

Article



Performance of Field-Scale Phosphorus Removal Structures Utilizing Steel Slag for Treatment of Subsurface Drainage

Chad Penn^{1,*}, Stan Livingston¹, Vinayak Shedekar², Kevin King³ and Mark Williams¹

- ¹ USDA-ARS National Soil Erosion Laboratory, 275 S. Russell St., West Lafayette, IN 47907, USA; stan.livingston@usda.gov (S.L.); mark.willliams2@usda.gov (M.W.)
- ² Department of Food, Agricultural and Biological Engineering, Ohio State University, 257 Agricultural Engineering, 590 Woody Hayes Drive, Columbus, OH 43210, USA; shedekar.1@osu.edu
- ³ USDA-ARS Soil Drainage Unit, 590 Woody Hayes Drive, Columbus, OH 43210, USA; kevin.king@usda.gov
- * Correspondence: chad.penn@usda.gov; Tel.: +1-765-494-0330

Received: 7 January 2020; Accepted: 4 February 2020; Published: 7 February 2020



Abstract: Reducing dissolved phosphorus (P) losses from legacy P soils to surface waters is necessary for preventing algal blooms. Phosphorus removal structures containing steel slag have shown success in treating surface runoff for dissolved P, but little is known about treating subsurface (tile) drainage. A ditch-style and subsurface P removal structure were constructed using steel slag in a bottom-up flow design for treating tile drainage. Nearly 97% of P was delivered during precipitation-induced flow events (as opposed to baseflow) with inflow P concentrations increasing with flow rate. Structures handled flow rates approximately 12 L s⁻¹, and the subsurface and ditch structures removed 19.2 (55%) and 0.9 kg (37%) of the cumulative dissolved P load, respectively. Both structures underperformed relative to laboratory flow-through experiments and exhibited signs of flow inhibition with time. Dissolved P removal decreased dramatically when treated water pH decreased <8.5. Although slag has proven successful for treating surface runoff, we hypothesize that underperformance in this case was due to tile drainage bicarbonate consumption of slag calcium through the precipitation of calcium carbonate, thereby filling pore space, decreasing flow and pH, and preventing calcium phosphate precipitation. We do not recommend non-treated steel slag for removing dissolved P from tile drainage unless slag is replaced every 4–6 months.

Keywords: phosphorus transport; dissolved phosphorus; algal bloom; phosphorus sorption materials; tile drainage; water quality; eutrophication

1. Introduction

Dissolved phosphorus (P) loss has been identified as the main culprit in the recent re-eutrophication of Western Lake Erie [1–3], where the dominant land use throughout the basin is agriculture. While various best management practices (BMPs) for reducing erosion and therefore particulate P losses are employed across much of the Western Lake Erie Basin (WLEB), dissolved P losses have been increasing for several years. In fact, dissolved P losses have increased despite decreases in total P [1]. The problem of dissolved P transport is not isolated to Lake Erie; water bodies around the world have also experienced increased eutrophication rates due to increased P loading [4,5].

Dissolved P losses to surface waters are in some ways more problematic than particulate P losses, as dissolved P is immediately bioavailable upon entering a water body compared with particulate P [2]. The magnitude of the effect of P bioavailability on eutrophication is evident from the fact that the best estimate of algal bloom biomass in Lake Erie is predicted from total bioavailable P loading that occurs during the spring and summer of that year (March through July), where total bioavailable P is the sum

of dissolved P and the proportion of particulate P that is bioavailable [6]. Transport of dissolved P is especially important in Western Lake Erie, because it has been shown that the internal lake sediment P alone does not provide enough P flux to the water column to cause an algal bloom [7]. The sources of non-point dissolved P can be broadly classified as occurring from "incidental" P loss events, i.e., P lost directly from recently applied manure or fertilizer [8–11], or from "legacy" P soils, i.e., soils that have soil test P concentrations well beyond that of plant needs and continue to release relatively low concentrations of dissolved P for decades [5,12–14]. Although incidental P losses can be prevented efficiently and at low cost by simple practices such as proper application timing, rate, and placement, preventing dissolved P losses from legacy P soils is more challenging. Other than reducing non-point flow volumes [15,16] and temporarily reducing soil P solubility through application of P sorption materials (PSMs) [17,18], BMPs are generally non-effective at reducing dissolved P losses, because they target particulate P [19]. For this reason, the P removal structure was developed. Phosphorus removal structures are landscape-scale dissolved P filters containing PSMs that have shown to be effective at trapping dissolved P in non-point source drainage and wastewater [20–29]. Briefly, a P removal structure distributes P-rich water over a bed of PSMs and forces it to flow through the PSMs at a rate high enough to treat all water produced from large flow events, while also allowing sufficient contact time for P removal reactions. Required contact times vary as a function of the P sorption mechanisms, and therefore the type of PSM. For example, P removal reactions involving precipitation usually require more contact time than surface adsorption (i.e., ligand exchange) reactions onto variable charged minerals. Structures are often diverse in appearance but still possess the same three necessary components: containing an effective PSM in sufficient quantity for treating a significant portion of the annual load, sufficient contact time and flow rate through the PSM, and the ability to retain and replace the PSM. Structures can be constructed in a variety of environments, such as urban, street drop inlets, stormwater retention basins, blind inlets, golf courses, agricultural runoff from crop fields or around animal production facilities, and subsurface tile drains. In a review by Penn et al. [27], the performance of P removal structures varied, but overall P removal among 40 studies was 33%. Structures are engineered for achieving a desired cumulative P removal and lifetime, as a function of PSM properties and site characteristics such as annual flow volume, dissolved P concentration, and peak flow rate [30].

While many PSMs have been shown to be effective in P removal structures, one of the most popular PSMs is steel slag, due to its low cost and widespread availability [24,28,31–36]. Electric arc furnace steel slag has proven effective at trapping dissolved P in surface runoff [25,27,33,36,37] and wastewater [20,38–41], but little to no research has been conducted on the use of steel slag for treating tile drainage water. A major challenge for design and construction of P removal structures on tile drains is the fact that many tile-drained fields have little relief and therefore do not provide the hydraulic head necessary for achieving appreciable flow rates through a structure and minimizing its footprint for a top-down flow design. This is especially challenging given the greater flow rates that are often observed for tile drains [16,42,43]. One solution is to design structures that flow from the bottom-upward [30], thereby allowing for any given depth of PSM, where the elevation of water inflow equals the elevation of treated outflow water (i.e., hydraulic head equals depth of media). Although several studies have utilized a bottom-up flow regime for slag and other PSMs [22,39,44–47], none were utilized on buried tile drains.

The objectives of this study were to (i) design, construct, and evaluate two P removal structures for treating tile drainage from high-P soils in a bottom-up flow regime; (ii) compare field performance to expected performance based on laboratory flow-through results; and (iii) assess the economics of P removal for each structure.

2. Materials and Methods

2.1. Site Characteristics

The field site selected for the construction of the subsurface P removal structure has been previously described in detail in several papers [48–51]. Specifically, this site is listed as "Field 3" in a study by Smith et al. [48] and is located in the St. Joseph Watershed in Northeast Indiana, USA. The site consists of two fields and contains a closed depression with about 4 ha that is tile drained, with laterals located approximately 0.9 m below the surface and drainage intensity of 0.005 m^{-1} , meaning that a tile drain is located every 200 m. The dominant soil series include Glynwood loam (fine, illitic, mesic Aquic Hapludalfs), Morley silty clay loam (fine, illitic, mesic Oxyaquic Hapludalfs), Pewamo silty clay (fine, mixed, active, mesic Typic Argiaquolls), and Wallkill silt loam (fine-loamy, mixed, superactive, nonacid, mesic Fluvaquentic Humaquepts). Soil Mehlich-3 P concentrations at the site were initially low (around 15 mg kg⁻¹), which produced very low dissolved P concentrations of at least 0.2 mg L⁻¹ in order to justify the construction of a P removal structure. Thus, the field was amended with 433 kg P ha⁻¹ in order to increase soil test P concentrations and thereby dissolved P concentrations in drainage water. Fertilizer P was broadcast applied on 23 April 2018, in the form of triple super phosphate, followed by incorporation with a disk. From that point, the crop rotation was oats followed by wheat.

The ditch P removal structure designed to treat a tile drain outlet was located on a poultry farm near Ft. Recovery, OH, USA. The contributing area was a 4.5 ha field that is tile drained at an intensity of approximately 0.02 m^{-1} . The dominant soil series is a Blount silt loam (fine, illitic, mesic Aeric Epiqualf), and soil Mehlich-3 concentrations range from 330 to 440 mg kg⁻¹ in the upper 30 cm. This site historically received greater application rates of animal manure for several years, thereby resulting in the excessive soil test P concentrations, but has not received P applications for at least 20 years. Tillage was conducted every other year and varied since 2010, with the use of vertical, disk, and chisel tillage. The general crop rotation was mainly a corn–soybean rotation with cover crops established during the non-growing season. However, established alfalfa was present while the P removal structure was constructed and evaluated.

