Evaluation of a universal flow-through model for predicting and designing phosphorus removal structures

Chad Penn^{a,*}, James Bowen^{a,b}, Joshua McGrath^{b,c}, Robert Nairn^d, Garey Fox^a, Glenn Brown^a, Stuart Wilson^a, Clinton Gill^c,

^a Department of plant and soil science, Oklahoma State University, 367 Agricultural Hall, Stillwater, OK, 74078

^b Department of plant and soil science, University of Kentucky, 1405 Veterans Drive, Lexington, KY, 40546

^c Department of environmental science and technology, University of Maryland, 0214 H.J. Patterson Hall, College Park, MD, 27042

^d School of civil engineering and environmental science, University of Oklahoma, 202 W. Boyd St. Room 334, Norman, OK, 73019

*Corresponding author. Email address: chad.penn@okstate.edu (C. Penn)

ABBREVIATIONS: P, phosphorus; PSM, phosphorus sorption material; RT, retention time; DP_{rem}, discrete phosphorus removed; CP_{rem}, cumulative phosphorus removed; CP_{add}, cumulative phosphorus added; PL_{annual}, annual phosphorus load; DL, desired lifetime; RG, removal goal; FGD, flue gas desulfurization; EAF, electric arc furnace; BMP, best management practice; TMDL, total maximum daily load; AMDR, acid mine drainage residual.

ABSTRACT

Phosphorus (P) removal structures have been shown to decrease dissolved P loss from agricultural and urban areas which may reduce the threat of eutrophication. In order to design or quantify performance of these structures, the relationship between discrete and cumulative removal with cumulative P loading must be determined, either by individual flow-through experiments or model prediction. A model was previously developed for predicting P removal with P sorption materials (PSMs) under flow-through conditions, as a function of inflow P concentration, retention time (RT), and PSM characteristics. The objective of this study was to compare model results to measured P removal data from several PSM under a range of conditions (P concentrations and RT) and scales ranging from laboratory to field. Materials tested included acid mine drainage residuals (AMDRs), treated and non-treated electric arc furnace (EAF) steel slag at different size fractions, and flue gas desulfurization (FGD) gypsum. Equations for P removal curves and cumulative P removed were not significantly different between predicted and actual values for any of the 23 scenarios examined. However, the model did tend to slightly over-predict cumulative P removal for calcium-based PSMs. The ability of the model to predict P removal for various materials, RTs, and P concentrations in both controlled settings and field structures validate its use in design and quantification of these structures. This ability to predict P removal without constant monitoring is vital to widespread adoption of P removal structures, especially for meeting discharge regulations and nutrient trading programs.

Keywords: phosphorus; phosphorus removal structures; phosphorus sorption materials; flow-through model; eutrophication; legacy phosphorus

1. INTRODUCTION

Eutrophication reduces the ability of surface water bodies to provide drinking water, serve as a means of recreation, and sustain a diverse group of organisms (Carpenter et al., 1998). While both nitrogen (N) and phosphorus (P) are required for algae growth, P cannot be fixed from the atmosphere, so P is typically the limiting nutrient for eutrophication (Schindler et al., 2008). Phosphorus sources to surface waters include effluent from wastewater treatment plants, runoff and subsurface drainage from agricultural land and urban areas, and domestic septic systems which release both dissolved and particulate P. Agriculture has been identified as a major contributor of P due to over application of chemical fertilizer or manure, allowing soil P levels to accumulate beyond plant needs. Soils with high P levels will release small amounts of dissolved P in runoff for years or even decades providing a “legacy” of P that will continue even after adoption of BMPs and cessation of P additions (Haygarth et al., 2014; Sharpley et al., 2013). The released dissolved P is relatively low in concentration (King et al., 2015; Smith et al., 2015), yet 100% bioavailable upon reaching an aquatic ecosystem.

Conventional BMPs focus on reducing particulate P through erosion prevention, but do little to reduce transport of dissolved P and potentially increase losses of dissolved P (Darch et al., 2015; Fox and Penn, 2013; Sharpley and Smith, 1994). Materials with a high affinity for P have been used to reduce solubility of soil P in efforts to reduce dissolved P transport in runoff, tile drainage, and other effluents (Ippolito, 2015; Dunets et al., 2015; Callery et al., 2015; Karczmarczyk and Bus, 2014; Claveau-Mallet et al., 2013; Uusitalo et al., 2012; McDowell et al., 2008; Penn et al., 2011). These P sorbing materials (PSMs) are able to reduce dissolved P concentrations in water, but have a finite ability to sorb P, requiring additional material for continued reductions. In order to facilitate this process, PSMs have been used as a replaceable

1 filter media in large landscape filters, or P removal structures, that are strategically placed in
2 areas receiving drainage water with high concentrations of dissolved P (Ibrahim et al., 2015;
3 Shipitalo et al., 2015; McDowell, 2015; Wang et al., 2014; Penn et al., 2014a; Bryant et al.,
4 2012) as a precision conservation BMP (Delgado et al., 2011). A P removal structure can take
5 the form of a ditch filter (Bryant et al., 2012), confined bed runoff filter (Penn et al., 2012),
6 riparian runoff filter (Kirkkala et al., 2012), surface inlets (Feyereisen et al., 2015), pond filter
7 (Penn and McGrath, 2011), subsurface drainage filter (McDowell et al., 2008), or bio-retention
8 cells (Zhang et al., 2008).

9 Most PSMs are able to remove P from solution by two main mechanisms: ligand
10 exchange onto Fe and Al materials and precipitation of Ca phosphates (Karczmarczyk and Bus,
11 2014; Klimeski et al., 2012; Lyngsie et al., 2015; Stoner et al., 2012). These mechanisms are a
12 function of the chemical characteristics of the PSM (Penn et al., 2011), which also provide a
13 means of modelling P removal (Stoner et al., 2012).

14 Using a series of flow-through experiments, Penn and McGrath (2011) and Lyngsie et al.
15 (2015) developed an approach for individual PSMs to predict P sorption onto steel slag and
16 manufactured PSMs under flow-through conditions as a function cumulative P loading. Briefly,
17 a flow-through experiment consisted of using a known mass of PSM in a flow-through cell and
18 maintaining a constant head of P solution at a known concentration as the solution was pulled
19 through the PSM using a pump at a constant rate for achieving a desired retention time (RT).
20 Discrete solution samples that passed through the PSM are taken at various time increments and
21 measured for dissolved P concentration in order to determine P removal. Flow-through
22 techniques are superior to batch P sorption tests in the context of P removal structures (Lyngsie
23 et al., 2015; Klimeski et al., 2014; Stoner et al., 2012; Penn and McGrath, 2011). Individual

models were later developed for other PSMs (Stoner et al., 2012). Each individual model took the form:

$$DP_{rem} (\%) = be^{m*CP_{add}} \quad (1)$$

Where DP_{rem} is discrete P removed as a function of cumulative P added to the PSM (mg P kg^{-1} PSM), CP_{add} . Coefficients b and m are simply the coefficients of an exponential equation that predicts DP_{rem} with respect to CP_{add} . Next, equation 1 is integrated with respect to CP_{add} to calculate cumulative P removal (CP_{rem} ; mg kg^{-1} PSM) as a function of CP_{add} (mg kg^{-1} PSM); details of this are further described in the Methods section. Stoner et al., (2012), Penn et al. (2012) and Penn and McGrath (2011) expanded this approach by conducting flow-through experiments on materials at different RTs and inflow P concentrations, which enabled prediction of log transformed coefficients m and b from equation 1 as a function of RT and P concentration:

$$\log(-m) = (\alpha RT) + (\beta P) + \chi \quad (2a)$$

$$\log(b) = (\delta RT) + (\varepsilon P) + \mu \quad (2b)$$

After log transformation, coefficients b and m from equation 1 become the y-intercept and slope, respectively, for the relationship between DP_{rem} and CP_{add} . The coefficients, α , β , χ , δ , ε , and μ are specific to each individual PSM. Therefore, each individual model was limited to the specific samples that it was developed for due to the high spatial and temporal variability within PSM types (Wang et al., 2014; Penn et al., 2012). As a result, when an individual model for a specific steel slag sample, for example, was applied to a different steel slag sample collected from the same steel mill, the individual model would fail at predicting P removal performance due to variation in PSM chemical character (Penn et al., 2012). This exposed the need for a

universal flow-through model that could be used to predict P removal for any PSM type as a function of PSM properties, in addition to considering RT and inflow P concentration.

