min) minimizing the amount of microbial activity possible.

Table 8. Dissolved nitrogen (N) concentrations (ammonium + nitrate) in runoff from slag and gravel treatments and the percentage of N removed by the gravel and slag treatments. Fertilizer applications of 49 kg ha^{-1} N were applied to all plots monthly to maintain a healthy turfgrass stand.

Event	Precipitation	N concentration				N removed	
		Slag		Gravel		Slag	Gravel
		Pre-filtered	Filtered	Pre-filtered	Filtered		
		——————— Mg L^{-1} ———————				——— % ———	
11 Apr 12	natural	2.388	2.363	2.787	2.805	3.298	-0.623 NS
15 May 12	simulated	2.214	2.152	2.088	2.188	2.558	-5.285 NS
9 Aug 12	simulated	2.656	2.723	2.727	2.802	-2.648	-2.942 NS

NS There is no significant difference ($P < 0.05$) between slag and gravel treatment

pH and metal concentrations

Runoff samples collected on 11 Apr 2012, 15 May 2012 and 9 Aug 2012 were tested for pH values. The average pH of pre-filtered and filtered runoff water from the slag treatment was 7.6 and 7.9, respectively. There was no pH difference between pre-filtered and filtered runoff water from the gravel treatment (pH=7.6). Runoff samples collected on 25 Aug 2012 and 30 Sep 2012 were tested for Zn, Cu and Mn concentrations before and following slag treatment. Pre-filtered and filtered runoff water samples did not differ in concentrations of Zn, Cu and Mn and were all below 0.01 mg L^{-1}.

CHAPTER IV

CONCLUSIONS AND FURTHER RESEARCH

During the seven months of the research period, the filter structures filled with slag significantly removed more P in runoff, reducing the dissolved P concentrations by 17 to 43 % compared with the control structures filled with gravel. Treating plots with P fertilizer increased the P concentration in the runoff inflow significantly compared with the unfertilized control. In general, the difference between P concentrations in runoff from the fertilized and unfertilized treatments declined with each runoff event following a P fertilizer application. Approximately 44.5 mg kg^{-1} dissolved P entered the steel slag filter systems (six plots) and 19% of the dissolved P was removed. Storm events were the main contributors to P losses in runoff. The previous P removal model developed by Penn and McGrath (2011) overestimated the maximum P loading capability of the slag filter structures (460 mg kg^{-1} vs. 269 mg kg^{-1} estimated using accumulated data) and the maximum P removal possible before the slag filters were spent (35.7 mg kg^{-1} vs 8.3 mg kg^{-1}). The overestimation of the performance of the P removal structures was believed to be due to the slag used in this study having "inferior" sorption properties than that used for the model development. The inferior slag probably had less water soluble Ca, higher pH, and higher alkalinity, which made it less useful for P removal.

The runoff produced by the storm of 14 Apr 12 delivered precipitation of 70 mm over 2 h, and accounted for over half of the P loss that occurred during the research period. Runoff produced in such extreme storm events has the potential to cause the filter structures to overflow. The hydraulic conductivity of the filter structures in extreme storm events might be improved if the

sand used to support the weight of the plastic containers was replaced by materials with higher hydraulic conductivity such as the inert river gravel used in the control structures. During the current study the runoff samples collected represented the average P concentration in runoff that occurred from each plot over an entire runoff event. Therefore, the relationship between runoff P concentration and flow rate at intervals within the precipitation period cannot be calculated. To further investigate this, the automatic samplers could be used to collect samples on a time interval basis to characterize the dynamics of runoff P concentrations as a function of flow rate during runoff events. In addition, the chemical properties of the slag used in this study were not investigated prior to use. In order to more accurately estimate the maximum P loading and maximum P removal potential of the slag filters, the previous flow-through model could have been adjusted by adding parameters based on the specific chemical properties of the slag used in this study.

REFERENCES

Agrawal, S. G., K. W. King, et al. (2011). "Use Of Industrial Byproducts To Filter Phosphorus And Pesticides In Golf Green Drainage Water." J. Environ. Qual. **40**(4): 1273-1280.

