

Article

EAF Steel Slag Filters for Phosphorus Removal from Milk Parlor Effluent: The Effects of Solids Loading, Alternate Feeding Regimes and In-Series Design

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Abstract: Electric arc furnace (EAF) steel slag filters were investigated for their efficiency at reducing the concentration of phosphorus (P) from dairy farm wastewater in Vermont. The primary objective for this study was to examine the use of in series design on filters' performance in P removal from dairy farm wastewater at subzero temperatures. Other research objectives were to investigate operational parameters such as the effects of total suspended solids (TSS) daily mass loading rates and of alternating feeding and resting periods on EAF steel slag filters' TSS, dissolved reactive phosphorus (DRP) and total phosphorus (TP) removal efficiencies and filter system life-span. The utilization of in series filter design increased filter DRP removal efficiency by 35%. In series design also allows for alternating feeding and resting periods, which resulted in a 16%, 57% and 74% increase in TSS, DRP and TP removal efficiencies, respectively, by the first filter in series over a single period. Additionally, the system life span was extended 3.25 fold (from 52 to 169 day). Based on this research, we recommend alternate feeding and resting cycles and in series design to be integrated in the design of EAF steel slag filter systems for highly concentrated agricultural effluents in cold climates.

Keywords: phosphorus removal; concentrated waste influent; steel slag filters; cold climate; total suspended solids (TSS); dissolved reactive phosphorus (DRP)

1. Introduction

Over the past decade the eutrophication of surface waters caused by excess phosphorus (P) pollution from agricultural operations has become one of the major water quality issues worldwide [1,2]. The use of confined animal feeding operations (CAFOs) results in the concentration of animals, and therefore their associated wastes, wastewater and storm runoff into increasingly smaller plots of land and regions of the U.S. This causes elevated levels of nutrients, suspended solids, oxygen demanding organisms and heavy metals in agricultural waste effluents, and poses a threat to surface and ground waters [3]. The pollution potential of CAFOs, however, depends on the number and type of animals, farm size, farm location, layout of facilities and fields, and practices used to collect and store wastes and choice of practices for waste management [3,4].

An increase in water pollution associated with agricultural operations has resulted in a more concerted national effort to enforce water quality regulations throughout the U.S. [1,5,6]. In 2003 the U.S. EPA revised the national Concentrated Animal Feeding Operations (CAFOs) rules to define which farms are required to obtain a National Pollutant Discharge Elimination System (NPDES) Permit [7,8]. The result of these revisions was the determination that all medium and large CAFOs are required to obtain a NPDES permit if they have any discharge of agricultural wastewater to any waters of the state [7]. Additionally, the Total Maximum Daily Load (TMDL) was created to establish the total maximum amount of a pollutant that a body of water can receive while still meeting water quality standards [9]. The TMDL regulation additionally requires all CAFOs to implement waste storage or treatment systems to prevent discharges from production areas and ensure that the farm is in compliance with state and federal regulations [8,9].

The newly revised federal CAFO and water quality rules will impact farming communities across the nation. Many farms will have difficulty preventing discharges of high P effluent from their production areas and disposing properly of animal wastes. The impact will be even more severe in small states, such as Vermont, where agricultural producers generally have much less arable land available for animal waste disposal in comparison to other US agricultural communities [10]. The financial burden that a family farm may have to bear to implement these waste management practices may strain the already tight economics of farming, resulting in an increase in the loss of farms. Alternative wastewater management systems are needed to provide relatively economical solutions to treat these wastewaters and prevent the discharge of P to surface waters.

Several actions have been taken across the nation regarding the management and treatment of animal wastes from CAFOs in order to mitigate the potential for nutrient pollution. The USDA-EPA Unified National Strategy for animal feeding operations (AFOs) proposed a requirement that all AFOs develop nutrient management plans (NMPs) to identify the methods to be used for management of animal wastes [11]. The NMPs often rely on agricultural best management plans (BMPs) to manage P on farms, and limit the risk of its movement to surface water. Sharpley *et al.* [12] recently provided an updated review of BMPs to minimize agricultural impacts on water quality. Most of the current P removal technologies and BMPs rarely achieve reductions greater than 50% [12]. At present the options for treatment of agricultural effluents are very limited, and so it is critical that new methods of effective treatment are sought [1-4,7-9]. The treatment technologies that are utilized for municipal and industrial wastewater are complex and very expensive. Chemical dosing, for example, a traditional P

removal technology, is an energy intensive method that requires constant monitoring and manipulation [13]. Agricultural producers lack the capital, manpower and technical training to build and maintain such systems.

Research on the potential use of natural and industrial by-products in on-site treatment systems for P removal from wastewater was initiated in the late 1980s, along with the development of constructed wetlands (CW), a low cost technology for point source pollution treatment [14,15]. Over 100 materials have been tested for P retention capacity in laboratory and pilot scale studies around the world. Comprehensive reviews of the published literature have compared the P removal efficiency of many of these materials [16,17]. Steel slags, a co-product of steel production, have demonstrated the greatest capacity to remove P from a variety of wastewaters [16,17]. Over the past 15 years there has been significant scientific evidence showing the efficiency of electric arc furnace (EAF), blast furnace (BF) and iron melter (IM) steel slags in P removal from a variety of wastewaters [16-20]. However, despite this evidence, apart from New Zealand [18,20,21], there are currently very few full-scale steel slag filters in operation for the removal of P from wastewater [22].