2.2. Slag Characterization

The steel slag used for both P removal structures was from Levy Co., located in Dearborn, MI, USA. Specifically, the slag was produced from the electric arc furnace (EAF) method for making steel. The slag was sieved at the facility with vibratory screens (3 × 9.5 mm). Bulk density was measured by filling a container of known volume with slag and weighing it. Porosity was determined by measuring the volume of water required to fill the pore space of a known volume of slag. Particle size distribution was obtained through sieving at the following sizes: 4.8, 1, 2, 0.5, 0.2, 0.15, and 0.12 mm. pH and electrical conductivity (EC) of the slag was measured in de-ionized (DI) water with a pH and EC meter after equilibrating slag for 30 min in a 1:5 solid/solution. Total concentrations of Ca, Mg, Fe, Al, Mn, P, K, Cr, Ni, Pb, Zn, B, and S were extracted by the EPA 3050 digestion [54], followed by analysis of digestate by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Dissolved P removal was characterized with flow-through experiments in order to produce the design curve necessary for designing the structures [30]. Briefly, 0.5 g of slag, sampled by obtaining a representative sample that contained a variety of particle sizes, was subjected to continuous flow in a flow-through cell with input of 0.5 and 2 mg dissolved P L⁻¹. Flow rate was adjusted to achieve a 10 min retention time, based on the total pore volume. All flow was collected and separated every 3 h and analyzed for dissolved P using the Murphy–Riley colorimetric method [55]. Discrete P removal (%) was calculated based on the difference between the inflow and outflow concentrations, and was

described as a function of cumulative P added to the slag (mg P added kg⁻¹ slag; variable x in Equation (1)) using an exponential model:

$$Discrete P removal = be^{mx}$$
(1)

where b is the Y intercept and m is the slope coefficient.

2.3. P Removal Structure Construction

2.3.1. Subsurface P Removal Structure

The subsurface P removal structure was designed to treat the tile drainage water from the field, plus surface runoff that flowed into a blind inlet via plumbing into the 15 cm diameter tile drain main (Figure 1). The blind inlet was located up-pipe of the P removal structure and constructed in a depression according to conservation practice Standard 620 of the Natural Resource Conservation Service. A back-flow preventer (Rectorseal, Houston, TX, USA) was installed where the blind inlet joined the tile drain main in order to prevent field tile drain water from back-flowing into the blind inlet. Because of a lack of hydraulic head via slope at the site, the structure was designed to flow from the bottom-upward, where the elevation of the inlet is equal to the outlet.



Figure 1. (a) Overhead view of the blind inlet/subsurface tile drain P removal structure, and (b) side view and details of the tile drain P removal structure. The blind inlet collects surface water at the site and is plumbed into the field tile drainage system, which is all treated by the subsurface P removal structure. The yellow and blue arrows indicate the flow path of the untreated and treated water, respectively. Water flows from the bottom-up and discharges at the same elevation as the inlet.

The structure was designed based on known flow inputs from over 10 years of monitoring at the site in addition to measured slag characteristics (see below). The design process is described in detail by Penn and Bowen [30]. The average annual flow volume was 12.6 million L y⁻¹ and typical dissolved P concentration was assumed to be 0.2 mg L⁻¹ after equilibration of applied fertilizer. Based on slag physical and P removal characteristics, plus a design goal for minimum peak flow rate of 19 L s⁻¹ with a minimum retention time of 10 min and 40% cumulative dissolved P removal over 20 years, 34.5 Mg of this particular steel slag material was required. In order to meet both the flow rate and retention time goal, the buried slag bed was dimensioned to approximately $7 \times 8 \times 0.43$ m deep. Because electric

arc furnace steel slag removes dissolved P by calcium phosphate precipitation, retention time is critical for proper function [27,56]. After excavating the area for the slag bed, a tarp (0.15 mm thick, 3.54 thread cm^{-1}) was placed on the bottom for the purpose of maintaining a clean working environment during construction, not for water retention. The 15 cm tile main was plumbed into a distribution manifold that consisted of a 0.76 m diameter × 1.3 m long pipe with ten 10 cm diameter perforated pipes that were plumbed from the manifold to the bottom of the slag bed (Figure 1). A by-pass pipe was also plumbed to the tile inlet, up-pipe of the distribution manifold in order to allow for excessive flow rates beyond the capacity of the structure to by-pass the slag bed. This by-pass pipe had a 15 cm rise in order to induce a minimum 15 cm head. A 15 cm gate valve was plumbed to this by-pass pipe and provided access from the surface in case the farmer ever wanted to open the valve.

In order to allow an open head space between the top of the slag bed and the drainage outlet, 21 Infiltrator H-20 septic chambers (Infiltrator Water Technologies, Old Saybrook, CT, USA) were placed on top of the slag bed. This permitted approximately 40 cm of head space to permit for settling of and prevent loss of precipitant/floc that would develop in the treated water. Preliminary pilot-scale experiments showed that using a traditional corrugated tile drainpipe near the top of the slag bed was not sufficient as an alternative to an open "dead space" for settling, as the corrugated pipe quickly clogged with the precipitant/floc. The Infiltrator H-20 septic chamber is specially designed to handle traffic, which was necessary in this case because the landowner would need to drive over the buried P removal structure without crushing the chambers. Three chambers were connected for seven rows, with a 10 cm diameter pipe plumbed to the chamber at the end of each row, which were then connected to a single 15 cm diameter manifold pipe that served to drain the entire slag bed (Figure 1).

The septic chambers were supported through gravel and a plastic geo-grid, according to company specifications. Briefly, 15–20 cm deep layer of clean limestone gravel (2.5 to 6.4 cm in diameter) was placed on top of the chambers and compacted. A geotextile was placed on top of the compacted gravel in order to prevent soil particles from leaching into the slag bed. This was followed by a 15–20 cm deep layer of compacted gravel (containing fines), geo-grid plastic (Tensar BX1100, Tensar Co. Alpharetta, GA, USA), 30 cm layer of compacted gravel containing fines, and 30 cm of soil.

2.3.2. Ditch P Removal Structure for Treating Tile Drainage

In July 2018, a ditch-style P removal structure was constructed in which the inlet water was treated from the bottom-up. Tile drainage water from a 10 mm diameter tile drain outlet flowed into a 72 m long ditch before entering into a wetland. The ditch bottom width was 2 m, while the top width and depth varied. Based on slag characterization and flow characteristics obtained from previous monitoring (annual flow volume of 5 million L y⁻¹, dissolved P concentration of 1 mg L⁻¹) and a P removal goal of 40% cumulative dissolved P removal over 15 y, the structure was constructed using 45 Mg slag. In order to meet the peak flow rate of 32 L s⁻¹ while attaining a retention time of at least 10 min, the slag was oriented approximately $72 \times 2 \times 0.33$ m deep within the ditch. A pond liner (2.3 mm thickness) was placed under the slag bed in order to prevent seepage loss between inlet and outlet flow monitoring/sampling equipment. At the upstream side of the ditch slag bed, a 76 cm tall dam was built with concrete and five 10-cm diameter elbows were set near the bottom, serving as the inlet into the slag bed (Figure 2). Five corrugated perforated drainpipes (10 cm diameter) were attached to each elbow on the downstream side of the dam and extended nearly 72 m where the ends were capped off.

On the downstream side of the ditch, a 50 cm tall concrete dam was constructed, serving as the outlet for treated water. In cases where flow rate exceeded the slag flow capacity, the inflow water could simply over-top the inflow dam and flow to the outlet without being treated (Figure 2). In May of 2019, a dye test was conducted by slowly releasing water with added dye (fluorescent yellow/green; Kingscote chemicals, Piqua, OH, USA) from a 2000 L tank at the upstream side of the inflow dam. The structure was then visually monitored for 90 min in order to assess preferential flow paths or potential clogging.



Figure 2. Schematic of the ditch phosphorus removal structure (**a**) and photograph taken during a dye test (**b**) illustrating the lack of uniform flow through the slag media and clogging of the ditch structure. Photograph (**c**) shows the flocculant/precipitant that forms through the dissolution and reprecipitation of calcium minerals that can fill the slag matrix and reduce pore connectivity (**d**).

2.4. Monitoring and Analysis

For the subsurface P removal structure, the inlet was monitored at the distribution manifold (i.e., 0.76 m diameter × 1.3 m unit shown in Figure 1) with an ISCO Signature 330 bubbler (Teledyne-ISCO, Lincoln, NE, USA) for pressure head and an ISCO 6712 autosampler for taking water samples before flowing into the slag bed. A composite vault (described in detail by Smith and Livingston; [50]) was buried near the outlet, with the 15 cm outlet pipe plumbed into it and connected to a 15 cm

Palmer-Bowlus flume with an ISCO Signature 330 bubbler and ISCO 350 area-velocity sensor. Samples were taken with an ISCO 6712 autosampler. Both inlet and outlet sampling were triggered based on the flow rate detected at the outlet based on a two-step program to allow for both baseflow and event flow sampling. Daily baseflow sampling occurred once per day, with a single draw of 1 L. Event flow sampling was triggered by the rate of change in flow at the outlet, specifically by a level increase of 50 mm h⁻¹ or faster. Event sampling was discrete, with samples taken every 2 h after initiation. Daily precipitation was monitored with a Vaisala WXT 510 Weather Transmitter (Vaisala Company, Helsinki, Finland).

For the ditch P removal structure, inflow (i.e., untreated) water at the inlet was monitored at the outlet of the 10 cm diameter tile drain that terminated at the inlet dam (Figure 2). Flow rate was monitored at 10 min intervals using an Isco 4230 pressure transducer and an Isco 2150 area-velocity sensor that were positioned with a Thelmar weir, inserted into a 30 mm diameter pipe attached to the end of the tile outlet. Monitoring of flow rate at the outlet of the ditch P removal structure was identical to the inflow, with the water directed back into a 30 cm diameter pipe containing a Thelmar weir and sensors. Isco 6712 autosamplers were used to obtain water samples at both the inlet and outlet for pretreated and treated water, respectively. Inflow water was sampled at two different stages: stage one consisted of a composite with 200 mL draw samples taken every 6 h, with a single composite representing 2 d. The second stage of sampling intended to capture precipitation-induced flow events was initiated when the level increased at a rate of 18 mm h⁻¹ or more. Event flow samples were composites comprised of 15 min draw samples (120 mLs per draw) with each composite representing 1 h of event flow. Outflow was sampled as 2 d composites with a 200 mL draw taken every 6 h and each composite representing 2 d.