Alleoni, L. R. F., G. A. O'Connor, et al. (2008). "Runoff and Leachate Losses of Phosphorus in a Sandy Spodosol Amended with Biosolids [electronic resource]." Journal of environmental quality **37**(1): 259-265.

ASAE. 1993. Procedure for sprinkler distribution testing for research purposes. ANSI/ASAE S330.1 SEP 91, St. Joseph, MO

Bowden, L. I., A. P. Jarvis, et al. (2009). "Phosphorus Removal from Waste Waters Using Basic Oxygen Steel Slag." Environmental Science & Technology **43**(7): 2476-2481.

Carpenter, S. R. (2005). "Eutrophication of aquatic ecosystems: bistability and soil phosphorus." Proceedings of the National Academy of Sciences of the United States of America **102**(29): 10002-10005.

Chan, S. Y., S. N. Sin, et al. (2008). "Performance study of vegetated sequencing batch coal slag bed treating domestic wastewater in suburban area [electronic resource]." Bioresource technology **99**(9): 3774-3781.

Chimney, M. J., D. V. Calvert, et al. (2007). "Minimizing phosphorus release from newly flooded organic soils amended with calcium silicate slag: a pilot study [electronic resource]." Wetlands ecology and management **15**(5): 385-390.

Correll, D. L. (1998). "The role of phosphorus in the eutrophication of receiving waters: a review." Journal of environmental quality **27**(2): 261-266.

Cucarella, V. and G. Renman (2009). "Phosphorus Sorption Capacity of Filter Materials Used for On-site Wastewater Treatment Determined in Batch Experiments-A Comparative Study [electronic resource]." Journal of environmental quality **38**(2): 381-392.

Daniel, T. C., J. L. Lemunyon, et al. (1998). "Agricultural phosphorus and eutrophication: a symposium overview [electronic resource]." Journal of environmental quality **27**(2): 251-257.

Fiener, P. and K. Auerswald (2009). "Effects of Hydrodynamically Rough Grassed Waterways on Dissolved Reactive Phosphorus Loads Coming from Agricultural Watersheds [electronic resource]." Journal of environmental quality **38**(2): 548-559.

Gallimore, L. E., R. H. Huhnke, et al. (1999). "Water treatment residual to reduce nutrients in surface runoff from agricultural land." Journal of environmental quality **28**(5): 1474-1478.

He, Z. L., X. E. Yang, et al. (2006). "Phosphorus Concentrations and Loads in Runoff Water under Crop Production [electronic resource]." Soil Science Society of America journal **70**(5): 1807-1816.

Hylander, L. D. and G. Siman (2001). "Plant availability of phosphorus sorbed to potential wastewater treatment materials." Biology and fertility of soils **34**(1): 42-48.

Kaasik, A., U. Mander, et al. (2008). "Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands [electronic resource]." Water Research **42**(4-5): 1315-1323.

King, K. W., R. D. Harmel, et al. (2007). "Nutrient Load Generated by Storm Event Runoff from a Golf Course Watershed [electronic resource]." Journal of environmental quality **36**(4): 1021-1030.

Murphy, J. and J. P. Riley (1962). "A modified single solution method for the determination of phosphate in natural waters." Analytica Chimica Acta **27**(0): 31-36.

Leytem, A. B. and D. L. Bjorneberg (2005). "Removing soluble phosphorus in irrigation return flows with alum additions." Journal of soil and water conservation **60**(4): 200-208.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

McDowell, R. W., W. Bourke, et al. (2008). "Treatment of Drainage Water with Industrial By-Products to Prevent Phosphorus Loss from Tile-Drained Land [electronic resource]." Journal of environmental quality **37**(4): 1575-1582.

Moss, J. Q., H. Zhang, et al. (2006). "Reducing nutrient runoff from golf course fairways using grass buffers of multiple heights." Crop science **46**(1): 72-80.

Murphy, J. and J. P. Riley (1962). "A modified single solution method for the determination of phosphate in natural waters." Analytica Chimica Acta **27**(0): 31-36.

Penn, C. J., A. L. Allen, et al. (2007). "Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials [electronic resource]." Journal of soil and water conservation **62**(4): 269-286.