As a result, a universal model was developed from over 1000 flow-through P removal experiments conducted on a variety of PSMs at five different RTs and inflow P concentrations (Stoner et al., 2012). The universal model (described in detail in Methods) predicts DP_{rem} and CP_{rem} as a function of cumulative P loading to the PSM (i.e. CP_{add}), based on flow conditions (inflow P concentration and RT) and chemical and physical properties unique to the individual sample. Essentially, the coefficients listed in equations 2a and 2b are predicted as a function of PSM properties. This model eliminates the need for time and cost consuming flow-through experiments that would need to be conducted for each RT and inflow P concentration of interest, for each PSM. Accurate prediction of DP_{rem} and CP_{rem} as a function of CP_{add} serves two purposes: it provides the necessary information for designing a site-specific and PSM-specific P removal structure to meet desired P removal goals and lifetime, or predict the P removal performance and lifetime of a previously constructed P removal structure (Lyngsie et al., 2015). The Natural Resource Conservation Service (NRCS) has adopted an interim standard on P removal structures as part of the environmental quality incentives program (EQIP) through Standard 782 (NRCS, 2015). On a watershed basis, this tool could be used for planning and implementing P removal structures to meet the total maximum daily load (TMDL) criteria for non-point P sources (Parry, 1998). A TMDL is a regulatory term from the U.S. Clean Water Act that describes the maximum mass of a pollutant that a water body can receive and still meet water quality standards. Thus, TMDLs for dissolved P are based on both the concentration of dissolved P and the flow volume.

The objectives of this study were to compare model results to measured P removal data from several PSMs, P removal structures, conditions (P concentrations and RT), and scales; illustrate how the model output is used to design or predict P removal structure performance; and present results from previously constructed P removal structures.

2. MATERIALS AND METHODS

2.1 Characterization of PSMs and solution analysis of effluent

All PSMs listed in Table 1 were characterized for chemical and physical characteristics necessary for input into the universal flow-through model described below. Due to the objectives of this manuscript, the results of this characterization are not shown since they were previously reported in each of the publications that correspond to the validation scenario. A description of PSM characterization for safety analysis is found in Penn et al. (2011). Briefly, chemical characterization required for input to the model included total digestable Ca, Fe, and Al (EPA Method 3050), amorphous Fe and Al by ammonium oxalate extraction (McKeague and Day, 1966), pH in water, and pH buffer capacity to 6. The pH buffer capacity to 6 was determined using a pH probe and titration with a concentration of HCl that varied as a function of the buffer capacity of the PSM (0.005 to 0.1M). This was determined by trial and error.

Particle size distribution curves were determined for each PSM using the ASTM D 422 standard method. The results from both the hydrometer and sieve testing were plotted with the diameter in mm versus the percent finer (by mass) and then subjected to a second order polynomial regression resulting in the particle distribution curve. Bulk density was determined by measuring material dry mass at a known total volume; particle density was determined by

measuring water displacement after adding a known mass of material. Porosity was then calculated from the bulk density and porosity.

All water samples collected from flow-through P removal experiments and monitored P removal structures were filtered through a 0.45 μm membrane and analyzed for dissolved P by the Murphy-Riley method and a Spectronic 21D at 880 μm (Murphy and Riley, 1962). When possible, samples were tested the same day as collected, and kept refrigerated at 4°C if testing was delayed.

2.2 Description of Validation Scenarios

Specifics regarding each PSM tested are listed in Table 1 and their use in each of the different experimental scenarios and conditions for each scenario are listed in Table 2. Photographs of the units are shown in Figure 1.

2.2.1 Laboratory flow-through measurements of PSMs

Materials listed in Table 2 under “Laboratory flow-through columns” were obtained, characterized and tested for dissolved P removal in a flow-through scenario in the laboratory at specified conditions listed that table, and then compared to predicted P removal using the flow-through P removal model described in equations 1, 3, and 4. The flow-through experiments were completed using a setup previously described by Fuchs et al. (2009) and Stoner et al. (2012), and are shown in Fig. 1a. The outflow concentration at each time (0, 30, 90, 120, 150, 180, 210, 240, 270, and 300 min) for each sample was tested and compared with the inflow P concentration to calculate discrete removal (%) at each sampling event. The P loading was calculated using the inflow P concentration, flow rate, and mass of PSM.

2.2.2 Pond Filter Structure

In order to test PSMs on a larger scale than a laboratory flow-through experiment, a P removal structure was constructed next to a 405 m² pond located at the Oklahoma State University Botanical Gardens. This is the same site as the P removal structure described in Penn and McGrath (2011), but the structure was update by replacing the tank with a 1136 L plastic stock tank. Two different PSMs were tested in this structure (Table 2 and Fig. 1b).

2.2.3 Golf Course Runoff Structure

A field runoff P removal structure was constructed in Stillwater, Oklahoma in 2010 in a ditch outlet that drained a 63 ha watershed with land uses that consisted of undeveloped area, residential, and a golf course (Penn et al., 2012). Two different PSMs were tested in this structure (Table 2). An example runoff P removal structure is shown in Fig. 1d.

2.2.4 Poultry Farm Runoff Structure

A P removal structure was constructed at an outlet that drained 3.6 ha of a poultry farm in eastern Oklahoma (Penn et al., 2014a; Fig. 1d). The site is located within the Illinois River Watershed which is designated as a scenic river. The P removal structure was designed and constructed as described in Penn et al. (2014a). Briefly, the structure was designed to remove 45% of the annual dissolved P load at the location (annual load ~ 20 kg yr⁻¹) and handle a maximum flow rate of 2.8 m³ min⁻¹ (1.6 ft³ s⁻¹) or one-tenth of the estimated peak flow rate from a 2-yr, 24-h storm. To date, this P removal structure is still being monitored (Table 2).

2.2.5 Runoff Plot Interception Trenches

Interception trenches containing un-treated EAF slag were constructed on six turfgrass runoff plots previously described in detail by Wang et al. (2014). The runoff plots were fertilized with P and designed to collect runoff from both natural and simulated rainfall events. All runoff samples were tested for dissolved P as previously described, and Cu, Zn, and Mn by ICP-AES.

2.2.6 Maryland Ditch P removal Structures and Storm-Water Basin Filter

Six ditch P removal structures (Fig 1d) were constructed at Barclay, Marion, and Westover, Maryland, located on the Eastern Shore of Maryland. While the ditch drainage system serves to prevent flooding of agricultural fields and roads, they also directly connect landscape nutrients to the surface waters (Pierce et al., 2012; Ahiablame et al., 2011). More detail on the ditch drainage system of Maryland can be found in Needelman et al. (2007) and Vadas et al (2007). Because of this connectivity, the ditches serve as a direct intercession point for removing dissolved P before the drainage water reaches the Chesapeake Bay (Buda et al., 2012). Three ditch filters were constructed with flue gas desulfurization (FGD) gypsum and three were constructed with EAF steel slag. The FGD gypsum and slag were obtained from U.S. Gypsum and Tube City IMS, respectively.

Ditches were scraped out with heavy equipment to remove sediment, geotextile was placed on the bottom of the ditch, and a shallow PSM layer was poured on the geotextile. Four tile drains were wrapped in geotextile and placed along the length of the ditch, leading to a perpendicular manifold into which each of the tiles drained. A layer of approximately 76 cm of PSM was then placed on top of the drainage tiles. The ditch filters utilized 60 to 80 Mg of PSM, depending on the size of the ditch and the density of the PSM. For structures constructed with

FGD gypsum, re-vegetation of the ditch occurred due to the physical and chemical environment of the FGD gypsum.