All water samples were collected within 48 h of a precipitation-induced event at both sites; baseflow samples from the subsurface tile drain structure were collected on a weekly basis. All samples were filtered through a 0.45 μ m membrane and refrigerated, except for an unfiltered aliquot removed from ditch structure samples that was digested with persulfate [57]. Filtered samples from the subsurface tile drain structure were analyzed for Mn, Cr, Ni, Pb, Zn, B, and S by ICP-AES. Filtered samples from both sites samples were tested for P by the Murphy–Riley method [55]. A calibrated pH electrode was used to measure pH in all samples.

Flow and sampling data were synchronized with Flow Link software (Teledyne Isco Inc., Lincoln, NE, USA). Discrete flow volume produced at each time interval was calculated by:

where discrete flow volume is expressed in L and flow rate in L s⁻¹. Discrete flow volume was calculated at every time interval for baseflow and each flow event. Total flow volume produced for a given time period was determined by the sum of all discrete flow volumes over that time period. Phosphorus loading to the structure was calculated by integrating P concentrations with respect to flow volume. The sum of all P loads for each sampling point interval represents the cumulative P load for an event. From this, flow weighted P concentrations (mg L⁻¹) were calculated:

where P load and total volume are in units of mg and L, respectively. After P loads were determined for both inflow and outflow (treated) water, the P removal (mg) could simply be calculated as a mass balance:

$$P removed = inlet P load - outflow P load$$
(4)

where inlet and outflow P load are expressed as mg. Retention time (min) of the structure at different flow rates was also estimated [56]:

Retention time = Total bed pore volume/Flow rate
$$(5)$$

where total pore volume and flow rate at outlet are in units of L and L min⁻¹, respectively. Total pore space was calculated for each P removal structure based on the known mass of slag, bulk density, and porosity.

3. Results and Discussion

3.1. Slag Characterization

The slag used in this study was typical of electric arc furnace steel slag [30,40,56]. Although the material was screened to remove all particles smaller than 3 mm diameter at the production facility, particle size analysis shown in Table 1 reveals that the screening was not complete, as an appreciable percentage of fines smaller than 2 mm was still present. This was likely a result of screening several tons of slag at a time, which were not sufficiently dry enough to allow for removal of fines that were adhered to the larger particles.

Parameter	Units	Value						
Physical properties								
>4.8 mm	%	43.3						
2–4.8 mm	%	35.5						
1–2 mm	%	17.6						
0.5 to 1 mm	%	0.77						
0.2 to 0.5 mm	%	0.62						
0.15 to 0.2 mm	%	0.33						
0.12 to 0.15 mm	%	0.26						
<0.12 mm	%	1.7						
Bulk density	g cm ⁻³	1.69						
	Chemical properties							
рН		11.53						
Buffer index	$eq L^{-1}$	0.104						
Electrical conductivity	$mS cm^{-1}$	3.40						
Ca	$ m g~kg^{-1}$	185						
Mg	$g kg^{-1}$	29.7						
Fe	$g kg^{-1}$	110						
Al	$g kg^{-1}$	9.49						
Mn	$g kg^{-1}$	14.6						
Р	$g kg^{-1}$	2.32						
K	$mg kg^{-1}$	226						
Cr	$mg kg^{-1}$	1727						
Ni	$mg kg^{-1}$	464						
Pb	$mg kg^{-1}$	3.03						
Zn	$mg kg^{-1}$	362						
В	$mg kg^{-1}$	75.7						
S	$mg kg^{-1}$	345						

Table 1. Physical and chemical properties of the slag used in both field P removal structures and laboratory flow-through experiments. Concentrations of elements are total values.

Due to incomplete screening, the pH, total Ca and Mg, and buffer index were similar to pure slag fines, because the smaller particles generally contain higher concentrations compared with large slag particles [56,58,59]. Several studies have shown that the fine fraction of electric arc furnace slag consists of portlandite, calcium oxide, calcium hydroxide, and calcium silicate minerals [60,61]. These minerals are highly soluble, which, combined with their ability to maintain an elevated pH, enable a high degree of dissolved P removal through the precipitation of calcium phosphate [40,62–64]. Similarly, the buffer index, which is a measurement of the ability of a PSM to maintain a pH above 6.0 [30], was of a

magnitude expected for an electric arc furnace slag sample containing some fines [56]. Based on the physical and chemical characterization, this particular slag sample was expected to be an effective PSM.

Total concentrations of trace metals were not excessive (Table 1) with levels falling below thresholds for land application of biosolids [65]. Although considered safe for land application under the USEPA 503 rule, the concentration of chromium and nickel are high enough that they would fall into the category of "non-exceptional quality". Regardless, the USEPA 503 rule is intended for biosolids and not industrial byproducts such as steel slag, so caution should be exercised. More important than the total concentrations of metals are their solubility. Regardless of their total concentrations, if excessive amounts of trace metals are released to solution, then a P removal structure containing such materials would become a source of trace metals downstream and therefore an environmental hazard. Trace metals were monitored in the outflow of the P removal structure for this study and are presented in Section 3.2.2.

3.2. Performance of the Tile Drain Phosphorus Removal Structure

3.2.1. Inflow Rates, Concentrations, and Loads

Figure 3 shows both the precipitation and the degree of pressure head at the inflow of the subsurface P removal structure, illustrated in Figure 1. An increase in pressure head indicates that water was "backed-up" above the P removal structure to some degree. Clearly, this is expected to occur during high flow events, but notice that not all instances of increases in pressure head were concomitant with large precipitation events, indicative of the importance of antecedent soil moisture conditions in influencing flow events. For example, the P removal structure nearly ceased flowing from July 2018 to September 2018 (Figure 4), even though appreciable rainfall events occurred during that time period. Williams et al. [42] showed that both rainfall amount and antecedent moisture controlled flow generation for these tile drainage systems. Next, notice that the baseline pressure head level slowly increased starting in November 2018 (Figure 3). This suggests that the slag contained in the P removal structure may have been slowly clogging, decreasing the ability of water to flow through it and therefore requiring a greater hydraulic head.

Inflow dissolved P concentrations ranged from less than 0.01 mg L⁻¹ at baseflow to 19.8 mg L⁻¹. Dissolved P concentrations were extremely elevated for the first flow event, which likely resulted from transport of incidental fertilizer P loss rather than P lost from equilibrated soil. This is probable because there was no precipitation for the first two weeks after fertilizer application, until a catastrophic event that resulted in one of the greatest peak flow rates observed over the course of the study (10.4 L s⁻¹). In other words, the applied fertilizer was unable to sufficiently dissolve and react/stabilize with the soil before the large flow event occurred, delivering the greatest P concentration to the structure. Based on a soil Mehlich-3 concentration in the 0–5 cm layer of 367 mg kg⁻¹, only about 1 mg L⁻¹ of dissolved P is expected to be lost in tile drainage and runoff, according to a relationship between soil test P and dissolved P lost for the first event was mostly from unreacted fertilizer. This was unintended, as the target of P removal structures is treatment of dissolved P lost from high P soils, not incidental P lost from recently applied unreacted fertilizer or manure.

Flow rates through the P removal structure ranged from nearly zero to about 12 L s⁻¹. Inflow dissolved P concentrations generally followed the same pattern as flow rate, with low concentrations observed during baseflow conditions and spikes occurring at event peak flow rates (Figure 4). In fact, there was a significant (p < 0.05) and positive relationship between flow rate and inflow dissolved P concentration: inflow P concentration = 0.52 * flow rate – 0.056, where P concentration and flow rate are in units of mg L⁻¹ and L s⁻¹, respectively. A similar trend was also evident in non-point drainage monitoring in several other studies [36,66,67]. Similarly, mean flow-weighted concentrations for precipitation-induced flow events were much greater than baseflow concentrations, which was only 0.17 mg L⁻¹ (Table 2).



Figure 3. Daily precipitation record at the site of the subsurface tile drain P removal structure (**a**) and inflow pressure head level (**b**) measured at the inflow distribution manifold, illustrated in Figure 1.



Figure 4. Hydrograph and associated inflow dissolved phosphorus (P) concentrations measured at the inlet of the subsurface tile drain P removal structure shown in Figure 1.