The first field testing of EAF steel slag filters (EAF SSF) as an innovative method for P reduction from mixed barnyard and milk parlor waste effluent was conducted at the University of Vermont (UVM) Constructed Wetlands Research Center (CWRC), [18,19]. The results from these investigations demonstrated that EAF SSF reduced the dissolved reactive phosphorus (DRP) by 75% and 72%, respectively, when treating dairy waste effluent with and without constructed wetland pretreatment [19]. However, in these studies the EAF SSF were located indoors in the UVM Phosphorus Research Facility. This facility provided a controlled environment that was heated during winter months to room temperature (20 °C), and therefore not representative of typical on-farm conditions that an EAF SSF technology would encounter in cold climates.

To assess the viability of EAF SSF application on dairy farms in Vermont and other cold climate areas, the primary objective in this study was to evaluate the performance of EAF SSF the removal of P from a high strength milk parlor wastewater at subzero temperatures. Other objectives were to: (i) investigate the effects of TSS daily mass loading rates on the premature clogging of P filters, P removal performance and life-span of filter system, and (ii) investigate the rejuvenation of EAF steel slag filters through the alternation of feeding and resting periods so as to maximize TSS, DRP and TP removal efficiencies and filter systems life-span.

2. Materials and Methods

2.1. Research Site and Wastewater Effluent

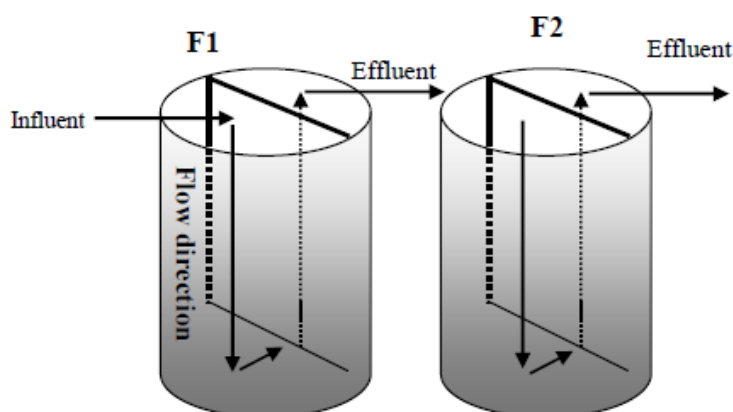
This experiment was conducted at the UVM CWRC, which was constructed to treat wastewater from the UVM Paul Miller Dairy farm. A full description of the UVM CWRC design is contained in Munoz *et al.* [23]. The filters were constructed to treat the wastewater effluents from both the milk parlor and milk house. Milk parlor effluent consists of milking equipment and other associated equipment wash water, rejected milk and animal waste and is of a much higher strength than the barnyard runoff. Wastewater from the milking operations is first stored in an underground 3.8 m³ (1,000 gallon) settling tank located outside the dairy parlor facility, where it undergoes

anaerobic digestion. The settling tank effluent is then gravity fed through an underground pipe (0.20 m diameter) to an 11.4 m³ (3,000 gallon) underground holding tank [23,24].

2.2. EAF Steel Slag Filters Construction

The construction of EAF steel slag filters at the UVM CWRC took place in November 2005 [24,25]. Two 1.2 m × 2.4 m × 1.2 m enclosures (Quazite[®], Strongewell, Lenoir City, TN) were buried in the ground next to the 11.35 m³ underground holding tank. Two 0.242 m³ (55 gallon) polypropylene drums (US Plastics, Lima, OH) were placed in each enclosure, making two replicates of two filters each connected in-series (F1 & F2 and F1' & F2'). The area around the filters was filled in with gravel to provide support for the barrels and insulation, with additional foam insulation placed around the outside of the enclosures and on the undersides of the enclosures lids. Each filter had a baffle installed in the middle, extending from the top of the column to 0.15 m from the bottom, creating the designed flow path (Figure 1). The influent for the filters was pulled directly from the CWRC milk house waste holding tank using a pump (Zoeller Z80 pump) controlled by a timer (Fisher Scientific).

Figure 1. Phosphorus filters design. In order to facilitate sampling, and maintain the same flow path baffles that were installed in each filter in series. The first half of each filter was fed from the top to the bottom, while the second half was fed from the bottom to the top of a filter.



The filters were filled with EAF steel slag (Multiserve, Quebec, Canada). Drizo *et al.* [18] recently provided a description of the chemical composition of this material. Based on the previous research conducted at the UVM CWRC [18,19] two different particle sizes of EAF steel slag material were employed: 5–10 mm and 10–20 mm, with the larger size used at the inlets to reduce the incidence of clogging. Slag particles were weighed and added to the filters in layers approximately 0.05 m in height. Each layer was leveled and compacted, and the remaining space in the filter height was recorded [18,19,25]. The average weight of the 5–10 mm EAF slag aggregates in each of the four filters was 340.6 kg, while the average weight of the 10–20 mm slag material aggregates was 74.13 kg, representing 82% and 18% of total filter weight, respectively. The theoretical pore volume of each filter was first estimated using known values from previous filter experiments. In January 2006, the filters were filled with fresh water and the exact pore volume of each filter was recorded. The average filter pore volume was 87.1 L, which was very close to the estimated theoretical volume (85.9 L). To

achieve the desired hydraulic retention time (HRT) of 18 h and to reduce the risk of freezing, each filter received 131 L of milk parlor wastewater per day spread over 6 separate pump cycles (Zoeller Z80 pump) lasting 28 minutes (flow rate of 1.553 L min^{-1}) and controlled by a timer (Fisher Scientific). The filters had a cross-sectional area of 0.106 m^2 , resulting in a hydraulic loading rate (daily flow to the filters divided by the cross sectional surface area of the filter) of 123 cm day^{-1} .