Penn, C. J. and R. B. Bryant (2006). "Application of phosphorus sorbing materials to streamside cattle loafing areas." Journal of soil and water conservation **61**(5): 303-310.

Penn, C.J. and J.M. McGrath. 2011. Predicting phosphorus sorption onto steel slag using a flow-through approach with application to a pilot scale system. J. Water Resour. Prot. 3:235–244.

Penn, C.J., Mcgrath, J.M., Bryant, R.B. 2010. Ditch drainage management for water quality improvement: Ditch drainage treatment structures. In: Moore, M. T., Kroger, R., editors. Agricultural Drainage Ditches: Mitigation Wetlands for the 21st Century. Kerala, India: Research Signpost. p. 151-172.

Penn, C. J., J. M. McGrath, et al. (2012). "Trapping Phosphorus In Runoff With A Phosphorus Removal Structure." J. Environ. Qual. **41**(3): 672-679.

Pratt, C., S. Pratt, et al. (2009). "Assessment of physical techniques to regenerate active slag filters removing phosphorus from wastewater [electronic resource]." Water Research 43(2): 277-282.

Pratt, C., A. Shilton, et al. (2007). "Effects of Redox Potential and pH Changes on Phosphorus Retention by Melter Slag Filters Treating Wastewater." Environmental Science & Technology 41(18): 6585-6590.

Renman, A., L. D. Hylander, et al. (2008). "Transformation and removal of nitrogen in reactive bed filter materials designed for on-site wastewater treatment." Ecological Engineering 34(3): 207-214.

Sakadevan, K. and H. J. Bavor (1998). "Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems." Water Research 32(2): 393-399.

Sharpley, A., P. Withers, et al. (2000). "Practical and innovative measures for the control of agricultural phosphorus losses to water: an overview [electronic resource]." Journal of environmental quality 29(1): 1-9.

Shilton, A. N., R. G. Haverkamp, et al. (2006). "Phosphorus removal by an'active' slag filter--a decade of full scale experience." Water Research 40(1): 113-118.

Shuman, L. M. (2004). "Runoff of Nitrate Nitrogen and Phosphorus from Turfgrass After Watering-In." Communications in Soil Science and Plant Analysis 35(1-2): 9-24.

Agrawal, S. G., K. W. King, et al. (2011). "Use Of Industrial Byproducts To Filter Phosphorus And Pesticides In Golf Green Drainage Water." J. Environ. Qual. 40(4): 1273-1280.

Alleoni, L. R. F., G. A. O'Connor, et al. (2008). "Runoff and Leachate Losses of Phosphorus in a Sandy Spodosol Amended with Biosolids [electronic resource]." Journal of environmental quality 37(1): 259-265.

ASAE. 1993. Procedure for sprinkler distribution testing for research purposes. ANSI/ASAE S330.1 SEP 91, St. Joseph, MO

Bowden, L. I., A. P. Jarvis, et al. (2009). "Phosphorus Removal from Waste Waters Using Basic Oxygen Steel Slag." Environmental Science & Technology **43**(7): 2476-2481.

Carpenter, S. R. (2005). "Eutrophication of aquatic ecosystems: bistability and soil phosphorus." Proceedings of the National Academy of Sciences of the United States of America **102**(29): 10002-10005.

Chan, S. Y., S. N. Sin, et al. (2008). "Performance study of vegetated sequencing batch coal slag bed treating domestic wastewater in suburban area [electronic resource]." Bioresource technology **99**(9): 3774-3781.

Chimney, M. J., D. V. Calvert, et al. (2007). "Minimizing phosphorus release from newly flooded organic soils amended with calcium silicate slag: a pilot study [electronic resource]." Wetlands ecology and management **15**(5): 385-390.

Correll, D. L. (1998). "The role of phosphorus in the eutrophication of receiving waters: a review." Journal of environmental quality **27**(2): 261-266.

Cucarella, V. and G. Renman (2009). "Phosphorus Sorption Capacity of Filter Materials Used for On-site Wastewater Treatment Determined in Batch Experiments-A Comparative Study [electronic resource]." Journal of environmental quality **38**(2): 381-392.