Flow					Inflow Dissolved P			Dissolved P Removed			
Event	Date	Peak Flow Rate	Total	Volume	Peak Concentration	Mean Flow-Weighted Concentration	Load	% of Total	Load	Discrete %	Minimum RT
		$L s^{-1}$	ML	% of total	mg L ⁻¹	$mg L^{-1}$	kg		kg		minutes
Storm 1	5/2/2018	10.4	949	4.32	19.80	14.4	13.69	39.0	13.7	100	13
Storm 2	5/13/2018	2.3	81	0.37	2.78	1.72	0.14	0.40	0.13	97	58
Storm 3	5/14/2018	7.2	161	0.73	12.53	7.95	1.28	3.65	1.28	100	19
Storm 4	5/15/2018	7.6	625	2.85	4.26	1.52	0.95	2.71	0.83	87	18
Storm 5	5/21/2018	5.3	172	0.78	2.25	1.31	0.22	0.64	0.21	96	25
Storm 6	6/1/2018	2.9	96	0.44	1.06	0.29	0.03	0.08	0.03	91	46
Storm 7	6/12/2018	1.2	40	0.18	0.33	0.13	0.01	0.01	0.01	100	110
Storm 8	6/22/2018	6.7	263	1.20	1.89	0.78	0.21	0.59	0.17	83	20
Storm 9	10/6/2018	3.9	351	1.60	1.39	0.55	0.19	0.55	0.18	91	35
Storm 10	11/1/2018	6.5	900	4.10	4.15	2.72	2.45	6.98	1.92	78	21
Storm 11	11/25/2018	11.7	540	2.46	3.90	2.47	1.89	5.38	0.26	13	12
Storm 12	12/1/2018	5.2	764	3.48	3.36	2.47	1.89	5.38	0.26	14	26
Storm 13	12/31/2018	7.4	739	3.37	4.27	2.64	1.95	5.57	0.15	8	18
Storm 14	2/3/2019	6.8	1721	7.84	3.85	1.89	3.25	9.25	0.65	20	20
Storm 15	2/12/2019	4.9	234	1.06	1.58	0.96	0.22	0.64	0.00	1	27
Storm 16	2/14/2019	3.7	364	1.66	1.82	0.96	0.35	1.00	-0.03	-9	36
Storm 17	2/20/2019	1.9	32	0.15	1.30	1.29	0.04	0.12	0.02	59	70
Storm 18	2/21/2019	3.5	144	0.65	1.50	0.90	0.13	0.37	-0.03	-20	39
Storm 19	2/24/2019	3.3	132	0.60	1.70	1.66	0.22	0.62	0.18	83	41
Storm 20	3/9/2019	9.5	1444	6.58	3.90	1.12	1.62	4.61	0.04	2	14
Storm 21	3/30/2019	7.6	642	2.92	1.62	1.20	0.77	2.20	-0.03	-3	18
Storm 22	4/18/2019	3.8	891	4.06	3.24	1.08	0.97	2.75	0.22	23	35
Storm 23	4/25/2019	11.7	2918	13.3	1.58	0.64	1.86	5.29	-0.45	-24	12
Storm 24	5/22/2019	1.4	86	0.39	0.44	0.13	0.01	0.03	0.00	-18	95
Baseflow	NA	NA	7673	34.9	NA	0.17	1.28	3.66	-0.40	-31	NA
Storm Event Total		NA	14,289	65.1	NA	2.37	33.8	96.3	19.6	58	NA
TOTAL		NA	21,962	NA	NA	1.60	35.1	NA	19.2	55	NA

Table 2. Flow characteristics, dissolved phosphorus (P) concentrations and loads, P removal, and distribution of flow volume and P among individual precipitation-induced events and baseflow for the subsurface tile drain P removal structure shown in Figure 1. RT: retention time. NA: not applicable.

While it is well understood that the greatest flow rates deliver the greatest dissolved and particulate P loads due to greater volumes of water, this phenomenon of the true dissolved P concentration increasing with flow rate is interesting, as it contradicts the notion of P dilution occurring as flow rates increase, i.e., "first flush" [68–70]. Penn et al. [36] attributed this to variable source areas [71] within the watershed that only become activated during intense rainfall events. However, in the current study, the field is always equally connected to the sampling point through the tile drainage system. Instead, there are two possibilities: First, greater flow rates translate to a shorter contact time between leaching water and subsurface soil, which could decrease sorption of P in the subsurface as the P-rich water at the surface moves downward into the tile. Similarly, these greater flow rates may activate preferential flow paths that permit water to move more directly to the tile with little to no soil contact [72,73]. A second possibility is that because the blind inlet within the system is capturing surface water (Figure 1), the high P concentrations coinciding with peak flow rates might be occurring only during major events that permit surface runoff to occur. Previous research in the region has shown that surface runoff generally produces greater dissolved P concentrations compared to tile drainage, among soils with similar surface soil P concentrations [74]. This is due to fact that tile drainage water is able to leach through several meters of lesser P soil, permitting sorption, before entering a tile. In the current study, it was not possible to separate tile drain flow from the surface runoff that entered the blind inlet before combining with the tile drain water.

Regarding dissolved P loads, about 35 kg of dissolved P was delivered over 23 precipitation-induced events, plus baseflow. Baseflow delivered nearly 35% of the total flow volume, but less than 4% of the dissolved P load (Table 2). Instead, precipitation-induced flow events delivered a disproportionate amount of the dissolved P load with nearly 97% of P transported with only 65% of the total flow volume. Again, this is indicative of how dissolved P transport mechanisms were drastically different under greater flow conditions vs. lesser flow and baseflow. While identifying specific mechanisms for P transport was outside the scope of the current study, it appears to be a function of contact time and the degree of soil contact, i.e., leaching rate through the soil, preferential flow, and surface runoff vs. leachate. Among precipitation-induced events, the majority of the total dissolved P load was delivered during the first event (nearly 14 kg; 39% of total load). As previously discussed, this first event was the result of incidental fertilizer loss due to the lack of sufficient soil reaction between fertilizer application and the first flow event [8,9]. This serves as an example of the magnitude of P lost from direct incidental transport of fertilizer compared with P lost from greater P soils. Outside of that first event, the greatest loss of P was 3.25 kg on February 3rd, comprising about 9% of the total P load. Excluding the three greatest P loads, all other events delivered less than 6% of the total load. Excluding the first event, mean flow-weighted concentration ranged from 0.13 to 7.65 mg L^{-1} , with all but six events less than $2 \text{ mg } \text{L}^{-1}$ (Table 2).

3.2.2. Phosphorus Removal, pH, and Metals

pH of the inflow water ranged from 7.2 to 8.9 and treated water from 7.4 to 13. The elevated pH of treated water was expected based on the typical minerals found in electric arc furnace steel slag [31,58,75]. Although not measured in this study, there is little concern about excessive pH levels, because treated water from electric arc furnace slag is generally not highly alkaline [36] and has been shown to not increase the pH of receiving waters [30,36]. pH of treated water decreased with time, with all values below 8.5 after event 8 (i.e., after about 3400 cumulative ML passed through the structure). Concentrations of cadmium, chromium, copper, manganese, nickel, lead, and zinc were all below detection limits. Although these elements were found in the slag itself (Table 1), they were apparently not soluble and therefore posed no hazard. Aluminum, boron, and molybdenum concentrations ranged from below detection limit to 1.25 mg L⁻¹, below detection limit to 0.315 mg L⁻¹, and from 0.016 to 0.017 mg L⁻¹, respectively. However, there was no statistically significant difference (p < 0.05) between inflow and treated water concentrations.

Overall dissolved P removal was 19.2 kg or about 55% of the total input to the structure (Table 2 and Figure 5). The structure removed 58% of the P that entered during precipitation-induced events, compared with -31% removal for baseflow. Poor baseflow P removal was likely due to the fact that baseflow provided relatively low concentrations of dissolved P compared with storm flow (Table 2); consider that P concentration partly dictates the chemical potential for calcium phosphate precipitation, which is the dominant P removal mechanism for EAF slag. Even though baseflow caused slag to behave as a net P source, recall that only a small amount of P was delivered during baseflow, so this only resulted in the loss of about 0.4 kg of P. The majority of the trapped P was removed during event 1 (Table 2).



Figure 5. Discrete (**a**) and cumulative (**b**) dissolved phosphorus (P) removal by the subsurface tile drain P removal structure as a function of cumulative dissolved P loading to the slag media. Laboratory flow-through discrete P removal curves for the same slag sample are shown in (**c**) and (**d**) for comparisons to field performance under the conditions of a ten-minute retention time and inflow dissolved P concentrations of 0.5 and 2 mg L⁻¹ (**c** and **d**, respectively). Discrete dissolved P removal for the structure (**a**) is shown excluding negative values in order to improve clarity, but cumulative dissolved and total P removal (**b**) is calculated with inclusion of those negative values. Note that the horizontal axes scales for (**a**) and (**b**) are different from (**c**) and (**d**).

Figure 5a illustrates that the structure removed 100% of all P input until the cumulative loading reached about 500 mg P kg⁻¹ slag; after that point, the P removal became quite variable. Table 2 also shows that discrete P removal by event, was nearly 90% or greater until event 8, and after event 10, the discrete event P removal drastically decreased, with some events resulting in net P release. The lowest retention time (total pore volume divided by flow rate) observed for the structure was 12 min (Table 2), occurring during the greatest measured flow rate. Note that the structure was designed to achieve a minimum retention time of 10 min during peak flow.

Figure 5c,d shows the discrete P removal flow-through curve determined in the laboratory for the same slag sample used in both P removal structures described in this study. Comparison of Figure 5a–d clearly indicate that the P removal structure greatly under-performed compared to

laboratory conditions. It is unknown exactly what caused the under-performance, although it could be due to chemical issues (discussed in detail in a later section), physical problems (i.e., partial clogging), or a combination of both. For example, the slowly increasing baseline pressure head at the inlet (Figure 3) suggests that the slag bed was slowly clogging. Such a partial clogging would prevent the water from interacting with the entire slag bed, effectively decreasing the mass of slag for treatment, and therefore reduce P removal. Further considerations of chemical issues are discussed in Section 3.4.