The filters were first put into operation in the winter of 2006, and therefore were frequently exposed to subzero temperatures (January 20th until March 13th, 2006). During this first feeding period, to reduce the risk of freezing, 6 separate pump cycles lasting 30 minutes (flow rate of approximately 1.5 L min^{-1}) were used for the feeding. At the end of the first 52 day feeding period, the EAF steel slag material was excavated from the first filters in series (F1 & F1') to a depth of approximately 0.3 m, placed on a plastic tarp and rinsed thoroughly with fresh water. The material was then placed back in the barrels, and left to rest for approximately 3 months (88 days).

In June 2006, a second pump was installed in the holding tank to feed each set of filters independently and ensure better control of flow rates. During this second feeding cycle, the feeding regime was simplified to 2 daily pump cycles of 44 minutes at approximately 3 L min^{-1} . To decrease the TSS loading, a metal screen ($5 \times 5 \text{ mm}$ mesh) was built and placed in the CWRC milk house waste holding tank in order to separate larger solids from the pump intakes. A synthetic material (geotextile) was placed at the pump intakes and a cheesecloth filter was placed around the inlet pipes for the first filters (F1 & F1') to further reduce solid particles in the filters influent.

The second feeding cycle was carried out during summer and fall warmer weather (9 June–4 October 2006) and lasted 117 days. Overall, filters were exposed to 2 feeding cycles (52 days and 117 days) with an 88 day resting period in between.

Water samples were taken from the holding tank and each filter's influent and effluent once a week and analyzed for total suspended solids (TSS), dissolved reactive phosphorus (DRP) and pH. Samples for total phosphorus (TP) determination were taken once every three weeks on average. TSS concentrations were determined gravimetrically by weighing samples before and after drying at $55 \text{ }^\circ\text{C}$ for 2–3 days [26]. DRP concentrations were determined using the molybdate—reactive P method [21]. TP was determined by a standard microwave assisted digestion method using 10 mL of sample and 10 mL of concentrated HNO_3 , which was then microwaved [26]. The sample was then diluted to 100 mL with 0.01 HNO_3 and the sample was analyzed by ICP-AES (Perkin Elmer 3000 DV). The pH was recorded for all samples using a standard pH probe (Hanna instruments, HI 223, Microprocessor pH meter).

The entire set of data was analyzed using the MIXED procedure of the SAS System for Windows [27]. Because the filter data are spatially correlated and the days are not equally spaced, a spatial covariance structure for both spatially and temporally correlated data points was used.

3. Results

TSS, DRP and TP removal efficiencies during the 1st Feeding Cycle (20 January–13 March 2006)

The average influent TSS, DRP and TP concentrations to the first filter (F1) was 3395.03 ± 2.67 mg TSS L⁻¹, 42.46 ± 12.75 mg DRP L⁻¹ and 54.77 ± 9.5 mg TP L⁻¹, respectively. The filters were fed at an average TSS, DRP and TP daily loading rates (LR) of 1.08 ± 0.004 g TSS kg⁻¹ EAF slag day⁻¹, 0.013 ± 0.001 g DRP kg⁻¹ EAF slag day⁻¹ and 0.02 ± 0.001 g TP kg⁻¹ EAF slag day⁻¹ respectively (Table 1).

Table 1. EAF steel slag filters life span, average hydraulic loading rates (q), TSS and DRP mass loading rates and DRP removal efficiencies.

Filters life span (days)	q (cm d ⁻¹)	TSS LR (g kg ⁻¹ d ⁻¹)	DRP LR (g kg ⁻¹ d ⁻¹)	DRP Removal Efficiency (%)	
Before resting		F1	F1	F1	F1F2
52 ^{a,1}	123	1.08 ± 0.004	0.013 ± 0.001	42.94 ± 2.60 %	76.11 ± 3.48 %
After resting					
169 ^{b,1}	123	0.24 ± 0.001	0.010 ± 0.003	39.7 ± 0.44 %	55.98 ± 7.59 %
Total					
175 ^{a,b,1}	123	0.53 ± 0.06	0.012 ± 0.003	42.80 ± 0.75 %	69.70 ± 1.48 %
180 ^{c,2}	43.2	0.285 ± 0.04	0.011 ± 0.002	72.00 ± 0.26	
over 260 ^{d,2}	43.2	0.024 ± 0.01	0.008 ± 0.001	75.00 ± 0.21	

^a Filters fed by milk parlor wastewater without any pre-treatment; ^b filters fed by milking operations wastewater, with a screen and synthetic material added as a pre-treatment; ^c filters fed by mixed barnyard runoff and milking operations wastewater, not receiving any pre-treatment; ^d filters fed by mixed barnyard runoff and milking operations wastewater, having constructed wetland as a pre-treatment; ¹ filters designed as two units connected in series; ² filters designed as single units.