An additional storm water basin P filter was constructed on a poultry farm in Centreville, MD using EAF steel slag (Fig 1e). Drainage from around the barns collected in the storm water basin, and the water was allowed to drain out of the basin through the steel slag into a drainage ditch. This system used custom made perforated steel boxes, designed with the concept of a cartridge system. Each box was 1.2 by 1.2 by 1.8 m with a perforated 16 cm plastic pipe in the center. Water flowed into the sides of the boxes, through the slag and into the plastic pipe, which ultimately drained into a nearby drainage ditch. Four of these boxes were used in this system, each containing approximately 0.9 Mg of slag. Over four years, the slag in the boxes was changed four times.

For the ditch P removal structures, the untreated water was restrained with a flow control structure (Agri-Drain, Adair, IA) prior to entering the P removal structure. The water backed up against the flow control structure and leached downward into the PSM (Fig. 1d). After exiting the filter, the treated water flowed into a concrete vault containing an H-flume where the flow rate was measured with an ISCO 720 submerged probe flow module and a water sample was taken with an ISCO 6712. At the same time, a sample was taken from the pre-treated ditch water to allow comparison between water entering the filter exiting the filter. Any flow over the flow control structure at the end of the ditch was also recorded. A 250 mL sample was taken every two hours, filling a 1-L bottle in eight hours.

The sampling for the storm water basin filter at Centreville was similar. The runoff water flowed into a ditch containing a flow control structure that diverted the water into the pond,

essentially collecting all the runoff from the poultry production section of the property. The water then flowed through the filters where it drained into a pipe that leads into the main ditch; this pipe contained a weir for measuring flow rate and also a sampler tube to capture treated water. An additional sampler was established to take simultaneous samples from the untreated pond water at the same time-pacing utilized in the ditch P removal structures.

The bottles from each site were collected once a week and the data from the samplers was downloaded. The samples were analyzed for pH, EC, and total solids. Two subsamples of water were then split off from the main sample for dissolved P analysis. Dissolved P was measured by the method previously described.

2.3 Data analysis and modelling

Discrete P removal (DP_{rem} ; in percent) was expressed as an exponential curve with discrete removal plotted as a function of the cumulative P added (CP_{add}) as previously described in equation 1. Dissolved P removal curves depicting actual removal data and curves based on model predictions are referred to as discrete P removal curves and design curves, respectively. Example design curves are shown in Figs 2a, 3a, and 4a.

The model was produced using data from flow-through experiments conducted on various PSMs tested at RTs of 0.5, 3, 6, 8, and 10 min and inflow P concentrations of 0.5, 1, 5, 10, and 15 mg L⁻¹ (Stoner et al., 2012). The model predicts the log of the coefficients, m and b of the discrete removal curves as a function of PSM chemical and physical characteristics, and flow conditions (RT and inflow flow-weighted P concentration). The PSMs are separated into two groups based on the dominant sorption mechanism, either ligand exchange onto Fe and Al materials or precipitation of Ca-phosphates in Ca materials (Klimeski et al., 2014, 2012; Lyngsie

et al., 2014; Wendling et al., 2013; Penn et al., 2011). Phosphorus sorption materials are classified in one of the two broad P sorption mechanism categories based on chemical characteristics (pH, buffer index, Total Ca, Al, and Fe). While there are two sets of models, one set per mechanism, the basic equation used is the same for both; equations 2a and 2b. The coefficients, α , β , χ , δ , ε , and μ from equations 2a and 2b differ for the two groups of materials (Fe/Al and Ca) due to differences in chemical characteristics relevant to their respective sorption mechanism. The universal model predicts these coefficients as a function of the PSM characteristics.

Within the Ca-P precipitation group, materials are further divided into RT sensitive and non-sensitive materials based on pH and buffer index. The Ca PSMs that are sensitive to RT are unable to strongly buffer the solution pH above 6 and therefore have slower Ca-P precipitation kinetics (Lyngsie et al., 2015, 2014; Stoner et al., 2012). Dissolved P removal by RT sensitive materials are appreciably affected by RT by increasing P removal with greater RT (Klimeski et al., 2012; Claveau-Mallet et al., 2011). The chemical characteristics used to estimate the coefficients listed in equations 2a and 2b include pH, buffer index, amorphous Fe and Al, mean particle size, and total Al, Ca, and Fe.

In addition, although both P sorption groups utilize an exponential P removal curve for the discrete design curve (equation 1), the Fe/Al PSM group additionally possesses a two-phase sorption model. Specifically, the Fe/Al model contains a linear P removal stage prior to the exponential portion of the P removal curve. An example of this is shown in Figs. 2a and 3a where the initial P removal decreases rapidly with increased cumulative P loading to the PSM before the change in P removal with loading decreases. The change in slope for P sorption among materials rich in Fe and Al is a common observation, and has been attributed to reasons

such as a change from bi-dentate to mono-dentate sorption and from ligand exchange to precipitation (Ler and Stanforth, 2003; Kafkafi et al., 1967; Taylor and Ellis, 1978; Syers et al., 1973). Therefore, the portion of the model that deals with the Fe/Al materials additionally involves a series of equations that predict the location of the junction point between the linear P removal line and the exponential line. Essentially, the coordinates of the junction point is estimated from the amount of ammonium oxalate extractable Fe and Al.

After the equation for the discrete removal curve (measured) or design curve (predicted) is determined (equation 1), it can be integrated to produce a CP_{rem} removal curve prior to use in designing or quantifying a P removal structure. Values of CP_{rem} in units of percent at any desired cumulative P loading (i.e. CP_{add}), is obtained by integrating equation 1:

$$CP_{rem} (\%) = \frac{\int_0^{CP_{add}} (be^{m*CP_{add}}) dCP_{add}}{CP_{add}} \quad (3)$$

Dividing the integrated discrete removal curve or design curve by 100 instead of CP_{add} results in CP_{rem} in $mg\ P\ kg^{-1}\ PSM$:

$$CP_{rem} (mg\ kg^{-1}) = \frac{\int_0^{CP_{add}} (be^{m*CP_{add}}) dCP_{add}}{100} \quad (4)$$

The loading at which the PSM's DP_{rem} (%) approaches 0, i.e. when the PSM is spent and inflow P equals outflow P concentration, can be determined by using the coefficients from the discrete removal curve or design curve:

$$Maximum\ P\ Added\ (mg\ kg^{-1}) = \frac{\ln(b)}{-m} \quad (5)$$

Input of the maximum P added into either equation 3 or 4 for CP_{add} will result in the maximum CP_{rem} in percent or $mg\ kg^{-1}$, respectively.

Twenty-two PSMs, which were not used in creation of the model, were chemically and physically characterized as previously described, with results input into the model for obtaining the predicted parameters of the design curve (i.e. the predicted discrete curve: cumulative P loading vs. percent discrete P removal). For Ca-based PSMs, this includes the slope (m) and y intercept (b), and for Fe/Al-based PSMs, this additionally includes the coordinates for the junction point between the linear and exponential phase of the discrete P removal curve. The measured curve parameters were obtained by performing an exponential regression on the measured data points. For the Fe/Al-based PSMs only, the data was additionally fit to a non-linear model using the PROC NLIN procedure (SAS Institute, 2011) in order to determine the x and y coordinates of the junction point previously described. The predicted and measured curve parameters were then statistically compared using a paired t-test conducted with SAS.

In addition, for each PSM used in this paper, a linear regression was conducted between measured and predicted DP_{rem} at each cumulative P loading point (i.e. CP_{add}), and between measured and predicted CP_{rem} at each cumulative P loading point. The analysis was conducted using SAS with the y intercept of the regression equation set to 0; this allowed us to compare the slope of the resulting linear regression to a value of 1. A slope value of 1 with an intercept of 0 indicates a perfect fit and therefore any deviance in slope from 1 was indicative if the model over or under-predicted P removal. The R^2 and slope value produced from the SAS output was reported, and a t-test was also conducted separately on grouped Ca-based and Fe/Al-based PSMs to determine if the slope of linear regression was significantly different from a value of 1. Last, a paired t-test was also conducted separately on Ca and Fe/Al-based PSMs to determine if the predicted and measured value of the total CP_{rem} (in both percent and $mg\ kg^{-1}$ PSM) for each experiment was statistically different.