3.3. Performance of Ditch-Style Phosphorus Removal Structure

The ditch-style P removal structure removed 37% of the cumulative dissolved P inflow load for a total of 0.9 kg removed (Figure 6). Similar to the subsurface tile drain P removal structure, dissolved P removal was near 100% for the first few events before drastically decreasing (Figure 6a). A comparison of Figure 6a to Figure 5c,d illustrate how the slag in the ditch P removal structure underperformed compared to testing the same slag under laboratory flow-through conditions. Discrete total P removal was highly variable (Figure 6c), but cumulative total P removal was 2.3 kg, equivalent to nearly 48% of the total P that flowed into the structure (Figure 6d).



Figure 6. Discrete and cumulative dissolved and total phosphorus (P) removal for the ditch P removal structure, shown as a function of cumulative P loading to the structure. Discrete dissolved and total P removal (**a** and **c**) are shown excluding negative values in order to improve clarity, but cumulative dissolved and total P removal (**b** and **d**) are calculated with inclusion of those negative values. Note that the horizontal axes scales for (**a**) and (**b**) are different from (**c**) and (**d**).

Inflow dissolved P concentrations varied from about 0.4 to 1.4 mg L⁻¹, with the highest concentrations delivered between July and October. About 21% of the cumulative dissolved P load was delivered during a single event that took place on September 7th, in which the structure removed 20%. Figure 7 clearly illustrates how the ditch structure was initially operating at a high P removal efficiency and then decreased with further loading. Total P concentrations entering the structure were fairly steady at around 2 mg L⁻¹, indicating that about 50% of the total P was in the dissolved form. Total P removal was also steady throughout the monitoring period, unlike dissolved P removal. This indicates that the structure was additionally removing particulate P through physical



mechanisms. 18% of the cumulative total P delivered to the structure occurred during an event on November 25th, during which 75% was removed.

Figure 7. Discharge and event mean concentrations (EMC) of dissolved phosphorus (P) (upper figure) and total P (lower figure) for both inflow and treated outflow water from the ditch P removal structure shown in Figure 2.

After approximately 11 months following installation, a dye test was conducted on the ditch structure as a qualitative assessment for clogging of the slag bed. After adding dye and water to the upstream side of the inflow dam (Figure 2a), it was observed that dye only appeared in several small areas, indicating that water flow through the slag bed was significantly limited due to clogging (Figure 2b). This indicated that during flow events, very little water would be able to flow through the slag bed and instead would over-top the inflow dam and flow directly on top of the slag bed to the outlet dam with little to no slag contact, therefore escaping treatment.

3.4. Potential Explantions for Underperformance of the Phosphorus Removal Structures

As previously discussed, both P removal structures displayed physical flow problems with time. Such clogging decreases the effective size of the slag bed, as the same volume of water becomes forced through a smaller mass of slag, which will decrease its ability to remove P. In the case of the ditch structure, after several months, there was nearly zero contact between the water and the slag before being discharged.

The ultimate cause of this partial clogging is a result of a chemical phenomenon. It is well known that electric arc furnace slag will produce relatively large amounts of floc resulting from the reprecipitation of various calcium minerals [20,30,75]; such precipitant can be seen at the surface of the ditch structure in Figure 2c. Claveau-Mallet et al. [20,75] showed that this precipitant readily formed in slag columns used to treat wastewater and was responsible for a gradual clogging. In fact, Claveau-Mallet et al. quantified this process and incorporated it into the P-hydroslag model [76]. Similarly, several authors showed that the minerals forming were generally calcite and hydroxyapatite [20,63,77]. The impact of the precipitation of the new calcium minerals are evident in Figure 2d, as the pore space between slag particles tends to become filled with the precipitant; total digest showed that >60% of the precipitated mass was calcium.

Not only can the formation of the calcite minerals fill the pore space, clogging the structure and reducing P removal through decreasing interaction between the slag and water, but we hypothesize that those same precipitation reactions are partly responsible for the decreased chemical potency of the slag, reducing the precipitation of calcium phosphate, the main P removal mechanism [62,63,78]. In essence, conversion of the slag calcium minerals into calcite will decrease the pH of the system and also depress the concentration of soluble calcium available for calcium phosphate precipitation. The precipitation of calcium phosphate shown in equilibrium Reaction (1) illustrates that increased concentrations of H+ (i.e., decreasing pH) and decreasing concentration of Ca^{2+} will reduce formation of brushite by pushing the equilibrium towards the reactants side [79]:

$$Ca^{2+} + H_2PO_4^- + 2H_2O \leftrightarrow CaHPO_4$$
 (brushite) + H⁺ Log K = -0.63 (reaction 1)

For example, consider a typical calcium mineral found in electric arc furnace slag that is highly soluble: portlandite. Equilibrium Reaction (2) [79] shows the standard dissolution reaction for portlandite, which not only produces the Ca^{2+} necessary for the precipitation of solution phosphate, but also consumes H+, which increases pH, thereby promoting the formation of calcium phosphate:

$$Ca(OH)_2 \text{ (portlandite)} + 2H^+ \leftarrow \rightarrow Ca^{2+} + 2H_2O \text{ Log } K = 22.8 \text{ (reaction 2)}$$

With high concentrations of Ca^{2+} and a sufficiently high pH, calcium phosphate is able to precipitate, thereby taking phosphate out of solution. However, if a system has appreciable concentrations of CO_2 , which is soluble in water, it will easily de-protonate in a high pH environment (pH > 9) and transform into carbonate [79]:

$$CO_2(g) + H_2O \leftrightarrow 2H^+ + CO_3^{2-} Log K = -18.15$$
 (reaction 3)

The problem with the formation of carbonate in the context of a slag P removal structure is that it results in the formation of protons (Reaction (3)), thereby decreasing pH. This decrease in pH will reduce the ability of calcium to precipitate with solution phosphate (Reaction 1). Several studies have demonstrated the importance of maintaining an elevated pH in a slag P removal structure; in fact, pH can be used as an indicator of effectiveness [34,80,81]. In addition, the newly formed carbonate will precipitate solution Ca^{2+} in the form of calcite, thereby preventing Ca^{2+} from precipitating with solution phosphate. The direct equilibrium between Ca^{2+} and CO_2 is shown in Reaction (4), which includes the de-protonation/hydrolysis of CO_2 to carbonate [79]:

$$Ca^{2+} CO_2(g) + H_2O \leftrightarrow CaCO_3 \text{ (calcite)} + H^+ Log K = -9.74$$
 (reaction 4)

Due to the poor solubility of calcite compared with calcium oxide and hydroxide minerals, the newly formed calcite is relatively poor at removing dissolved P. In an assessment of P sorption by several byproducts and natural materials, Johansson (1999) showed that materials containing CaCO₃ were less effective at P removal than CaO.

In summary, the highly soluble and alkaline minerals found in slag, such as portlandite, produce an ideal environment for the formation of carbonate if CO_2 is present in the system, and this carbonate will compete with phosphate for precipitation with Ca^{2+} and also depress the pH of the system, which reduces the chemical potential for calcium phosphate precipitation. For example, Liira et al. [82] showed that for a Ca-rich oil shale ash, the formation of carbonate precipitates reduced the solubility of calcium and thereby reduced P removal. Similarly, Claveau-Mallet et al. [77] conducted precipitation/speciation modeling on a wastewater P removal slag system and concluded that longevity was drastically influenced by simply increasing inflow alkalinity from 50 to 210 mg $CaCO_3 L^{-1}$. Formation of calcite is also responsible for partially filling the pore space of the slag and clogging [34]. Tile drainage water is generally richer in CO_2 compared with surface water, because it leaches through several meters of soil (where respiration occurs). For example, Omernik et al. [83] reported surface water alkalinities of the United States occurring over a range of less than 2.5 to greater than 20 mg $CaCO_3 L^{-1}$. Tile drainage, on the other hand, is typically much greater, with typical values reported in the range of 250 to over 300 mg $CaCO_3 L^{-1}$ [84,85].

Consider that the laboratory flow-through experiments conducted on the slag used in this study (Figure 5c,d) were executed using a P solution made from pure de-ionized water, which therefore contained little dissolved CO₂, bicarbonate, or carbonate. However, in field application, this slag was used to treat tile drainage water, which will contain appreciable amounts of various forms of carbonate. This difference in water chemistry may be partly responsible for the underperformance of the slag contained in both P removal structures, evident when comparing Figures 5a and 6a (field-measured P removal) to Figure 5c,d (laboratory flow-through P removal). Further evidence for the hypothesis of calcite formation reducing calcium phosphate precipitation in the slag beds is found in the observation of changes in treated water pH with time. Initially, when the highly soluble and alkaline slag minerals were dominant, the treated water pH was >9. Indeed, Figure 8 indicates that event P removal was around 80% or greater and then drastically decreased when pH dropped to less than 9, which occurred during event 11 in the subsurface P structure, resulting in P removal of 13%. Notice that the pH of the treated water appeared to stabilize at around 8.2 (Figure 8), which is the equilibrium pH for calcite. Similarly, Dunets et al. [80] showed that P removal of greenhouse wastewater with slag decreased dramatically at a pH of around 8.5.



Figure 8. Impact of treated water pH on discrete dissolved phosphorus (P) removal for the subsurface tile drain P removal structure shown in Figure 1.

Not only can dissolved forms of carbonate (such as dissolved CO₂, carbonic acid, and bicarbonate) in inflow water reduce P removal efficiency of slag P removal structures, it can also act to dissolve calcium phosphate minerals that are already present on the slag. In fact, this is how the Olsen soil test is designed to extract P from soils of arid and semi-arid regions that contain calcium phosphates [86]. This would explain why some of the later flow events resulted in net removal of P from the slag bed (Table 2).