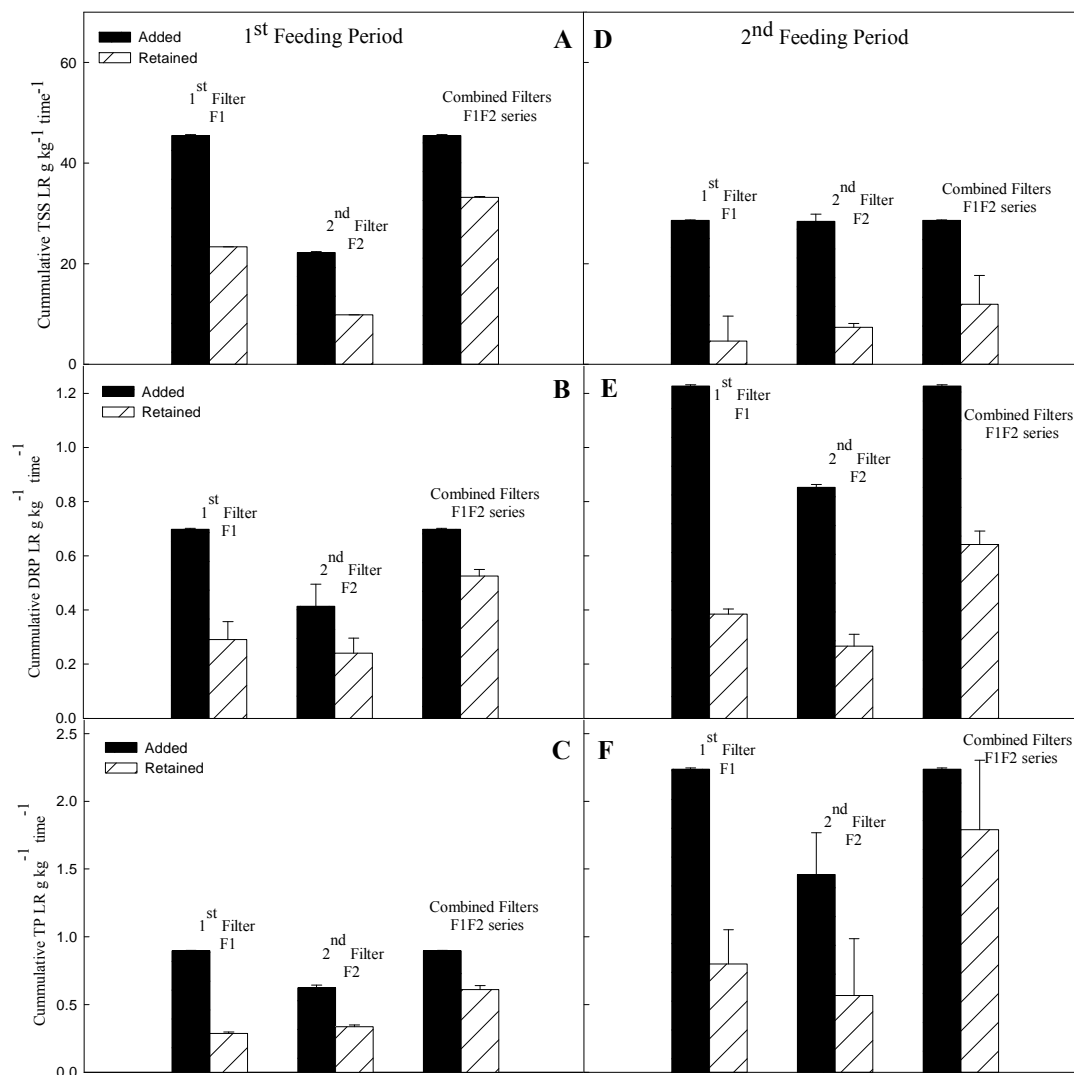
The cumulative amount of TSS fed to the first filter in series (F1) during the first feeding cycle was 45.44 ± 0.18 g TSS kg⁻¹ EAF slag (18.7 kg total) (Figure 2A). Filter F1 retained 23.34 ± 0.004 g TSS kg⁻¹ EAF slag (9.60 kg total) resulting in a TSS removal efficiency of 51% (Figure 2A). The second filter in series (F2) retained an additional 9.84 ± 0.004 g TSS kg⁻¹ EAF slag (3.98 kg total), resulting in an overall TSS removal efficiency by the filter series of 73% (Figure 2A). Although the use of in-series design improved TSS removal efficiency by 21%, the filters became clogged and inoperable after only 52 days.

During the first feeding period filter F1 received 0.7 ± 0.003 g DRP kg⁻¹ EAF slag (0.287 kg total) and of that it retained 0.29 ± 0.066 g DRP kg⁻¹ EAF slag (0.119 kg total), for a cumulative DRP removal efficiency of 43% (Figure 2B). The second filter in series (F2) received 0.41 ± 0.08 g DRP kg⁻¹ EAF slag (0.167 kg total) and retained 0.24 ± 0.06 g DRP kg⁻¹ EAF slag (0.098 kg total) resulting in a cumulative DRP removal efficiency of 66% (Figure 2B).

The F1F2 filter series received 0.70 ± 0.003 g DRP kg⁻¹ EAF slag (0.287 kg) and retained 0.53 ± 0.03 g DRP kg⁻¹ EAF slag (0.217 kg) resulting in a cumulative DRP removal efficiency of 76%

(Figure 2-2B). The filters in-series increased the system's DRP removal efficiency by 44% when compared to the single filter unit's performance (Figure 3A, Table 1).

Figure 2. Cumulative total suspended solids (TSS)(A, D), dissolved reactive phosphorus (DRP)(B, E) and total phosphorus (TP) (C, F) loading rates to the filters during the first 52 day feeding cycle (A, B, C) and during the second 117 day feeding cycle (D, E, F).

