WATER RESEARCH 44 (2010) 4077–4086

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Evaluating the efficiency and temporal variation of pilot-scale constructed wetlands and steel slag phosphorus removing filters for treating dairy wastewater

Martin S. Lee[a,*], Aleksandra Drizo[b], Donna M. Rizzo[a], Greg Druschel[c], Nancy Hayden[a], Eamon Twohig[b]

[a] College of Engineering and Mathematical Sciences, University of Vermont, 33 Colchester Avenue, Burlington, VT 05405, USA
[b] Department of Plant and Soil Science, University of Vermont, 105 Carrigan Drive, Burlington, VT 05405, USA
[c] Department of Geology, University of Vermont, 180 Colchester Avenue, Burlington, VT 05405, USA

ARTICLE INFO

Article history:
Received 22 November 2009
Received in revised form
1 April 2010
Accepted 13 May 2010
Available online 24 May 2010

Keywords:
Agricultural livestock wastewater
Hybrid systems
Slag filter systems
Pulse flow
Continuous flow
Seasonal variation

ABSTRACT

The performance and temporal variation of three hybrid and three integrated, saturated flow, pilot-scale constructed wetlands (CWs) were tested for treating dairy farm effluent. The three hybrid systems each consisted of two CWs in-series, with horizontal and vertical flow. Integrated systems consisted of a CW (horizontal and vertical flow) followed by a steel slag filter for removing phosphorus. Time series temporal semivariogram analyses of measured water parameters illustrated different treatment efficiencies existed over the course of one season. As a result, data were then divided into separate time period groups and CW systems were compared using ANOVA for parameter measurements within each distinct time period group. Both hybrid and integrated CWs were efficient in removing organics; however, hybrid systems had significantly higher performance ($p < 0.05$) during peak vegetation growth. Compared to hybrid CWs, integrated CWs achieved significantly higher DRP reduction ($p < 0.05$) throughout the period of investigation and higher ammonia reduction ($p < 0.05$) in integrated CWs was observed in late summer. Geochemical modeling demonstrates hydroxyapatite and vivianite minerals forming on steel slag likely control the fate of phosphate ions given the reducing conditions prevalent in the system. The model also demonstrates how the wastewater:slag ratio can be adjusted to maximize phosphorus removal while staying at a near-neutral pH.

1. Introduction

Research for improving constructed wetland (CW) nutrient removal capabilities is motivated by the increasingly stringent worldwide water quality regulations and the often varying treatment performance of existing CWs for treating nutrient rich livestock wastewater (Hunt and Poach, 2001). Treating livestock wastewater with CWs has become recognized as a viable technology; however, data on systems treating dairy wastewater, especially in temperate climates, are fairly limited (e.g. Knight et al., 2000; Newman et al., 2000; Schaafsma et al., 2000). While CWs are generally effective at removing organic matter and total suspended solids (TSS), nutrient removal needs to be improved (Hunt and Poach, 2001) due to the effects of eutrophication (Schindler, 1977).

Constructed wetlands have relatively low start-up costs and less maintenance requirements compared to other types of wastewater treatment systems making them attractive for

---

* *Corresponding author*. Tel.: +1 201 788 3583; fax: +1 802 656 4656.
E-mail address: martin.lee84@gmail.com (M.S. Lee).

0043-1354/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2010.05.020

small and medium-scale farms (Knight et al., 2000). However, their limited ability to remove nutrients, in particular phosphorus (P), from highly concentrated agricultural wastewater has created concerns over the applicability and longevity of these systems.