3.5. Economics of Dissolved Phosphorus Removal

The total cost of the subsurface P removal structure was nearly USD 11,000, including professional services for installation. This total cost also includes the blind inlet used to capture surface water at the site and direct it into the subsurface P removal structure. The majority of the cost associated with the materials was from the septic chambers and the associated materials necessary for their proper installation (nearly 50% of the cost of materials). Note that this cost is specific to using regular slag (i.e., not aluminum-coated slag) to prevent the loss of flocculant/precipitant that develops. If a different PSM were used, this extra cost would not be incurred. Professional services during installation were only 23% of the total cost. Overall, the cost of dissolved P removal for the subsurface tile drain P removal structure was USD 562 per kg of dissolved P removed. This cost falls within the magnitude of wastewater treatment [87], but consider that wastewater treatment plants are mostly removing particulate P (as opposed to dissolved), which is much less costly or difficult to treat. Consider also that a wastewater treatment plant is treating a fairly constant point source with relatively high P concentrations and lesser volumes compared with non-point P sources. Together, this makes the cost of dissolved P removal by the P removal structure appear more reasonable. While the cost of removing particulate P from non-point sources (i.e., reducing erosion) is much less expensive, dissolved P is not only more difficult to capture, but it is a more potent eutrophication agent than particulate P.

The ditch-style P removal structure was much less expensive to construct compared with the buried tile drain structure, because it was above ground, and it was not necessary to construct it to allow for tractor traffic. Total cost was about USD 6000, with most of the cost associated with professional installation. However, due to the poor performance of the structure, overall dissolved P removal was over USD 6000 per kg removed, which is unacceptable.

4. Summary and Conclusions

Both P removal structures monitored in this study treated tile drainage water, constructed to flow from the bottom up, and underperformed relative to laboratory flow-through P experiments. Although trace metals were present in the slag, concentrations in the drainage water were below detection limits. For the subsurface P removal structure/blind inlet combination, inflow dissolved P concentrations were significantly correlated to flow rate, with concentrations ranging from less than 0.01 to nearly 20 mg L⁻¹. This indicated that greater flow rates leading to preferential flow or short contact time between leaching water and soil had a strong influence on P concentrations, large flow events dominated by surface flow into the blind inlet caused elevated P concentrations, or some combination of both. Of the 35 kg of dissolved P delivered to the P removal structure, 97% was delivered disproportionately by precipitation-induced events that produced only 65% of the total flow volume, with less than 4% delivered during baseflow, indicative of the low dissolved P concentrations in baseflow). In addition, 39% of the total dissolved P inflow load was delivered during the first event, which was an extreme rainfall/flow event that occurred shortly after the application of P fertilizer, thereby delivering a large amount of incidental P rather than soil-equilibrated P.

Overall, the subsurface structure removed 55% of the cumulative dissolved P input, although 71% of that P was removed during the first event that delivered a large amount of incidental P loss. While it is certainly a benefit that the structure was able to perform so well for an incidental P loss event, it should be noted that the target of P removal structures is soil-equilibrated "legacy" P sources,

because incidental P loss events are not only difficult to predict, but can be effectively reduced with more simple and inexpensive best management practices related to P fertilizer and manure application. The ditch P removal structure removed 37% of the cumulative dissolved P inflow load (0.9 kg removed). Regarding economics, the subsurface structured cost USD 562 per kg dissolved P removed, and over USD 6000 per kg for the ditch structure. This high cost is a result of the relatively poor performance of the structures compared with expected performance based on laboratory flow-through results.

Both P removal structures removed >90% of inflow dissolved P for several events, then drastically decreased. Thus, the predicted P removal determined by laboratory flow-through experiments highly overestimated field performance. The reason for this appears to be a combination of chemical and physical problems, specifically chemical issues that additionally caused physical clogging. We hypothesize that the highly soluble and alkaline calcium minerals found in slag produced an ideal environment for formation of carbonate, through input of CO₂-rich tile drainage water, which then competed with phosphate for precipitation with Ca²⁺ and depressed the pH, further reducing the chemical potential for calcium phosphate precipitation. The formation of calcium carbonate not only represents a chemical inefficiency in dissolved P removal, but the mineral also acted to fill the slag pore space and decrease water flow through the slag beds. Evidence for this was found in visual observations of the precipitant, an increase in pressure head at the inlet, dye test results, and a negative correlation between treated water pH and discrete P removal.

We hypothesize that the laboratory flow-through experiment overpredicted P removal because that experiment was conducted using DI water with low concentrations of bicarbonate or dissolved CO_2 compared with tile drainage water. DI water in contact with the atmosphere is only expected to have 0.7 mg L⁻¹ of carbonate alkalinity, whereas tile drainage water can have 200 to 300 mg L⁻¹ of alkalinity, expressed as CaCO₃. The fact that surface water only contains a fraction of the alkalinity compared to tile drainage would explain why previous studies have reported success in removing dissolved P from surface waters with steel slag [25,27]. While useful for treating less alkaline surface water, we do not recommend the use of electric arc furnace steel slag for treating tile drainage water for long-term structures. It would be appropriate to use this material for treating tile drainage if structures are designed for replacing media at a high frequency, which based on this study would be every 4–6 months; such a scenario might be more cost-efficient than what was demonstrated in this study. The problems with treating bicarbonate-rich tile drainage water are likely not isolated to steel slag alone, but any PSM that removes P via calcium phosphate precipitation such as fly ash or flue gas desulfurization gypsum. Because of the unique chemistry of tile drainage water, we recommend using PSMs that remove P via ligand exchange reactions onto Al and Fe oxide/hydroxide minerals, such as mine drainage residuals [26,56], manufactured PSMs [21], or aluminum-coated steel slag [30].

Author Contributions: Conceptualization, C.P. and S.L.; Formal analysis, C.P. and V.S.; Funding acquisition, K.K.; Investigation, C.P., V.S., and M.W.; Methodology, C.P., S.L., and K.K.; Project administration, K.K.; Writing—original draft, C.P.; Writing—review and editing, S.L., V.S., K.K., and M.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the USDA-ARS 211 program.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Baker, D.B.; Confesor, R.; Ewing, D.E.; Johnson, L.T.; Kramer, J.W.; Merryfield, B.J. Phosphorus loading to Lake Erie from the Maumee, Sandusky and Cuyahoga rivers: The importance of bioavailability. *J. Great Lakes Res.* 2014, 40, 502–517.
- 2. Kane, D.D.; Conroy, J.D.; Richards, R.P.; Baker, D.B.; Culver, D.A. Re-eutrophication of Lake Erie: Correlations between tributary nutrient loads and phytoplankton biomass. *J. Great Lakes Res.* **2014**, *40*, 496–501. [CrossRef]
- Scavia, D.; Allan, J.D.; Arend, K.K.; Bartell, S.; Beletsky, D.; Bosch, N.S.; Brandt, S.B.; Briland, R.D.; Daloğlu, I.; DePinto, J. V Assessing and addressing the re-eutrophication of Lake Erie: Central basin hypoxia. *J. Great Lakes Res.* 2014, 40, 226–246. [CrossRef]