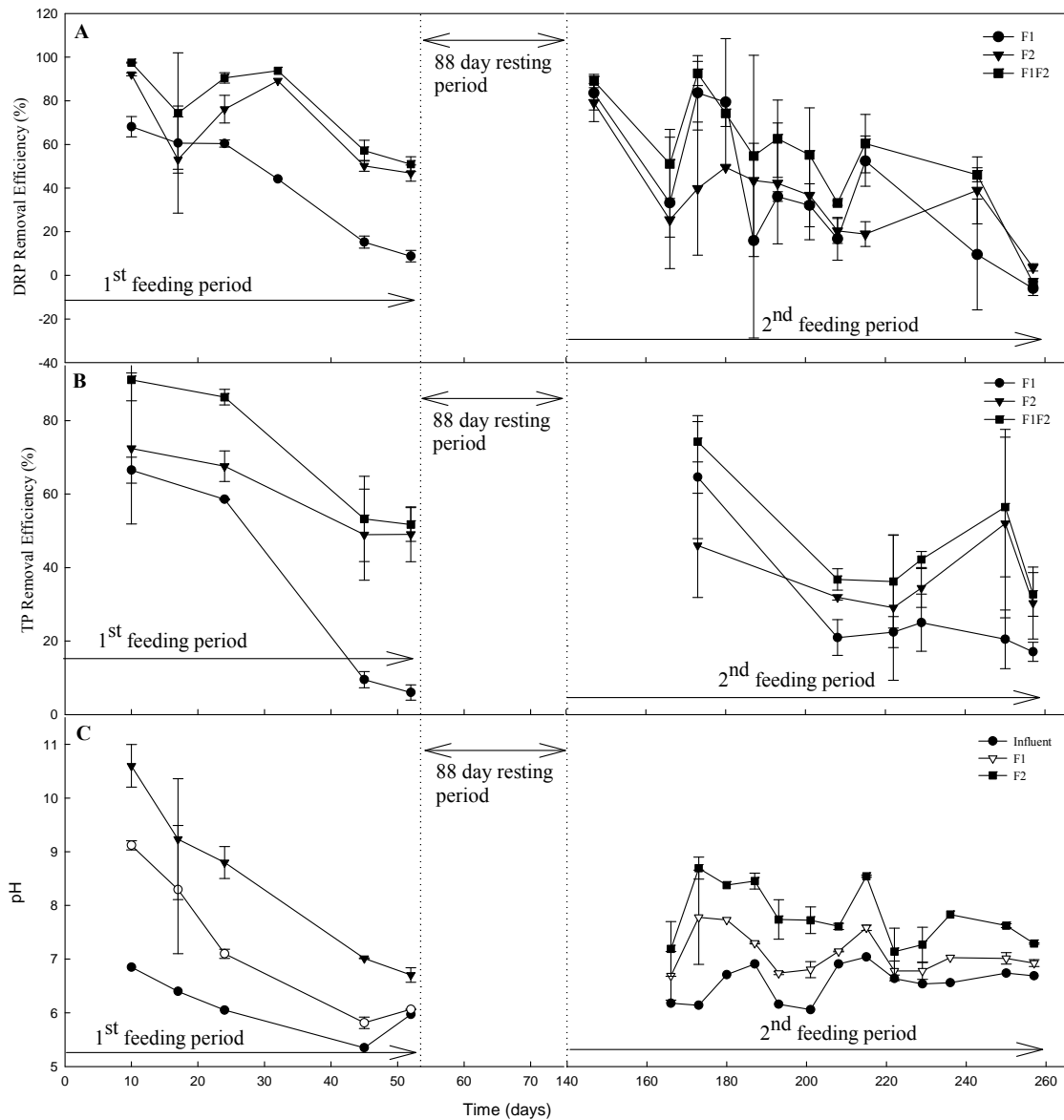


The amount of total phosphorus (TP) added to filter F1 during the first feeding cycle was 0.896 ± 0.003 g TP kg⁻¹ EAF slag (0.368 kg total) with the filter retaining 0.287 ± 0.01 g TP kg⁻¹ EAF slag (0.118 kg total), for a TP removal efficiency of 43% (Figure 2C). The second filter in series (F2) received 0.623 ± 0.02 g TP kg⁻¹ EAF slag (0.253 kg total) and retained 0.336 ± 0.013 g TP kg⁻¹ EAF slag (0.137 kg total), resulting in a TP removal efficiency of 57%. In total the F1F2 filter series received 0.88 ± 0.001 g TP kg⁻¹ EAF slag (0.368 kg) and retained 0.61 ± 0.03 g TP kg⁻¹ EAF slag (0.255 kg) resulting in a cumulative TP removal efficiency of 74% (Figure 2C). As with DRP, the use of series design for the EAF steel slag filters increased TP removal efficiency by 23% (Figure 3B).

The pH of the influent remained fairly consistent throughout the investigation, ranging from 5.13 to 6.85 (average 5.96 ± 0.64) (Figure 3C). Filter F1's effluent pH values ranged from 5.13 to 9.18 (average 7.02 ± 1.4) and the second filter in series (F2) effluent pH values were slightly higher and

ranged from 5.47 to 10.88 (average 8.2 ± 1.75) (Figure 3C). The effluent pH values of the first and second filters in series followed a similar trend with higher values observed during the first 20 days of investigation which then stabilized gradually at lower values (7 and 7.3, respectively) (Figure 3C).

Figure 3. DRP and TP removal efficiencies (A, B) and pH (C) over the entire 257 days of investigation. The first feeding cycle had a duration of 52 days with the second feeding cycle having a length of 117 days. There was additionally an 88 day resting period between the two feeding cycles.