Daniel, T. C., J. L. Lemunyon, et al. (1998). "Agricultural phosphorus and eutrophication: a symposium overview [electronic resource]." Journal of environmental quality **27**(2): 251-257.

Fiener, P. and K. Auerswald (2009). "Effects of Hydrodynamically Rough Grassed Waterways on Dissolved Reactive Phosphorus Loads Coming from Agricultural Watersheds [electronic resource]." Journal of environmental quality **38**(2): 548-559.

Gallimore, L. E., R. H. Huhnke, et al. (1999). "Water treatment residual to reduce nutrients in surface runoff from agricultural land." Journal of environmental quality **28**(5): 1474-1478.

He, Z. L., X. E. Yang, et al. (2006). "Phosphorus Concentrations and Loads in Runoff Water under Crop Production [electronic resource]." Soil Science Society of America journal **70**(5): 1807-1816.

Hylander, L. D. and G. Siman (2001). "Plant availability of phosphorus sorbed to potential wastewater treatment materials." Biology and fertility of soils **34**(1): 42-48.

Kaasik, A., U. Mander, et al. (2008). "Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands [electronic resource]." Water Research **42**(4-5): 1315-1323.

King, K. W., R. D. Harmel, et al. (2007). "Nutrient Load Generated by Storm Event Runoff from a Golf Course Watershed [electronic resource]." Journal of environmental quality **36**(4): 1021-1030.

Murphy, J. and J. P. Riley (1962). "A modified single solution method for the determination of phosphate in natural waters." Analytica Chimica Acta **27**(0): 31-36.

Leytem, A. B. and D. L. Bjorneberg (2005). "Removing soluble phosphorus in irrigation return flows with alum additions." Journal of soil and water conservation **60**(4): 200-208.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

McDowell, R. W., W. Bourke, et al. (2008). "Treatment of Drainage Water with Industrial By-Products to Prevent Phosphorus Loss from Tile-Drained Land [electronic resource]." Journal of environmental quality **37**(4): 1575-1582.

Moss, J. Q., H. Zhang, et al. (2006). "Reducing nutrient runoff from golf course fairways using grass buffers of multiple heights." Crop science **46**(1): 72-80.

Murphy, J. and J. P. Riley (1962). "A modified single solution method for the determination of phosphate in natural waters." Analytica Chimica Acta **27**(0): 31-36.

Penn, C. J., A. L. Allen, et al. (2007). "Removing dissolved phosphorus from drainage ditch
water with phosphorus sorbing materials [electronic resource]." Journal of soil and water
conservation **62**(4): 269-286.

Penn, C. J. and R. B. Bryant (2006). "Application of phosphorus sorbing materials to streamside
cattle loafing areas." Journal of soil and water conservation **61**(5): 303-310.

Penn, C.J. and J.M. McGrath. 2011. Predicting phosphorus sorption onto steel slag using a flow-
through approach with application to a pilot scale system. J. Water Resour. Prot. 3:235–
244.

Penn, C.J., Mcgrath, J.M., Bryant, R.B. 2010. Ditch drainage management for water quality
improvement: Ditch drainage treatment structures. In: Moore, M. T., Kroger, R., editors.
Agricultural Drainage Ditches: Mitigation Wetlands for the 21st Century. Kerala, India: Research
Signpost. p. 151-172.

Penn, C. J., J. M. McGrath, et al. (2012). "Trapping Phosphorus In Runoff With A Phosphorus
Removal Structure." J. Environ. Qual. **41**(3): 672-679.

Pratt, C., S. Pratt, et al. (2009). "Assessment of physical techniques to regenerate active slag
filters removing phosphorus from wastewater [electronic resource]." Water Research
43(2): 277-282.

Pratt, C., A. Shilton, et al. (2007). "Effects of Redox Potential and pH Changes on Phosphorus
Retention by Melter Slag Filters Treating Wastewater." Environmental Science &
Technology **41**(18): 6585-6590.

Renman, A., L. D. Hylander, et al. (2008). "Transformation and removal of nitrogen in reactive
bed filter materials designed for on-site wastewater treatment." Ecological Engineering
34(3): 207-214.