3. RESULTS AND DISCUSSION

3.1 Conformity of the Model to Actual Discrete and Cumulative Phosphorus Removal Curves

Statistical results of the paired t-tests for comparing measured and predicted design curve parameters (equation 1) are shown in Table 3. Examples of design curves are shown in Figs. 2a, 3a, and 4a. For both the Ca and Fe/Al-based model, there was no statistical difference between measured and predicted P removal curve parameters ($p = 0.05$), or for the final amount of CP_{rem} (equations 3 and 4). However, based on the p values for comparison between predicted and observed CP_{rem} , the Fe/Al-based model appeared to perform better than the Ca-based PSM model. Because the design curve slope parameters for both the Ca and Fe/Al-based model were not significantly different between predicted and measured values, it is not surprising that the CP_{rem} values were also well predicted (Tables 3 and 4). This is due to the fact that cumulative P is determined by integration of the design curve.

Further assessments of the model for specific scenarios are shown in Table 4. In general, the individual DP_{rem} points for each design curve were well predicted as assessed by the R^2 values of 0.74 and higher, indicating good model fit. Table 4 also shows the slope for the linear regression between measured and predicted DP_{rem} values for each scenario. While the average slope for Ca-based PSMs was not significantly different from 1 (i.e. a perfect fit), the average slope value of 1.31 for Fe/Al PSMs was significantly different from 1 at $p = 0.1$, although not significantly different at $p = 0.05$. In this case a slope significantly >1 indicates that overall, the model was over-predicting discrete P removal for Fe/Al-based PSMs. However, AMDR 1, 3, and 5 were somewhat skewing the data with slope values greater than 2.

The R^2 values obtained from linear regression between individual measured and predicted CP_{rem} points for each scenario were greater than 0.96 and always larger than the R^2 values for the DP_{rem} points (Table 4). Examples of CP_{rem} curves are shown in Figs 2b, 2c, 3b, 3c, 4b, and 4c. Calculation CP_{rem} tends to minimize occasional large differences in DP_{rem} points that may have occurred between measured and predicted values. While accurate prediction of the DP_{rem} curve parameters are needed to calculate the absolute lifetime of a P removal structure (i.e. the cumulative P loading point at which P is no longer able to be removed; equation 5), the CP_{rem} curve provides the information necessary for estimating/predicting how much P will be removed at a certain point within the lifetime of the P removal structure. For example, even though the DP_{rem} for AMDR 1 was over-predicted by the model (discrete slope = 2.4), the CP_{rem} at the final measured loading point was reasonably well predicted (11 vs. 16% and 1413 vs. 2001 $mg\ kg^{-1}$; Table 4). For Fe/Al-based PSMs, the average slope of the linear regression between measured and estimated CP_{rem} points was not significantly different from 1. Overall, the average slope for the linear regression between measured and estimated CP_{rem} points for Ca-based PSMs was 1.39, which was significantly greater than 1. Again, this indicates that the Ca-based PSM model was generally over-predicting CP_{rem} . Regardless, the final measured CP_{rem} at the final P loading point (CP_{add}) for the Ca-based materials shown in the final two columns of Table 4 were not significantly different from predicted values ($p = 0.1$ and 0.28 for CP_{rem} expressed as percent of total input and $mg\ kg^{-1}$ PSM, respectively; Table 3).

3.2 Practical use of the model and illustration of validation scenarios

The universal flow-through model did a reasonable job of predicting the design curve when compared with actual removal data in a variety of settings with both Fe/Al-based materials and Ca-based materials. The ability to predict the design curve reduces the effort required to

design a P removal structure or quantify an existing structure by eliminating the need for time consuming flow-through experiments, which must be conducted separately for each RT and input P concentration of interest. However, by using the model, various scenarios can be easily investigated requiring only the characterization of the PSM and site conditions.

When designing a structure for a specific PSM, inflow P concentration, RT, and removal goal, the mass of PSM required (Mg) to meet the desired P removal goal is calculated by: (6)

$$PSM\ mass = \frac{PL_{annual} * DL}{CP_{add}(RG)} \quad (6)$$

Where PL_{annual} is the annual P loading for the site (g), DL is desired lifetime (yr) of the structure, and CP_{add} (RG) is the cumulative P load to the PSM (in mg P kg^{-1} PSM) as a function of the desired removal goal (RG, in percent). The CP_{add} corresponding with the desired RG is determined from the equation of the CP_{rem} curves (Figs 2b, 3b, and 4b). This process is illustrated in several examples below. Note that the CP_{rem} curve used to make this calculation is specific to the PSM, inflow P concentration, and RT. The CP_{rem} curve is determined by integration of the predicted DP_{rem} curve (i.e. design curve) as described in equations 3 and 4. On the other hand, for quantification of P removal for an existing structure, the current value of CP_{add} is input into the design curve equation (equation 1) resulting in the current value of DP_{rem} , which is then integrated to determine CP_{rem} to that point. The accuracy for either design or prediction of performance is dependent on the model's ability to predict the equation for the design curve and the quality of the inputs, including the characteristics of PSM, annual flow volume, RT, and average P concentration. Six of the 16 scenarios listed in Table 4 are field P

removal structures (Slag 1, 2, 3, 4, 5, and 7) that possess this inherent variability, yet the model still provided an accurate estimate of P removal.

Several examples are shown below that illustrate how the model is used in designing P removal structures, as well as a demonstration of how well the model fits actual measured P removal data. Examples for four different types of scenarios are presented: laboratory flow-through, pond filter, runoff bed filter, and ditch filters.

3.2.1 Example of Laboratory Flow-Through Data

Figure 2 shows an example of the laboratory flow-through validation scenarios, specifically for AMDR 4 listed in Table 4. The inflow P concentration was 1 mg L^{-1} . Each point shown on the DP_{rem} curve in Fig.2a represents the percentage of P removed at that sampling time, as a function of the cumulative load of P that has flowed through the PSM (i.e. CP_{add}). The solid line is the design curve estimated by using the universal flow-through model which predicted the m and b values for the exponential portion of the curve (equation 1), and additionally the coordinates for the junction point since this was a Fe/Al-based PSM. Based on the design curve for AMDR 4 in Fig. 2a, this material will be able to remove P until the CP_{add} reaches $80,000 \text{ mg P kg}^{-1}$ (from equation 5). For a known mass of PSM and annual site P loading (i.e. PL_{annual}), this value can be used to determine the amount of time in which a structure will be able to remove P, at the specified inflow P concentration and RT (if the material is sensitive to RT). For example, at a PL_{annual} value of 30 kg yr^{-1} to 2 Mg of AMDR 4, it would be effective at removing P for 5.3 yrs.

The cumulative curve, determined by integration of the DP_{rem} curve (equations 3 and 4), removes some of the noise present in the discrete curve and presents a useful picture of the

PSM's ability to sorb P from the context of designing a P removal structure. The points plotted in Fig. 2b and 2c are measured data points, which are compared to the predicted CP_{rem} curve (solid line). If this curve was to be used in sizing a P removal structure, continuing with the same hypothetical example of P loading at a site of 30 kg yr^{-1} , the CP_{rem} curve in Fig 2b shows that a RG of 50% corresponds with a value of CP_{add} of $6000 \text{ mg P kg}^{-1}$ i.e. $CP_{add} \text{ (RG)}$, under those conditions. Inserting this value of CP_{add} and a PL_{annual} value of 30 kg yr^{-1} into equation 6 results in a mass requirement of 5 Mg of AMDR 4 to achieve the RG of 50% over one year (DL) for this hypothetical site and set of conditions.