TSS, DRP and TP removal efficiencies during the 2nd Feeding Period (9 June– 4 October 2006)

The second feeding cycle of the filters commenced after a resting period of 88 days, and lasted for 117 days. Although the filters were fed at the same HLR (123 cm day^{-1}) as during the first feeding cycle, the placement of a screen inside of the holding tank reduced the influent TSS concentration to filter F1 by 87% (from an average of 3,395.03 to 910.09 mg TSS L^{-1}). Additionally, the installation of a geotextile material around the pumps' inlet and a cheesecloth filter on the filters' inlet pipes reduced

TSS concentration by a further 5% (from 915.09 to 865.86 mg TSS L⁻¹). As a result, the first filter in series (F1) received 37% lower amount of TSS (28.59 ± 0.11 g kg⁻¹ EAF slag) (Figure 2D) when compared to the previous feeding cycle (Figure 2A), and had a much lower retention (4.59 ± 4.96 g TSS kg⁻¹ EAF slag). Overall, the first filter in series (F1) received a total of 73.95 ± 0.11 g TSS kg⁻¹ EAF slag (31.97 kg TSS) during the entire period of investigation (both feeding periods 1 and 2), and retained 27.93 ± 4.96 g TSS kg⁻¹ EAF slag (14.9 kg TSS) resulting in a TSS removal efficiency of 62% (Figure 3A). The second filter in series (F2) retained an additional 17.19 ± 0.77 g TSS kg⁻¹ EAF slag (11.33 kg TSS) (both feeding cycles 1 and 2) for a total removal by the F1F2 filter series of 45.12 ± 0.49 g TSS kg⁻¹ EAF slag (25.52 kg TSS) with a TSS removal efficiency of 61% (Table 1).

During the second feeding cycle the first filter in series (F1) received an additional 1.23 ± 0.005 g DRP kg⁻¹ EAF slag (0.504 kg DRP) and retained 0.385 ± 0.02 g DRP kg⁻¹ EAF slag (0.158 kg DRP) resulting in an average DRP removal efficiency of 40% (Figure 2E). The second filter in series (F2) was fed 0.852 ± 0.012 g DRP kg⁻¹ EAF slag (0.346 kg total) and retained 0.27 ± 0.04 g DRP kg⁻¹ EAF slag (0.109 kg total) for an average DRP removal efficiency of 38% (Figure 2D). When viewed as a single unit, the filter series F1F2 received 1.23 ± 0.005 g DRP kg⁻¹ EAF slag (0.504 kg) and retained 0.64 ± 0.05 g DRP kg⁻¹ EAF slag (0.267 kg) resulting in an average DRP removal efficiency of 56% (Figure 3A) during the second feeding cycle. During the entire 169 days of operation the F1F2 filter series received a total of 1.93 ± 0.008 g DRP kg⁻¹ EAF slag (0.791 kg) and retained 1.18 ± 0.09 g DRP kg⁻¹ EAF slag (0.489 kg) resulting in a DRP removal efficiency of 63%. The use of the series filter design improved the DRP removal efficiency by 35% (Table 1).

The amount of TP added to filter F1 during the second feeding cycle was 2.24 ± 0.009 g TP kg⁻¹ EAF slag (0.920 kg total), with the filter retaining 0.799 ± 0.253 g TP kg⁻¹ EAF slag (0.329 kg total), resulting in a cumulative TP removal efficiency of 11% (Figure 2F). Filter F2 received 1.46 ± 0.309 g TP kg⁻¹ EAF slag (0.591 kg total) of which it retained 0.566 ± 0.42 g TP kg⁻¹ EAF slag (0.227 kg total), for a cumulative TP removal efficiency of 34%. In total, during the second feeding cycle the F1F2 filter series received 2.37 ± 0.009 g TP kg⁻¹ EAF slag (0.920 kg) and retained 1.79 ± 0.512 g TP kg⁻¹ EAF slag (0.556 kg) resulting in a cumulative TP removal efficiency of 42% (Figure 2F). As was seen with DRP, the use of series design improved TP removal efficiency by nearly 73% (Figure 3B).

During the second feeding cycle the pH of the influent ranged from 6.06 to 7.04 (average 6.57 ± 0.30). The pH of the effluent of the first filter in series (F1) ranged from 6.37 to 7.73 (average 7.02 ± 1.4) and the second filter in series (F2) effluent pH values were slightly higher, ranging from 6.83 to 8.84 (average 7.71 ± 0.56). This followed the same trend exhibited during the first feeding period (Figure 3C).

This linear mixed models analysis showed no statistically significant difference between filters F1 (the first filter in series) and F2 (the second filter in series), even though F1 retained 23% more DRP per kg of materials than did F2. The interaction between filter and feeding period also was not statistically significant, indicating that any difference between filters was similar in each period. However, there was a statistically significant difference ($p < 0.05$) between feeding periods in DRP removal. Both terms involving day of experiment were statistically significant (day within period, $p = 0.04$ and day by filter within period, $p = 0.01$), as expected, since the DRP removal performance

changes from day to day. A simplified model analyzing total DRP removal was also run using the MIXED procedure. This removes any “day” effect from the model and compares the total DRP removal performance between filters and between feeding periods. This analysis found a statistically significant difference between filters in their total DRP removal performance ($p < 0.05$). No significant difference was found between periods, nor was the filter by period interaction significant.

Due to the restriction of the available space at the University dairy farm, it was not possible to install and investigate performance of a single large filter unit against two smaller filter units installed in series. Therefore, we were unable to perform a statistical comparison of the effect of series construction *versus* a single filter on the DRP removal efficiency. The mean DRP removal rate of both filters was significantly different from zero ($p < 0.001$), indicating that both filters in series had a statistically significant effect on DRP removal efficiency.