Sakadevan, K. and H. J. Bavor (1998). "Phosphate adsorption characteristics of soils, slags and
zeolite to be used as substrates in constructed wetland systems." Water Research **32**(2):
393-399.

Sharpley, A., P. Withers, et al. (2000). "Practical and innovative measures for the control of
agricultural phosphorus losses to water: an overview [electronic resource]." Journal of
environmental quality **29**(1): 1-9.

Shilton, A. N., R. G. Haverkamp, et al. (2006). "Phosphorus removal by an'active' slag filter--a
decade of full scale experience." Water Research **40**(1): 113-118.

Shuman, L. M. (2004). "Runoff of Nitrate Nitrogen and Phosphorus from Turfgrass After
Watering-In." Communications in Soil Science and Plant Analysis **35**(1-2): 9-24.

Sibrell, P. L., T. W. Tucker, et al. (2009). "Removal of phosphorus from agricultural wastewaters
using adsorption media prepared from acid mine drainage sludge [electronic resource]."
Water Research **43**(8): 2240-2250.

Sims, J. T., B. C. Joern, et al. (1998). "Phosphorus loss in agricultural drainage: historical
perspective and current research." Journal of environmental quality **27**(2): 277-293.

Soldat, D. J. and A. M. Petrovic (2008). "The Fate and Transport of Phosphorus in Turfgrass
Ecosystems [electronic resource]." Crop science **48**(6): 2051-2065.

Sims, J.T., Kleinman, P.J. 2005. Managing agricultural phosphorus for environmental protection.
In Sims, J. T. and Sharpley, A.N. Phosphorus: Agriculture and the Environment. Madison, W.I:
Soil Science Society of America Special Publication. o, 1021-1068.

Stoner, D., C. Penn, et al. (2012). "Phosphorus removal with by-products in a flow-through
setting." J Environ Qual **41**(3): 654-663.

USEPA. 1993. Guidance specifying management measures for sources of nonpoint pollution in
coastal waters. United States Environmental Protection Agency, publication EPA 840-B-
92-002. Online. Available at: http://www.epa.gov/owow/nps/MMGI/index.html (verified
17 Aug 2012).

USEPA W. (2002). Water quality conditions in the United States [electronic resource] : a profile
from the 2000 national water quality inventory, [Washington, D.C.] : U.S. Environmental
Protection Agency, Office of Water, [2002].

Vietor, D. M., T. L. Provin, et al. (2010). "Biosolid and Alum effects on runoff losses during turfgrass establishment [electronic resource]." <u>Bioresource technology</u> **101**(9): 3246-3252.

Vohla, C., S. Baatz, et al. (2007). "Dynamics of phosphorus, nitrogen and carbon removal in a horizontal subsurface flow constructed wetland [electronic resource]." <u>The science of the total environment</u> **380**(1-3): 66-74.

Wagner, D. J., D. Jaiswal, et al. (2008). "Managing Biosolids Runoff Phosphorus Using Buffer Strips Enhanced with Drinking Water Treatment Residuals [electronic resource]." <u>Journal of environmental quality</u> **37**(4): 1567-1574.

Walker, W.J., and B. Branham. 1992. Environmental impacts of turfgrass fertilization. p. 105-219. In J.C. Balogh and W.J. Walker (ed.) Golf course management and construction: environmental issues. Lewis Publ., Chelsea, MI.

Watts, D. B. and H. A. Torbert (2009). "Impact of Gypsum Applied to Grass Buffer Strips on Reducing Soluble P in Surface Water Runoff [electronic resource]." <u>Journal of environmental quality</u> **38**(4): 1511-1517.

Wei, X., S. Bhojappa, et al. (2008). "Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants [electronic resource]." <u>Water Research</u> **42**(13): 3275-3284.

Westholm, L. J. (2006). "Substrates for phosphorus removal--potential benefits for on-site wastewater treatment?" <u>Water Research</u> **40**(1): 23-36.

Yamada, H., M. Kayama, et al. (1986). "A fundamental research on phosphate removal by using slag." <u>Water Research</u> **20**(5): 547-557.

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