3.2.2 Example of Pond Filter Structure Data

The second validation scenario tested was pond filter data produced in Penn and McGrath (2011). The data shown in Fig 3 is for a treated steel slag material, specifically Slag 2 listed in Table 4. Again, Figs. 3a, 3b, and 3c show the DP_{rem} , CP_{rem} in %, and CP_{rem} in mg kg^{-1} , respectively, compared to model predictions. The predicted DP_{rem} and CP_{rem} was not significantly different from measured values, with some slight over-prediction of CP_{rem} . The treated and sieved slag material is often favored over other PSMs in certain situations due to the large hydraulic conductivity of the material, thereby allowing a large amount of water to pass through it quickly during peak flow events. Here we present an example design for a future site located in Grand Lake St. Mary's Watershed, Ohio, using the CP_{rem} curve (Fig. 3). The drainage water at this site is from subsurface tile drainage that has an average annual flow volume of 1.27 million L. Thus, PL_{annual} is about 8.87 kg. Assuming that the RG was 35% of the cumulative 2-yr P load, Fig 3b shows that the corresponding value of $CP_{add} \text{ (RG)}$ is 385 mg kg^{-1} . Inserting this information and value of 2y for DL into equation 6, it would require 46 Mg of this particular treated slag material to meet the RG. Also, P removal after the first year would correspond to a

1 cumulative P loading of 192 mg P kg^{-1} PSM, which would result in CP_{rem} value of about 50% of
2 the PL_{annual} (Fig. 3b). Notice that for the last two example scenarios, the PSMs were not
3 sensitive to RT, therefore RT was not considered.

4 *3.2.3 Example of Runoff Bed Structure Data*

5 The third validation scenario examined one of the three field runoff bed P removal
6 structures (Slag 1-Poultry farm, Slag 3-Golf course filter, and Slag 7-Golf course filter; Table 4).
7 This particular structure, Slag 3-Golf course filter, was constructed using a sieved ($>6.35 \text{ mm}$)
8 and non-treated EAF steel slag, and therefore had less capacity to remove P compared to the
9 treated slag. Specifics of this slag filter and measured data set were presented in detail in Penn et
10 al. (2012). The flow-weighted inflow dissolved P concentration and RT was 0.69 mg L^{-1} and 10
11 min, respectively. The DP_{rem} by the structure (Fig. 4a) showed discrepancies from the expected
12 exponential decay observed in more controlled settings, which is likely explained by the
13 differing RTs that occurred for various flow events. The PSM was sensitive to RT and thus for
14 individual flow events with low flow rates, the RT of the structure will increase, causing
15 increased sorption, which explains the sampling events with almost 100% DP_{rem} halfway through
16 the life of the PSM (Stoner et al., 2012).

17 As discussed in the introduction, Penn et al. (2012) highly overestimated the P removal of
18 this data set through use of a previous model that considered only inflow P concentration and
19 RT, and not the chemical characterization of the slag material i.e. the previous model was
20 specific to a single specific slag sample only. Figure 4 illustrates the benefit of the current
21 universal model in predicting discrete and cumulative P removal. Although the current model
22 slightly over-predicted P removal, the prediction was dramatically improved compared to Penn

et al. (2012) by considering individual chemical characterization. For example, use of the previous model resulted in prediction of CP_{rem} of nearly 80 mg kg^{-1} at a value of CP_{add} of 100 mg kg^{-1} compared to the predicted value of 35 mg kg^{-1} by the current model (Fig. 4c). Although the RT varied between individual flow events, input of a flow-weighted RT allowed for reasonable prediction of CP_{rem} .

The non-treated slag material differs from the example PSMs illustrated in Figs. 2 and 3 in that this PSM is Ca-based. After 1.5 years, Slag 3 was replaced with the same mass (2.7 Mg) of a smaller size fraction of non-treated slag (Slag 7) and monitored for approximately 16 months (Penn et al., 2014b). The smaller sized fraction of slag possessed a greater pH buffer capacity, total Ca, and smaller mean particle diameter, resulting in about twice as much P removal ($53 \text{ vs. } 26 \text{ mg kg}^{-1}$) under similar conditions, which was well predicted by the model (Table 4; Slag 7-Golf course). The current model was able to capture the differences in the chemical characteristics that are critical to P removal, while also taking into account inflow P concentration and RT.

3.2.4 Maryland Ditch Filters and Storm Water Basin Structure

The ditch P filters represented the largest P removal structures constructed in this validation set as the mass of PSM varied from 46 to 80 Mg (Table 5). In general, the model did a reasonable job at predicting the cumulative mass of P removed over the 3-yr monitoring period. The storm water basin P removal structure (Centreville; Table 5) represented a scenario with easily moveable PSM boxes that were replaced annually over 4 years. When the y-intercept was set to 0, the R^2 value between predicted and measured cumulative mass of P removed was 0.78 ($p < 0.01$) with a slope of 0.92, thus only a slight overall under-prediction. The statistical t-test

also showed that the predicted values were not different from the measured cumulative mass of P removed ($p < 0.01$).

The average mass of P removed by the large ditch filters was 0.79 kg, with final P concentrations on the PSMs ranging from 8 to 25 mg kg⁻¹; values similar to the untreated slag materials used in the Golf course filter (Slag 3) and runoff plots (Slag 4) listed in Table 4. Note that the use of the untreated slag and FGD gypsum are generally much less potent at removing P on a per mass basis compared to the other materials examined, specifically the treated slag and AMDRs (Table 4). However, the model was able to capture this through differences in PSM chemical characterization. It is difficult to directly compare the performance of the non-treated slag ditch filters to the FGD gypsum filters in Table 5 because of the differences in filter size, inflow P concentrations, RT, and the cumulative inflow P load. Regardless, notice that the slag ditch filters had a much greater cumulative inflow P load compared to the FGD gypsum ditch filters; this is due to the high hydraulic conductivity of the sieved slag (~1 cm s⁻¹) compared to FGD gypsum (~0.01 cm s⁻¹), thereby allowing a greater volume of water and mass of P to enter into the structure (Canga et al., 2014).

4. SUMMARY AND IMPLICATIONS

P removal structures have been proven as an effective means of reducing dissolved P loss from sites, but in order to design or quantify their P removal, the PSM's ability to sorb P under the respective flow-through conditions must be known. The design curve, which is the relationship between the DP_{rem} and CP_{add} to a PSM, is used for designing structures to meet performance goals or to quantify existing structures. The ability to accurately predict the design curve for a specific PSM and set of conditions is not only necessary to properly design or evaluate a P removal structure, but it also avoids the need for costly and time consuming flow-through experiments and constant monitoring of constructed P removal structures. The universal flow-through model was able to predict P removal in 23 different scenarios, which included a diversity in chemical characteristics, conditions (P inflow concentration and RT), and ranged in scale from laboratory flow-through to 80 Mg ditch filters. Although CP_{rem} curves were slightly over-predicted by the model for Ca-based PSMs, the design curves predicted by the universal flow-through model were not significantly different from the experimentally determined design curves from the 15 sets of Ca-based PSM observations used in this validation.

The flexibility and utility of the model is due to the fact that any PSM can be used in design of a P removal structure through a chemical and physical characterization. This is especially important since certain PSMs are only available in narrow geographic regions, and because the chemical characteristics within specific types of PSMs will vary, even within the same source (Penn et al., 2012). Not only can the model be applied to PSMs that result from by-products, but also manufactured PSMs. The universal flow-through model presented here is currently utilized as a component in the design software, Phrog (Phosphorus removal online guidance; Oklahoma State University, 2015). The ability to predict P removal without constant

1 monitoring makes the P removal structure a viable means of meeting TMDL P discharge
2 regulations and could be used in nutrient trading programs.

3 It is important to keep in mind that P removal structures are intended to treat “hot spots”
4 of periodic flow containing high dissolved P concentrations before they reach surface waters,
5 rather than treating a constant flowing water source with relatively lower P concentrations such
6 as a stream or canal. Targeting dissolved P hot spots is much more efficient both from the
7 perspective of thermodynamics and design. Also, implementing P removal structures under
8 constant-flow scenarios may result in the formation of biofilms on the surfaces of the PSMs
9 which would likely reduce P sorption.