The initiation of a resting period combined with the installation of the filters for TSS removal extended the life-span of the system by 3.25 fold (from 52 to 169 days). Moreover, exposing the filters to a prolonged resting period enabled the rejuvenation of the EAF steel slag filters' P retention capacities, which occurred in all filters (Figures 2 and 3). At the end of the first feeding cycle, the DRP and TP removal efficiencies of the first filter in series (F1) had decreased to only 9% and 6%, respectively. At the beginning of the second feeding cycle, the same filter's (F1) DRP and TP removal efficiencies had increased to 84% and 75%, respectively, an approximately 10 fold increase over the values prior to the resting period. The resting period also resulted in an increase in removal efficiency of the filter series (F1F2). The DRP and TP removal efficiencies increased 1.8 fold after the resting period, from 51% to 89% (DRP) and 52% to 89% (TP), respectively (Figure 3).

4. Discussion

The effects of solids and DRP daily mass loading rates on DRP and TP removal efficiency

TSS mass loading rates: The first feeding cycle was carried out during the winter of 2006 (January until mid March) represented a test of the EAF steel slag filters' P removal efficiency under the worst case scenario: subzero temperatures, extremely high effluent strength (organic matter $\sim 6,000$ g BOD5 m^{-3} , total suspended solids $\sim 3,400$ g TSS m^{-3}). By comparison, the U.S. EPA [7] reported that to achieve P removal, a wastewater treatment systems influent TSS concentration should not exceed 100 g m^{-3} . Apart from being fed at an over 30 fold higher TSS concentration, the HLR employed in this study (123 $cm\ day^{-1}$ HLR) were 22.4 fold higher than the recommend rates for similar on-site treatment systems in North America [28]. Given this extreme feeding regime, it is not surprising that the filters became clogged after only 52 days of operation (Figure 3).

The clogging of a filters substrate material caused by development of biofilm has been identified as one of the biggest operational problems in similar on-site wastewater treatment systems, such as constructed wetlands and rock and sand filters [29-31]. Langergraber *et al.* [29] stated that developing operational methods for the treatment of high HLRs in constructed wetlands without clogging of the systems represents one of the most important unsolved problems in this area of research.

To investigate the effects of TSS and DRP daily mass loading rates, alternate feeding and resting regimes and in-series design on the removal efficiencies of DRP and TP, data from the present study was compared to results reported by Weber *et al.* [19]. Weber *et al.* [19] investigated EAF steel slag

filters' treatment performance of dairy effluent combined with stormwater, and with and without the use of a constructed wetland pretreatment unit. Consequently, the TSS loading rates reported for the waste effluent with constructed wetland pretreatment were 11.9 fold lower than without the pretreatment (0.024 and 0.285 g TSS g kg⁻¹ EAF slag day⁻¹ respectively, Table 1). In that study, the filters fed at the higher TSS loading rates became clogged after 180 days in operation while filters fed at a lower rate (0.024 g TSS g kg⁻¹ EAF slag day⁻¹) were in operation for 270 days before their efficiency dropped to below 60%, and went on to have a total life-span of 499 days before they became fully saturated with P [16]. Similarly the filters in this study, which were fed at a 3.3 fold higher TSS loading rate (1.08 ± 0.004 g TSS g kg⁻¹ EAF slag day⁻¹), had a 3.4 fold shorter life-span (52 days) in comparison to the filters fed without wetland pretreatment as described by Weber *et al.* [19] (Table 1).

Further comparison of the TSS influent mass loading rates with the filters' life-span in each study revealed that EAF steel slag filters will become clogged with biofilm when they have been fed approximately 50 g TSS kg⁻¹ EAF steel slag (Table 1).

DRP mass loading rates: A comparison of the DRP daily mass loading rates between the present study and that of Weber *et al.* [19] shows that unlike the TSS loading rates, they were very similar (Table 1). This suggests therefore, that the TSS loading rate, not the DRP loading rate is the predominant parameter affecting the filters' DRP treatment efficiency. The filter F1, which was fed at 3.3 fold higher TSS loading rate, achieved a DRP removal efficiency of 38%, being 1.9 fold lower than the DRP efficiency of 72% achieved by filters fed at the lower TSS loading rates (Table 1). Similarly, Weber *et al.* [19] reported that there was not a significant difference in the DRP loading rates and removal efficiencies between filters fed with wastewater that had been pretreated by a constructed wetland (75%) *versus* untreated effluent (72%) (Table 1). However, the filters fed with pretreated effluent (at lower TSS loading rates) had a 2.2 fold longer life-span than filters fed without a constructed wetland pretreatment [18,19].

The effects of in-series design and the use of alternating feeding and resting periods

Drizo *et al.* [18] recently showed EAF steel slag material has the ability to rejuvenate its P removal efficiency. They also found that the implementation of a resting period when their DRP removal efficiency decreases below the design objective results in the largest increase in DRP removal efficiency and significantly prolongs the filters' operational life-span. However the effect of altering the feeding and resting periods on filters' TSS removal efficiency has not been previously investigated.

The results from this study show that after resting period of over 12 weeks the first filter in series (F1) retained an additional 4.59 ± 4.96 g TSS kg⁻¹ EAF slag, which is much lower than the amount retained during the first feeding cycle (23.34 ± 0.004 g TSS kg⁻¹ EAF slag) (Figure 2A, 2D). Similarly, the quantities of TSS retained by the filter series during the second feeding cycle were much lower than in the first feeding period (11.94 and 33.18 g TSS kg⁻¹ EAF slag respectively) (Figure 2B, 2E). Therefore with TSS, the incorporation of a resting period in the design of EAF steel slag filters does not have any effect on their treatment efficiency and system longevity. The increase in treatment efficiency and longevity of the filters observed during the second feeding cycle can also be attributed to two other operational factors. The first is that the TSS daily mass loading rates were 4.5 fold lower (0.24 ± 0.0001 g kg⁻¹ EAF slag day⁻¹) when compared to the first feeding period (1.08 ± 0.004 g kg⁻¹

EAF slag day⁻¹) due to the TSS filters that had been installed and the effect of washing the EAF steel slag between feeding cycles.