- 4. Turner, R.E.; Rabalais, N.N.; Justic, D. Predicting summer hypoxia in the northern Gulf of Mexico: Riverine, N., P., and Si loading. *Mar. Pollut. Bull.* **2006**, *52*, 139–148. [CrossRef] [PubMed]
- Vadas, P.A.; Fiorellino, N.M.; Coale, F.J.; Kratochvil, R.; Mulkey, A.S.; McGrath, J.M. Estimating legacy soil phosphorus impacts on phosphorus loss in the Chesapeake Bay watershed. *J. Environ. Qual.* 2018, 47, 480–486. [CrossRef] [PubMed]
- 6. Stumpf, R.P.; Johnson, L.T.; Wynne, T.T.; Baker, D.B. Forecasting annual cyanobacterial bloom biomass to inform management decisions in Lake Erie. *J. Great Lakes Res.* **2016**, *42*, 1174–1183. [CrossRef]
- Matisoff, G.; Kaltenberg, E.M.; Steely, R.L.; Hummel, S.K.; Seo, J.; Gibbons, K.J.; Bridgeman, T.B.; Seo, Y.; Behbahani, M.; James, W.F. Internal loading of phosphorus in western Lake Erie. *J. Great Lakes Res.* 2016, 42, 775–788. [CrossRef]
- 8. Preedy, N.; McTiernan, K.; Matthews, R.; Heathwaite, L.; Haygarth, P. Rapid incidental phosphorus transfers from grassland. *J. Environ. Qual.* **2001**, *30*, 2105–2112. [CrossRef]
- 9. McDowell, R.W.; Catto, W. Alternative fertilisers and management to decrease incidental phosphorus loss. *Environ. Chem. Lett.* **2005**, *2*, 169–174. [CrossRef]
- Penn, C.J.; Mullins, G.L.; Zelazny, L.W.; Warren, J.G.; McGrath, J.M. Surface runoff losses of phosphorus from Virginia soils amended with Turkey manure using phytase and high available phosphorus corn diets. *J. Environ. Qual.* 2004, 33, 1431–1439.
- 11. Haygarth, P.M.; Sharpley, A.N. Terminology for phosphorus transfer. J. Environ. Qual. 2000, 29, 10–15. [CrossRef]
- 12. Haygarth, P.M.; Jarvie, H.P.; Powers, S.M.; Sharpley, A.N.; Elser, J.J.; Shen, J.; Peterson, H.M.; Chan, N.-I.; Howden, N.J.K.; Burt, T. *Sustainable Phosphorus Management and the Need for a Long-Term Perspective: The Legacy Hypothesis*; ACS: Washington, DC, USA, 2014.
- 13. Jarvie, H.P.; Sharpley, A.N.; Spears, B.; Buda, A.R.; May, L.; Kleinman, P.J.A. *Water Quality Remediation Faces Unprecedented Challenges from Legacy Phosphorus*; ACS: Washington, DC, USA, 2013.
- 14. Qin, Z.; Shober, A. The Challenges of Managing Legacy Phosphorus Losses from Manure-Impacted Agricultural Soils. *Curr. Pollut. Rep.* **2018**, *4*, 265–276. [CrossRef]
- Ross, J.A.; Herbert, M.E.; Sowa, S.P.; Frankenberger, J.R.; King, K.W.; Christopher, S.F.; Tank, J.L.; Arnold, J.G.; White, M.J.; Yen, H. A synthesis and comparative evaluation of factors influencing the effectiveness of drainage water management. *Agric. Water Manag.* 2016, 178, 366–376. [CrossRef]
- 16. Williams, M.R.; King, K.W.; Fausey, N.R. Drainage water management effects on tile discharge and water quality. *Agric. Water Manag.* **2015**, *148*, 43–51. [CrossRef]
- 17. Penn, C.J.; Bryant, R.B.; Callahan, M.P.; Mcgrath, J.M. Use of industrial by-products to sorb and retain phosphorus. *Commun. Soil Sci. Plant Anal.* **2011**, *42*, 633–644. [CrossRef]
- 18. Penn, C.J.; Bryant, R.B. Application of phosphorus sorbing materials to streamside cattle loafing areas. *J. Soil Water Conserv.* **2006**, *61*, 303–310.
- 19. Inamdar, S.P.; Mostaghimi, S.; Mcclellan, P.W.; Brannan, K.M. BMP impacts on sediment and nutrient yields from an agricultural watershed in the Coastal Plain Region. *Trans. ASAE* **2001**, *44*, 1191–1200. [CrossRef]
- 20. Claveau-Mallet, D.; Courcelles, B.; Comeau, Y. Phosphorus removal by steel slag filters: Modeling dissolution and precipitation kinetics to predict longevity. *Environ. Sci. Technol.* **2014**, *48*, 7486–7493. [CrossRef]
- 21. Allred, B.J.; Martinez, L.R.; Gamble, D.L. Phosphate removal from agricultural drainage water using an iron oxyhydroxide filter material. *Water Air Soil Pollut.* **2017**, *228*, 240. [CrossRef]
- 22. Sibrell, P.L.; Kehler, T. Phosphorus removal from aquaculture effluents at the Northeast Fishery Center in Lamar, Pennsylvania using iron oxide sorption media. *Aquac. Eng.* **2016**, *72*, 45–52. [CrossRef]
- 23. Groenenberg, J.E.; Chardon, W.J.; Koopmans, G.F. Reducing phosphorus loading of surface water using iron-coated sand. *J. Environ. Qual.* **2013**, *42*, 250–259. [CrossRef] [PubMed]
- 24. McDowell, R.W.; Sharpley, A.N.; Bourke, W. Treatment of drainage water with industrial by-products to prevent phosphorus loss from tile-drained land. *J. Environ. Qual.* **2008**, *37*, 1575–1582. [CrossRef] [PubMed]
- Penn, C.; Bowen, J.; McGrath, J.; Nairn, R.; Fox, G.; Brown, G.; Wilson, S.; Gill, C. Evaluation of a universal flow-through model for predicting and designing phosphorus removal structures. *Chemosphere* 2016, 151, 345–355. [CrossRef] [PubMed]
- 26. Penn, C.J.; Bryant, R.B.; Kleinman, P.J.A.; Allen, A.L. Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials. *J. Soil Water Conserv.* **2007**, *62*, 269–276.

- 27. Penn, C.; Chagas, I.; Klimeski, A.; Lyngsie, G. A review of phosphorus removal structures: How to assess and compare their performance. *Water* **2017**, *9*, 583. [CrossRef]
- Weber, D.; Drizo, A.; Twohig, E.; Bird, S.; Ross, D. Upgrading constructed wetlands phosphorus reduction from a dairy effluent using electric arc furnace steel slag filters. *Water Sci. Technol.* 2007, *56*, 135–143. [CrossRef]
- 29. Erickson, A.; Gulliver, J.; Weiss, P. Phosphate removal from agricultural tile drainage with iron enhanced sand. *Water* **2017**, *9*, 672. [CrossRef]
- Penn, C.J.; Bowen, J.M. Design and Construction of Phosphorus Removal Structures for Improving Water Quality; Springer: Berlin/Heidelberg, Germany, 2017; ISBN 3319586580.
- 31. Drizo, A.; Forget, C.; Chapuis, R.P.; Comeau, Y. Phosphorus removal by electric arc furnace steel slag and serpentinite. *Water Res.* **2006**, *40*, 1547–1554. [CrossRef]
- 32. Karczmarczyk, A.; Bus, A.; Baryła, A. Filtration curtains for phosphorus harvesting from small water bodies. *Ecol. Eng.* **2016**, *86*, 69–74. [CrossRef]
- 33. Penn, C.; McGrath, J.; Bowen, J.; Wilson, S. Phosphorus removal structures: A management option for legacy phosphorus. *J. Soil Water Conserv.* **2014**, *69*, 51A–56A. [CrossRef]
- 34. Klimeski, A.; Uusitalo, R.; Turtola, E. Screening of Ca-and Fe-rich materials for their applicability as phosphate-retaining filters. *Ecol. Eng.* **2014**, *68*, 143–154. [CrossRef]
- 35. Canga, E.; Heckrath, G.J.; Kjaergaard, C. Agricultural drainage filters. II. Phosphorus retention and release at different flow rates. *Water Air Soil Pollut.* **2016**, 227, 276. [CrossRef]
- 36. Penn, C.J.; McGrath, J.M.; Rounds, E.; Fox, G.; Heeren, D. Trapping phosphorus in runoff with a phosphorus removal structure. *J. Environ. Qual.* **2012**, *41*, 672–679. [CrossRef] [PubMed]
- 37. Wang, Z.; Bell, G.E.; Penn, C.J.; Moss, J.Q.; Payton, M.E. Phosphorus reduction in turfgrass runoff using a steel slag trench filter system. *Crop Sci.* **2014**, *54*, 1859–1867. [CrossRef]
- 38. Shilton, A.N.; Elmetri, I.; Drizo, A.; Pratt, S.; Haverkamp, R.G.; Bilby, S.C. Phosphorus removal by an 'active'slag filter—A decade of full scale experience. *Water Res.* **2006**, *40*, 113–118. [CrossRef]
- 39. Claveau-Mallet, D.; Lida, F.; Comeau, Y. Improving phosphorus removal of conventional septic tanks by a recirculating steel slag filter. *Water Qual. Res. J.* **2015**, *50*, 211–218. [CrossRef]
- 40. Claveau-Mallet, D.; Wallace, S.; Comeau, Y. Removal of phosphorus, fluoride and metals from a gypsum mining leachate using steel slag filters. *Water Res.* **2013**, *47*, 1512–1520. [CrossRef]
- 41. Vohla, C.; Kõiv, M.; Bavor, H.J.; Chazarenc, F.; Mander, Ü. Filter materials for phosphorus removal from wastewater in treatment wetlands—A review. *Ecol. Eng.* **2011**, *37*, 70–89. [CrossRef]
- Williams, M.R.; Livingston, S.J.; Penn, C.J.; Smith, D.R.; King, K.W.; Huang, C.-H. Controls of event-based nutrient transport within nested headwater agricultural watersheds of the western Lake Erie basin. *J. Hydrol.* 2018, 559, 749–761. [CrossRef]
- Smith, D.R.; King, K.W.; Johnson, L.; Francesconi, W.; Richards, P.; Baker, D.; Sharpley, A.N. Surface runoff and tile drainage transport of phosphorus in the midwestern United States. *J. Environ. Qual.* 2015, 44, 495–502. [CrossRef]
- 44. Kõiv, M.; Liira, M.; Mander, Ü.; Mõtlep, R.; Vohla, C.; Kirsimäe, K. Phosphorus removal using Ca-rich hydrated oil shale ash as filter material–the effect of different phosphorus loadings and wastewater compositions. *Water Res.* **2010**, *44*, 5232–5239. [CrossRef] [PubMed]
- Dobbie, K.E.; Heal, K.V.; Aumonier, J.; Smith, K.A.; Johnston, A.; Younger, P.L. Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater. *Chemosphere* 2009, 75, 795–800. [CrossRef] [PubMed]
- 46. Klimeski, A.; Uusitalo, R.; Turtola, E. Variations in phosphorus retention by a solid material while scaling up its application. *Environ. Technol. Innov.* **2015**, *4*, 285–298. [CrossRef]
- 47. Kirkkala, T.; Ventelä, A.-M.; Tarvainen, M. Long-term field-scale experiment on using lime filters in an agricultural catchment. *J. Environ. Qual.* **2012**, *41*, 410–419. [CrossRef] [PubMed]
- 48. Smith, D.R.; Francesconi, W.; Livingston, S.J.; Huang, C. Phosphorus losses from monitored fields with conservation practices in the Lake Erie Basin, USA. *AMBIO* **2015**, *44*, 319–331. [CrossRef]
- 49. Feyereisen, G.W.; Francesconi, W.; Smith, D.R.; Papiernik, S.K.; Krueger, E.S.; Wente, C.D. Effect of replacing surface inlets with blind or gravel inlets on sediment and phosphorus subsurface drainage losses. *J. Environ. Qual.* **2015**, *44*, 594–604. [CrossRef]