10

11

REFERENCES

- Ahiablame, L.M., Chaubey, I., Smith, D.R., Engel, B.A. 2011. Effect of tile effluent on nutrient concentration and retention efficiency in agricultural drainage ditches. *Ag. Wat. Man.* 98:1271-1279.
- American Society for Testing and Materials (ASTM). 1963. D422–63 (2007) Standard test method for particle-size analysis of soils. ASTM International, West Conshohocken. doi 10:1520.
- Bryant R.B., Buda A.R., Kleinman P.J.A., Church C.D., Saporito L.S., Folmar G.J., Bose S., Allen A.L. 2012. Using Flue Gas Desulfurization Gypsum to Remove Dissolved Phosphorus from Agricultural Drainage Waters. *Journal of Environmental Quality* 41:664-671. DOI: 10.2134/jeq2011.0294.
- Callery, O., Brennan, R.B., Healy, M.G. 2015. Use of amendments in a peat soil to reduce phosphorus losses from forestry operation. 85:193-200.
- Carpenter S.R., Caraco N.F., Correll D.L., Howarth R.W., Sharpley A.N., Smith V.H. 1998. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen. *Ecological Applications* 8:559-568. DOI: 10.2307/2641247.
- Canga, E., Iversen, B.V., Kjaergaard, C. 2013. A simplified transfer function for estimating saturated hydraulic conductivity of porous drainage filters. *Wat. Air Soil Pol.* 225:1-13.
- Claveau-Mallet D., Wallace S., Comeau Y. 2011. Model of Phosphorus Precipitation and Crystal Formation in Electric Arc Furnace Steel Slag Filters. *Environmental Science & Technology* 46:1465-1470. DOI: 10.1021/es2024884.

- Claveau-Mallet D., Wallace S., Comeau Y. 2013. Removal of phosphorus, fluoride and metals from a gypsum mining leachate using steel slag filters. *Water Research* 47:1512-1520.
DOI: <http://dx.doi.org/10.1016/j.watres.2012.11.048>.
- Darch T., Carswell A., Blackwell M.S.A., Hawkins J.M.B., Haygarth P.M., Chadwick D. 2015. Dissolved Phosphorus Retention in Buffer Strips: Influence of Slope and Soil Type. *Journal of Environmental Quality*. DOI: 10.2134/jeq2014.10.0440.
- Delgado, J.A., Khosla, R., Mueller, T. 2011. Recent advances in precision (target) conservation. *J. Soil Wat. Cons.* 66:167A-170A.
- DeSutter T.M., Pierzynski G.M., Baker L.R. 2006. Flow-Through and Batch Methods for Determining Calcium-Magnesium and Magnesium-Calcium Selectivity. *Soil Science Society of America Journal* 70:550-554.
- Feyereisen, G.W., Francesconi, W., Smith, D.R., Papiernik, S.K., Krueger, E.S., Wentz, C.D. 2015. Effect of replacing surface inlets with blind or gravel inlets on sediment and phosphorus subsurface drainage losses. *J. Environ. Qual.* 44:594-604.
- Fox, G.A., Penn, C.J. 2013. Empirical model for quantifying total phosphorus reduction by vegetative filter strips. *Trans. ASABE* 56(4):1461-1469.
- Fuchs, J.W., Fox, G.A., Storm, D.E., Penn, C.J., Brown, G.O. 2009. Subsurface transport of phosphorus in riparian floodplains: Influence of preferential flow paths. *J. Environ. Qual.* 38(2):473-484.
- Haygarth, P.M., Jarvie, H.P., Powers, S.M., Sharpley, A.N., Elser, J.J., Shen, J., Peterson, H.M., Chan, N., Howden, N.J.K., Burt, T., Worrall, F., Zhang, F., Liu, X. 2014. Sustainable

- phosphorus management and the need for a long-term perspective: the legacy hypothesis. Environ. Sci. Tech. 48:8417-8419.
- Ibrahim, T.G., Goutelle, A., Healy, M.G., Brennan, R., Tuohy, P., Humphreys, J., Lanigan, G., Brechignac, J., Fenton, O. 2015. Mixed agricultural pollutant mitigation using woodchip/pea gravel and woodchip/zeolite permeable reactive interceptors. Wat. Air Soil Pol. 226: 51 DOI 10.1007/s11270-015-2335-4.
- Ippolito, J.A. 2015. Aluminum-based water treatment residual use in a constructed wetland for capturing urban runoff phosphorus: column study. Wat. Air Soil Pol. 226: 334 DOI 10.1007/s11270-015-2604-2
- Kafkafi, U., Posner, A.M., Quirk, J.P. 1967. Desorption of phosphate from kaolinite. Soil Sci. Soc. Am. Proc. 31:348-353.
- Karczmarczyk A., Bus A. 2014. Testing of reactive materials for phosphorus removal from water and wastewater—comparative study. Annals of Warsaw University of Life Sciences-SGGW. Land Reclamation 46:57-67.
- King, K.W., Williams, M.R., Macrae, M.L., Fausey, N.R., Frankenberger, J., Smith, D.R., Kleinman, P.J.A., Brown, L.C. 2014. Phosphorus transport in agricultural subsurface drainage: a review. J. Environ. Qual. 44:467-485.
- Kirkkala, T., Ventela, A., Tarvainen, M. 2012. Long-term field-scale experiments on using lime filters in an agricultural catchment. J. Environ. Qual. 41:410-419.
- Klimeski A., Chardon W.J., Turtola E., Uusitalo R. 2012. Potential and limitations of phosphate retention media in water protection: A process-based review of laboratory and field-scale tests. Agricultural and Food Science 21:206-223.

- Klimeski, A., Uusitalo, R., Turtola, E. 2014. Screening of Ca- and Fe-rich materials for their applicability as phosphate-retaining filters. *Ecol. Eng.* 68:143-154.
- Ler, A., Stanforth, R. 2003. Evidence for surface precipitation of phosphate on goethite. *Environ. Sci. Technol.* 37:2694-2700.
- Lyngsie G., Penn C.J., Pedersen H.L., Borggaard O.K., Hansen H.C. 2015. Modelling of phosphate retention by Ca-and Fe-rich filter materials under flow-through conditions. *Ecological Engineering* 75:93-102.
- Lyngsie, G., Penn, C.J., Hansen, H.C.B., Borggaard, O.K. 2014. Phosphate sorption by three potential filter materials as assessed by isothermal titration calorimetry. *J. Environ. Man.* 143:26-33.
- McDowell R., Sharpley A., Bourke W. 2008. Treatment of drainage water with industrial by-products to prevent phosphorus loss from tile-drained land. *Journal of environmental quality* 37:1575-1582.
- McDowell, R. 2015. Treatment of pasture topsoil with alum to decrease phosphorus losses in subsurface drainage. *Ag. Eco. Environ.* 207:178-182.
- McGrath, J.M., Penn, C.J., and Coale F.J. 2012. A modeling approach to the design of *in situ* agricultural drainage filters. *Soil Use and Management*. doi: 10.1111/j.1475-2743.2011.00381.x
- McKeague J., Day J.H. 1966. Dithionite-and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science* 46:13-22.
- Murphy J., Riley J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27:31-36. DOI: [http://dx.doi.org/10.1016/S0003-2670\(00\)88444-5](http://dx.doi.org/10.1016/S0003-2670(00)88444-5).

- Needelman, B.A., Kleinman, P.J.A., Strock, J.S., Allen, A.L. 2007. Improved management of agricultural drainage ditches for water quality protection: an overview. *J. Soil Wat. Cons.* 62:171-178.
- Nguyen, T.A.H., Gno, H.H., Guo, W.S., Zhang, J., Liang, S., Lee, D.J., Nguyen, P.D., Bui, X.T. 2014. *Biores. Technol.* 169:750-762.
- NRCS, 2015. Natural Resources Conservation Service Interim Conservation Practice Standard: Phosphorus Removal System, Code 782.
http://efotg.sc.egov.usda.gov/references/public/WI/782_Standard.pdf. Verified November 2nd, 2015.
- Oklahoma State University. 2015. Phosphorus removal online guidance (Phrog) software. Oklahoma Technology Development Center, Stillwater, OK.
- Parry, R. 1998. Agricultural phosphorus and water quality: a U.S. Environmental Protection Agency Perspective. *J. Environ. Qual.* 27:258-261.
- Penn C., McGrath J., Bowen J., Wilson S. 2014a. Phosphorus removal structures: A management option for legacy phosphorus. *Journal of Soil and Water Conservation* 69:51A-56A.
- Penn, C.J., Bell, G., Wang, Z., McGrath, J., Wilson, S., Bowen, J. 2014b. Improving the ability of steel slag to filter phosphorus from runoff. *Turfgrass and environmental research online.* 13(5):1-5.
- Penn C.J., McGrath J.M., Rounds E., Fox G., Heeren D. 2012. Trapping Phosphorus in Runoff with a Phosphorus Removal Structure. *J. Environ. Qual.* 41:672-679. DOI: 10.2134/jeq2011.0045.