During the resting period, because the filters were clogged, the EAF steel slag material had to be removed from the filters. The formation of biofilm had caused the slag material to solidify, therefore the large clumps had to be broken up and the material was then washed with tap water to remove some of the solids. It has been shown that DRP and TP sorbed to the EAF steel slag material does not readily desorb to surface runoff, therefore this action would not have significantly affected the P sorption capacity of the slag material in this study [25]. The material was then returned to the respective filters, and left to rest.

The resting period increased the first filter in series (F1) DRP capacity by 57%, which is higher than the 28% increase that was observed after a 12 week resting period in EAF steel slag filters also fed by a dairy effluent until reaching their P saturation point [18]. The resting period had an even greater effect on the filters' TP retention capacity, which increased 74% (from 0.29 ± 0.01 g TP kg⁻¹ EAF slag at the end of the first feeding cycle to 1.09 ± 0.24 g TP kg⁻¹ EAF slag after the second feeding cycle).

Overall, the incorporation of a second filter unit into in-series design increased DRP and TP removal efficiencies by 44% and 42%, respectively, in the first feeding period and by 29% and 73% in the second feeding period, contributing significantly to the filters' treatment performances (Figures 2 and 3). This has been expected given that it has been well established that multiple and hybrid CW systems have fewer problems with preferential flows and thus generally exhibit better performances in pollutant reduction when compared to that of single cell units [32]. One of the prime advantages of a multi-stage filter system over a similarly sized single filter is that with time as clogging occurs in the filter system and biofilm develops over the slag particles, the first filter in series can be drained and left to rest (in a case of EAF steel slag material) or removed (if other materials are used) [18,33]. The remaining filter unit or units, which will have had significantly less TSS loading, can then become the primary P treatment filters. Therefore, the life-span of a filter system could be prolonged by draining and resting individual treatment cells while the system as a whole continues to operate. On the contrary, if the system consists of just one larger single cell, once the inlet zone of the filter becomes clogged with solid material, the entire system would have to be switched off while the filter material is replaced. Additionally, in this research we demonstrated that in real on-farm applications of EAF steel slag filters, with basic solid separation techniques the TSS loads can be dramatically reduced. As stated above, with the use of a metal screen around the pumps feeding the filters and a geotextile material placed around the pump's intake, the mass loading of TSS in the second period was reduced by 3.7 fold in comparison to the first period. However, during the second period, the TSS concentration in the influent was actually 2 fold higher ($6,968.99$ mg L⁻¹) than in the first period, and the solid separation techniques employed was able to reduce this by 88%.

EAF steel slag filters treatment efficiency under sub-zero temperatures

During much of the first feeding cycle the EAF steel slag filters were operated under subzero temperatures. Many steps were made to reduce the incidence of freezing in the filter system, and the few times that freezing did occur it was mostly in the connecting piping between filters, which were more exposed. Some freezing did occur in the actual filters themselves, however this was the result of the clogging causing shortcutting of the flow path, creating areas of stagnant flow vulnerable to the

effects of freezing. The observed removal efficiency of the EAF steel slag system (41% for the first filter, F1 and 63% for the in-series system, F1F2) is impressive considering that P retention capacity of EAF steel slag filters is decreased at such low temperatures [34,35]. This demonstrates that with simple design modifications to provide insulation and protection from cold, an EAF steel slag filter system can function effectively in northern climates.

EAF steel slag filters effects on pH

The results from this research provide further evidence that when fed at the HRT of 24 h or less, EAF steel slag filter's effluent pH is within the range of US water quality regulations [36]. Moreover, the results also show that both DRP and TP removal efficiencies are positively correlated to filter's effluent pH values, which is consistent with the previous findings as presented in Bird *et al.* [34], Drizo *et al.* [18], and Weber *et al.* [19].

5. Conclusions

The results described here enhances our knowledge of EAF steel slag filters and further demonstrates their potential for the treatment of milk parlor effluents. We showed that at hydraulic retention time of 18 h filters are able to achieve high DRP and TP removal efficiencies while maintaining pH levels of the effluent below 8, thus in compliance with the environmental regulations. Furthermore, we determined average hydraulic loading (q), TSS and DRP mass loading rates to achieve >75% DRP removal efficiencies all year around (including during subzero temperatures). We demonstrated that TSS daily mass loading rates represent the most limiting factor to the EAF steel slag filters treatment efficiency and longevity. TSS daily loading should not exceed $0.020 \text{ g kg}^{-1} \text{ EAF steel slag day}^{-1}$ ($50 \text{ g TSS m}^{-2} \text{ filter day}^{-1}$) in order to prevent clogging and ensure long term functioning of the filter system.

Implementation of a resting period in a filter's design increases the total DRP and TP retention capacities through rejuvenation of the EAF steel slag material, resulting in higher pollutant treatment performances, and a significantly increased system life-span. The EAF steel slag filter systems P treatment performances were further enhanced by incorporation of an in-series design of multiple treatment units. The filters still showed impressive DRP removal rates when subjected to sub-zero temperatures, showing that they are an appropriate treatment technology for areas in cold climates.

Based on this research, we recommend that alternate feeding and resting cycles and the use of multiple filter units arranged in series should be integrated into the design of EAF steel slag filters used for the treatment of highly concentrated agricultural effluents in cold climates.

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