- 50. Smith, D.R.; Livingston, S.J. Managing farmed closed depressional areas using blind inlets to minimize phosphorus and nitrogen losses. *Soil Use Manag.* **2013**, *29*, 94–102. [CrossRef]
- Gonzalez, J.M.; Smith, D.R.; Livingston, S.; Warnemuende-Pappas, E.; Zwonitzer, M. Blind inlets: Conservation practices to reduce herbicide losses from closed depressional areas. *J. Soils Sediments* 2016, 16, 1921–1932. [CrossRef]
- 52. Sims, J.T.; Maguire, R.O.; Leytem, A.B.; Gartley, K.L.; Pautler, M.C. Evaluation of Mehlich 3 as an agri-environmental soil phosphorus test for the Mid-Atlantic United States of America. *Soil Sci. Soc. Am. J.* **2002**, *66*, 2016–2032. [CrossRef]
- 53. Duncan, E.W.; King, K.W.; Williams, M.R.; LaBarge, G.; Pease, L.A.; Smith, D.R.; Fausey, N.R. Linking soil phosphorus to dissolved phosphorus losses in the Midwest. *Agric. Environ. Lett.* **2017**, 2. [CrossRef]
- 54. USEPA. Acid Digestion of Sediments, Sludges, and Soils (Method 3050B). In *Test Methods Eval. Solid Waste, Physic Methods*; USEPA: Washington, DC, USA, 1996.
- 55. Murphy, J.; Riley, J.P. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* **1962**, *27*, 31–36. [CrossRef]
- 56. Stoner, D.; Penn, C.; McGrath, J.; Warren, J. Phosphorus removal with by-products in a flow-through setting. *J. Environ. Qual.* **2012**, *41*, 654–663. [CrossRef]
- 57. Nelson, N.S. An acid-persulfate digestion procedure for determination of phosphorus in sediments. *Commun. Soil Sci. Plant Anal.* **1987**, *18*, 359–369. [CrossRef]
- 58. Penn, C.J.; McGrath, J.M. Predicting phosphorus sorption onto steel slag using a flow-through approach with application to a pilot scale system. *J. Water Resour. Prot.* **2011**, *3*, 235. [CrossRef]
- 59. National Slag Association. *A Guide For The Use Of Steel Slag in Agriculture and for Reclamation of Acid Lands;* National Slag Association: Pleasant Grove, UT, USA, 2019.
- Yildirim, I.Z.; Prezzi, M. Chemical, mineralogical, and morphological properties of steel slag. *Adv. Civ. Eng.* 2011, 2011. [CrossRef]
- 61. Zuo, M.; Renman, G.; Gustafsson, J.P.; Klysubun, W. Phosphorus removal by slag depends on its mineralogical composition: A comparative study of AOD and EAF slags. *J. Water Process Eng.* **2018**, 25, 105–112. [CrossRef]
- 62. Drizo, A.; Comeau, Y.; Forget, C.; Chapuis, R.P. Phosphorus saturation potential: A parameter for estimating the longevity of constructed wetland systems. *Environ. Sci. Technol.* **2002**, *36*, 4642–4648. [CrossRef]
- 63. Bowden, L.I.; Jarvis, A.P.; Younger, P.L.; Johnson, K.L. Phosphorus removal from waste waters using basic oxygen steel slag. *Environ. Sci. Technol.* **2009**, *43*, 2476–2481. [CrossRef]
- Eveborn, D.; Gustafsson, J.P.; Hesterberg, D.; Hillier, S. XANES speciation of P in environmental samples: An assessment of filter media for on-site wastewater treatment. *Environ. Sci. Technol.* 2009, 43, 6515–6521. [CrossRef]
- 65. Usepa, A. Plain English Guide to the EPA Part 503 Biosolids Rule. U.S. Patent 93003A, 04 Febuary 2020.
- King, K.W.; Williams, M.R.; Johnson, L.T.; Smith, D.R.; LaBarge, G.A.; Fausey, N.R. Phosphorus availability in Western Lake Erie Basin drainage waters: Legacy evidence across spatial scales. *J. Environ. Qual.* 2017, 46, 466–469. [CrossRef]
- Sharpley, A.N.; Kleinman, P.J.A.; Heathwaite, A.L.; Gburek, W.J.; Folmar, G.J.; Schmidt, J.P. Phosphorus loss from an agricultural watershed as a function of storm size. *J. Environ. Qual.* 2008, *37*, 362–368. [CrossRef] [PubMed]
- 68. Larsen, T.; Broch, K.; Andersen, M.R. First flush effects in an urban catchment area in Aalborg. *Water Sci. Technol.* **1998**, *37*, 251–257. [CrossRef]
- 69. Kato, T.; Kuroda, H.; Nakasone, H. Runoff characteristics of nutrients from an agricultural watershed with intensive livestock production. *J. Hydrol.* **2009**, *368*, 79–87. [CrossRef]
- 70. Bertrand-Krajewski, J.-L.; Chebbo, G.; Saget, A. Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon. *Water Res.* **1998**, *32*, 2341–2356. [CrossRef]
- 71. Pionke, H.B.; Gburek, W.J.; Sharpley, A.N. Critical source area controls on water quality in an agricultural watershed located in the Chesapeake Basin. *Ecol. Eng.* **2000**, *14*, 325–335. [CrossRef]
- 72. Williams, M.R.; King, K.W.; Duncan, E.W.; Pease, L.A.; Penn, C.J. Fertilizer placement and tillage effects on phosphorus concentration in leachate from fine-textured soils. *Soil Tillage Res.* **2018**, *178*, 130–138. [CrossRef]
- 73. Williams, M.R.; King, K.W.; Ford, W.; Buda, A.R.; Kennedy, C.D. Effect of tillage on macropore flow and phosphorus transport to tile drains. *Water Resour. Res.* **2016**, *52*, 2868–2882. [CrossRef]

- 74. Pease, L.A.; King, K.W.; Williams, M.R.; LaBarge, G.A.; Duncan, E.W.; Fausey, N.R. Phosphorus export from artificially drained fields across the Eastern Corn Belt. *J. Great Lakes Res.* **2018**, *44*, 43–53. [CrossRef]
- 75. Claveau-Mallet, D.; Wallace, S.; Comeau, Y. Model of phosphorus precipitation and crystal formation in electric arc furnace steel slag filters. *Environ. Sci. Technol.* **2012**, *46*, 1465–1470. [CrossRef]
- 76. Claveau-Mallet, D.; Courcelles, B.; Pasquier, P.; Comeau, Y. Numerical simulations with the P-Hydroslag model to predict phosphorus removal by steel slag filters. *Water Res.* **2017**, *126*, 421–432. [CrossRef]
- 77. Claveau-Mallet, D.; Boutet, É.; Comeau, Y. Steel slag filter design criteria for phosphorus removal from wastewater in decentralized applications. *Water Res.* **2018**, *143*, 28–37. [CrossRef] [PubMed]
- 78. Qin, Z.; Shober, A.L.; Scheckel, K.G.; Penn, C.J.; Turner, K.C. Mechanisms of Phosphorus Removal by Phosphorus Sorbing Materials. *J. Environ. Qual.* **2018**, *47*, 1232–1241. [CrossRef] [PubMed]
- 79. Lindsay, W.L. Chemical Equilibria in Soils.; John Wiley and Sons Ltd.: Hoboken, NJ, USA, 1979; ISBN 0471027049.
- 80. Dunets, C.S.; Zheng, Y.; Dixon, M. Use of phosphorus-sorbing materials to remove phosphate from greenhouse wastewater. *Environ. Technol.* **2015**, *36*, 1759–1770. [CrossRef]
- Kostura, B.; Kulveitova, H.; Leško, J. Blast furnace slags as sorbents of phosphate from water solutions. *Water Res.* 2005, 39, 1795–1802. [CrossRef] [PubMed]
- Liira, M.; Kõiv, M.; Mander, Ü.; Mõtlep, R.; Vohla, C.; Kirsimäe, K. Active filtration of phosphorus on Ca-rich hydrated oil shale ash: Does longer retention time improve the process? *Environ. Sci. Technol.* 2009, 43, 3809–3814. [CrossRef] [PubMed]
- Omernik, J.M.; Powers, C.F. Total alkalinity of surface waters—A national map. Ann. Assoc. Am. Geogr. 1983, 73, 133–136. [CrossRef]
- 84. Fausey, N.R.; Brown, L.C.; Belcher, H.W.; Kanwar, R.S. Drainage and water quality in Great Lakes and cornbelt states. *J. Irrig. Drain. Eng.* **1995**, *121*, 283–288. [CrossRef]
- Jones, C.S.; Kult, K.J. Use alkalinity monitoring to optimize bioreactor performance. J. Environ. Qual. 2016, 45, 855–865. [CrossRef]
- 86. Olsen, S.R. *Estimation of Available Phosphorus in Soils by Extraction with Sodium Bicarbonate;* US Department of Agriculture: Washington, DC, USA, 1954.
- 87. Jiang, F.; Beck, M.B.; Cummungs, R.G.; Rowles, K.; Russell, D.L. Estimation of costs of phosphorus removal in wastewater treatment facilities: Adaptation of existing facilities. *Water Policy Work. Pap.* 2005, *11*, 1–45.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).