- Penn C.J., Bryant R.B., Callahan M.P., McGrath J.M. 2011. Use of Industrial By-products to Sorb and Retain Phosphorus. *Communications in Soil Science and Plant Analysis* 42:633-644. DOI: 10.1080/00103624.2011.550374.
- Penn C.J., McGrath J.M. 2011. Predicting Phosphorus Sorption onto Steel Slag Using a Flow-through approach with Application to a Pilot Scale System. *Journal of Water Resource and Protection* 03:235-244.
- Pierce, S.C., Kroger, R., Pezeshki, R. 2012. Managing artificially drained low-gradient agricultural headwaters for enhanced ecosystem functions. *Biological Conservation* 151:794-856.
- SAS. (2011) SAS/IML 9.3 User's Guide SAS Institute.
- Schindler D.W., Hecky R.E., Findlay D.L., Stainton M.P., Parker B.R., Paterson M.J., Beaty K.G., Lyng M., Kasian S.E. 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences of the United States of America* 105:11254-11258. DOI: 10.1073/pnas.0805108105.
- Sharpley A., Jarvie H.P., Buda A., May L., Spears B., Kleinman P. (2013) Phosphorus Legacy: Overcoming the Effects of Past Management Practices to Mitigate Future Water Quality Impairment. *J. Environ. Qual.* 42:1308-1326. DOI: 10.2134/jeq2013.03.0098.
- Sharpley A.N., Smith S. 1994. Wheat tillage and water quality in the Southern Plains. *Soil and Tillage Research* 30:33-48.
- Shipitalo, M.J., Bonta, J.V., Owens, L.B. 2012. Sorbent-amended compost filter socks in grassed waterways reduce nutrient losses in surface runoff from corn fields. *J. Soil Wat. Cons.* 67:433-441.

- Smith, D.R., King, K.W., Johnson, L., Francesconi, W., Richards, P. 2015. Surface runoff and tile drainage transport of phosphorus in the midwestern United States. *J. Environ. Qual.* 44:495-502
- Stoner D., Penn C., McGrath J., Warren J. 2012. Phosphorus Removal with By-Products in a Flow-Through Setting. *J. Environ. Qual.* 41:654-663. DOI: 10.2134/jeq2011.0049.
- Syers, J.K., Browman, M.G., Smillie, G.W., Corey, R.B. 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. *Soil Sci. Soc. Am. Proc.* 37:358-363.
- Taylor, R.W., Ellis, B.G. 1978. A mechanism of phosphate adsorption on soil and anion exchange resin surfaces. *Soil Sci. Soc. Am. J.* 42:432-436.
- USEPA. 1996. Method 3050B Acid Digestion of Sediments, Sludges, and Soils, Environmental Protection Agency.
- Uusitalo, R. Ekholm, P., Lehtoranta, J., Klimeski, A., Konstari, O., Lehtonen, R., Turtola, E. 2012. Ca-Fe oxide granules as potential phosphate barrier material for critical source areas: a laboratory study of P retention and release. *Ag. Food Sci.* 21:206-223.
- Vadas, P.A., Srinivasan, M.S., Kleinman, P.K., Schmidt, J.P., Allen, A.L. 2007. Hydrology and groundwater nutrient concentrations in a ditch-drained agroecosystem. *J. Soil Wat. Cons.* 62:178-188.
- Wang, Z., Bell, G.E., Penn, C.J., Moss, J.Q., Payton, M.E. 2014. Phosphorus reduction in turfgrass runoff using a steel slag trench filter system. *Crop Sci.* 54:1859-1867.
- Wendling, L.A., Blomberg, P., Sarlin, T., Priha, O., Arnold, M. 2013. Phosphorus sorption and recovery using mineral-based materials: Sorption mechanisms and potential phytoavailability. *App. Geochem.* 37:157-169.

Zhang, W., Brown, G.O., Storm, D., Zhang, H. 2008. Fly-ash amended sand as filter media in bioretention cells to improve phosphorus removal. *Wat. Environ. Res.* 80:507-516.

ACKNOWLEDGEMENTS: With regard to funding of P removal structure construction, we would like to thank the Natural Resource Conservation Service, United States Golf Association, and the Maryland Department of Agriculture. With regard to funding of model development, we would like to thank the Oklahoma Technology Development Center.

Table 1. Source, location, preparation, and the dominant phosphorus (P) sorption component of the P sorption materials (PSMs) used in each P removal scenario listed in Table 2. AMDR: acid mine drainage residual.

PSM	Dominant basis for P sorption	Source of PSM	Location	Preparation
AMDR 1	Fe/Al	Passive treatment of coal mine drainage. Vertical anoxic limestone drain	Huntington, AR	Air dry
AMDR 2	Fe/Al	Natural attenuation of coal mine drainage	Gowen, OK	Air dry
AMDR 3	Fe/Al	Passive treatment of coal mine drainage. Vertical anoxic limestone drain	Hartshorne, OK	Air dry
AMDR 4	Fe/Al	Natural attenuation of coal mine drainage	Howe, OK	Air dry
AMDR 5	Fe/Al	Passive treatment of coal mine drainage. Vertical anoxic limestone drain	Fanshawe, OK	Air dry
AMDR 6	Fe/Al	Ten-cell passive treatment of Pb-Zn mine drainage	Commerce, OK	Air dry
AMDR 7	Fe/Al	Same as AMDR 6, but from different location within site	Commerce, OK	Air dry
AMDR 8	Fe/Al	Passive treatment of coal mine drainage using fly-ash injection	Red Oak, OK	Air dry
Slag 1	Fe/Al	Tube City IMS, electric arc furnace slag. Collected Oct, 2013.	Ft. Smith, AR	Treated. Excluded particles < 6.35 mm
Slag 2	Fe/Al	Tube City IMS, electric arc furnace slag. Collected July, 2013.	Ft. Smith, AR	Treated. Excluded particles < 6.35 mm
Slag 3	Ca	Tube City IMS, electric arc furnace slag. Collected June, 2010	Ft. Smith, AR	Excluded particles < 6.35 mm
Slag 4	Ca	Tube City IMS, electric arc furnace slag. Collected January, 2010.	Ft. Smith, AR	Excluded particles < 6.35 mm
Slag 5	Ca	Tube City IMS, electric arc furnace slag. Collected July, 2010	Ft. Smith, AR	Excluded particles < 6.35 mm
Slag 6	Ca	Edwin Levy Co., blast furnace slag. Collected Jan. 2013.	Butler, IN	Excluded particles < 4 mm
Slag 7	Ca	Tube City IMS, electric arc furnace slag. Collected Sep., 2012	Ft. Smith, AR	Excluded particles < 0.5 mm

Table 2. Location and description of conditions for each phosphorus (P) removal scenario examined in this study (Figure 1), utilizing P sorption materials (PSMs) described in Table 1.

Experimental scenario	Location	Retention Time (min)	Inflow weighted dissolved P concentration (mg L ⁻¹)	PSMs utilized	PSM mass	Size	Reference
Laboratory flow-through columns	Oklahoma State University	0.5 to 3	1	†AMDRS 1 to 8, Slag 1 and 6	0.1 to 2 g	173 mm ²	Stoner et al., 2012
Poultry farm runoff filter	Westville, OK	16.8	4.2	Slag 1	36 Mg	36 m ²	Penn et al., 2014a
Pond filter	Oklahoma State University Botanical Gardens	10	0.5	Slag 2 and 4	453 kg	1.2 m ²	Penn and McGrath, 2011
Golf course runoff filter	Stillwater Country Club, Stillwater, OK	9.5	0.69	Slag 3 and 7	2.7 Mg	7.4 m ²	Penn et al., 2012
Runoff interception trenches	Oklahoma State University Turf Grass Research Farm	1	4.3	Slag 5	1 Mg per trench	3.1 m ² per trench	Wang et al., 2014
Ditch filter structures	Barclay, Marion, and Westover, MD	>10	0.48 to 1.58	‡FGD gypsum and electric arc furnace slag	46 to 80 Mg	65 to 84 m ²	McGrath et al., 2012
Storm water basin filter	Centreville, MD	>10	1.04	Electric arc furnace slag	§15 Mg over 4 yr	2.6 m ³ per box	NA

† Acid mine drainage residuals

‡ Flue gas desulfurization gypsum

§ The slag contained in the four perforated metal boxes at the site was annually replaced with new slag over a four-year time period. Each box contained 0.94 Mg slag

Table 3. Statistical p values for the hypothesis test: measured value = predicted value, for parameters of the equations (equations 2a and 2b) for the discrete phosphorus removal curve (example: Figs. 2a, 3a, and 4a). Parameters include m (equation 1), x and y coordinates for the joint (for Al/Fe materials only), and b (for Ca materials only; equation 1). Statistical p values for overall differences between measured and predicted cumulative phosphorus removed (CP_{rem} as % and $mg\ kg^{-1}$; equations 3 and 4) are shown separately for the Ca and Fe/Al based phosphorus sorption materials (PSMs) groups listed in Table 1.

<u>P value (measured = predicted)</u>								
m		Joint: Al/Fe		b	CP_{rem} (%)		CP_{rem} ($mg\ kg^{-1}$ PSM)	
Al/Fe	Ca	X	Y	Ca	Al/Fe	Ca	Al/Fe	Ca
0.11	0.53	0.29	0.14	0.10	0.47	0.10	0.40	0.28

Table 4. Slope and R^2 values for the linear relationship between measured and predicted discrete phosphorus (P) removal (DP_{rem}), and between measured and predicted cumulative P removal (CP_{rem}) for several different acid mine drainage residuals (AMDRs), normal slag, and treated slag samples, with y-intercept set to zero. Final measured and predicted CP_{rem} is presented as both a percentage of cumulative inflow P load and $mg\ kg^{-1}$ P sorption material (PSM).

PSM	Scenario	Measured vs. predicted DP_{rem}		Measured vs. predicted CP_{rem}		Final measured CP_{rem}		Final predicted CP_{rem}	
		R^2	slope	R^2	slope	%	$mg\ kg^{-1}$	%	$mg\ kg^{-1}$
AMDR 1	Laboratory	0.99**	2.4	0.99**	1.4	11	1413	16	2001
AMDR 2	Laboratory	0.90**	0.62	0.99**	0.6	36	4274	21	2494
AMDR 3	Laboratory	0.99**	2.32	0.99**	1.67	16	1984	28	3495
AMDR 4	Laboratory	0.96**	1.08	0.99**	1.03	36	4498	40	5031
AMDR 5	Laboratory	0.94**	2.37	0.99**	1.76	17	2212	32	3969
AMDR 6	Laboratory	0.86**	1.09	0.99**	0.96	24	3005	21	2670
AMDR 7	Laboratory	0.83**	1.03	0.99**	1	24	2983	21	2671
AMDR 8	Laboratory	0.85**	0.9	0.99**	0.91	42	5010	32	3978
Slag 1 [†]	Laboratory	0.99**	0.74	0.99**	0.7	45	265	31	184
Slag 1	Poultry farm	0.99**	0.95	0.99**	1.07	58	54	63	59
Slag 2	Pond filter	0.85**	0.94	0.99**	1.25	22	169	28	213
Slag 3	Golf course	0.83**	0.73	0.99**	1.44	25	26	34	35
Slag 4	Pond filter	0.90**	0.7	0.99**	0.77	34	59	25	43
Slag 5	Runoff plots	0.95*	1.28	0.99**	1.89	18	8	34	15
Slag 6	Laboratory	0.79**	1.11	0.96**	1.39	23	45	27	52
Slag 7	Golf course	0.74**	0.66	0.98**	1.46	33	53	61	61
<u>Average slope: Fe/Al PSMs</u>			1.31 (0.07) [†]		1.12 (0.13)				
<u>Average slope: Ca PSMs</u>			0.90 (0.80)		1.39 (0.01)				

[†] Slag 1 and 2 – sieved and treated electric arc furnace (EAF) steel slag (>6.35 mm)

Slag 3, 4, 5, and 6: sieved EAF steel slag (>6.35 mm)

Slag 7: sieved EAF steel slag (>0.5 mm)

‡ Value in parentheses is statistical P value for hypothesis test: slope = 1

Table 5. Summary of dissolved phosphorus (P) removal by six ditch filter structures (example picture Fig. 1d) and one storm water basin filter (Centreville; example picture Fig. 1e) after four years. All structures were located in Maryland, USA, and contained either flue gas desulfurization (FGD) gypsum or electric arc furnace steel slag as the P sorption material (PSM)

Site	PSM	Cumulative inflow P load	Flow- weighted inflow P concentration	PSM mass	Average P removal per event	Predicted P load removed	Measured P load removed
		kg	mg L ⁻¹	Mg	g	kg	kg
Barclay	FGD gypsum	3.8	0.48	58	75.9	0.77	1.06
Marion	FGD gypsum	0.86	1.58	46	16.4	0.62	0.31
Westover	FGD gypsum	7.2	1.3	49	132.4	1.09	1.06
Barclay	Slag	3.4	0.57	80	25.5	1.13	0.84
Marion	Slag	4.6	1.49	62	29.8	1.19	0.51
Westover	Slag	7.1	0.88	67	133.2	0.91	1.73
Centreville	Slag	0.53	1.04	15	12.9	0.32	0.14

FIGURE CAPTIONS

Figure 1. Photographs of example phosphorus (P) removal structures and experiments: (a) laboratory flow-through experiment for P removal; (b) pond filter with inset showing P sorption material (PSM) bed located inside building; (c) confined bed runoff structure; (d) ditch filter with inset showing drainage pipe installed prior to addition of PSM; (e) storm water basin filter, with inset showing the perforated metal box containing PSM.

Figure 2. Predicted and measured values for phosphorus (P) removal by an acid mine drainage residual (AMDR: Fe/Al-based), as a function of P loading (cumulative P added; CP_{add}), under laboratory flow-through conditions using a P concentration of 1 mg L^{-1} and a retention time (RT) of 3 min. (a) discrete P removal (DP_{rem}), (b) cumulative P removal (CP_{rem}) expressed as a %, and (c) CP_{rem} expressed as mg kg^{-1} PSM. Statistics for model fit to actual data shown in Table 4 (AMDR 4).

Figure 3. Predicted and measured values for phosphorus (P) removal by a treated slag material (i.e. Fe/Al-based slag) as a function of P loading (cumulative P added; CP_{add}) for a pond P removal structure with a P concentration of 0.5 mg L^{-1} and a retention time (RT) of 10 min. (a) discrete P removal (DP_{rem}), (b) cumulative P removal (CP_{rem}) expressed as a %, and (c) CP_{rem} expressed as mg kg^{-1} PSM. Statistics for model fit to actual data shown in Table 4 (Slag 2-Pond Filter).

Figure 4. Predicted and measured values for phosphorus (P) removal by a non-treated slag material (i.e. Ca-based slag) as a function of P loading (cumulative P added; CP_{add}) for a confined bed runoff structure with a flow-weighted P concentration and retention time (RT) of 0.69 mg L^{-1} and 10 min, respectively. (a) discrete P removal (DP_{rem}), (b) cumulative P removal (CP_{rem}) expressed as a %, and (c) CP_{rem} expressed as mg kg^{-1} PSM. Statistics for model fit to actual data shown in Table 4 (Slag 3-Golf Course).

FIGURES

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4