As a consequence, CW design has evolved to accommodate the various wastewater treatment needs. Over the past decade, hybrid CW systems became well-established systems efficient at removing organic matter, suspended solids, and nitrogen species when properly designed (Vymazal, 2007). To improve P removal, various natural and industrial waste materials containing Ca, Fe, or Al oxides have been tested (e.g. Mann, 1997; Arias et al., 2001; Westholm, 2006; Drizo et al., 2008). Of these, steel slag materials showed great efficiency in P reduction from municipal, domestic and agricultural effluents (Westholm, 2006; Drizo et al., 2008; Vohla et al., 2009). The use of an electric arc furnace (EAF) steel slag column-scale filter as an add-on unit to improve CW P removal performance in dairy effluent treatment was recently investigated by Weber et al. (2007) and Drizo et al. (2008). They showed that EAF steel slag filters achieved an average of 70% dissolved reactive phosphorus (DRP) reduction over a period of 400 days, resulting in P retention capacity of 2.15 g DRP/kg slag (Drizo et al., 2008). However, the mechanisms involved in P removal via these systems, especially when used to treat highly concentrated dairy effluents, are not well understood. Previous research by Drizo et al. (2006) using laboratory-made solutions suggested that precipitation with Ca oxides in a form of hydroxyapatite represents the principal P removal mechanisms via EAF steel slag. However, more research is needed to elucidate P removal mechanisms in EAF steel slag filters, especially at higher (5 days) hydraulic retention times.

The primary goal of this research was to investigate the most appropriate CW design for treating highly concentrated dairy effluent. The specific objectives were to (i) investigate pollutant removal efficiencies of the four pilot-scale CW designs when fed under different hydraulic regime (pulse and continuous flow); (ii) examine temporal variation in the systems performances using time series analyses; and (iii) use geochemical modeling to examine P removal mechanisms in EAF steel slag and to illustrate the importance of properly sizing slag filters.

This research moves forward the study of CWs integrated with slag P filters (integrated CW systems) by analyzing (1) treatment differences between the pilot-scale hybrid and integrated CW systems while (2) considering temporal variation. We compare the differences in DRP, BOD_5, TSS and NH_4^+ removal in these systems and discuss the pros and cons associated with both integrated and hybrid CWs for treating dairy farm wastewater.

2. Methods and materials

2.1. Experimental setup

The CW pilot-scale systems were built at the University of Vermont Constructed Wetlands Research Center (CWRC) located at the Paul Miller Dairy Farm in Burlington, Vermont USA. The influent wastewater was a combination of feedlot runoff and milk parlor wash water. The feedlot runoff has an area of approximately 1750 m^2; the concentration and flow from this wastewater source depended mostly on precipitation. Milk parlor and milk house wastewater is generated during two or three events each day: two milkings and one washing event.

The CW pilot-scale systems were constructed to treat the dairy wastewater, consisting of the mixed barnyard runoff and milk house wash water. The pilot-scale systems (Fig. 1) were classified as either hybrid or integrated systems. The three hybrid CW systems (Fig. 1a) combine two CWs in-series. The two integrated CW systems (Fig. 1b) use a combination of a CW followed by an EAF steel slag filter for removing P. Within the hybrid and integrated systems, different flow regimes were also implemented. Two of the hybrid systems consisted of a vertical flow (VF) CW, followed by a subsurface horizontal flow (HF) CW; while the third hybrid system consisted of two subsurface HF flow CWs connected in-series (Fig. 1). Two of the integrated systems consisted of a VF CW, followed by a subsurface HF steel slag filter, and the third integrated system consisted of a subsurface HF CW followed by a steel slag filter (Fig. 1b). Overall, there were four individual VF CWs and two HF CWs constructed as the first treatment units and three HF CWs and three HF EAF steel slag filters constructed as the second treatment units (Fig. 1).

Wastewater samples were collected weekly at the influent of the first in-series CWs (CWs 1–6), and at the outlet of all twelve CWs. The 13 sampling locations are identified by solid circles in Fig. 1.

All CWs had the same dimensions (length, width, and height of 1.7 m, 1.1 m, and 0.5 m, respectively). Nine of the CWs (CWs 1–9) were packed with gravel (2.5–5 cm diameter) which was calculated to have a porosity of approximately 40%. The top 3 cm of these CWs were layered with compost and planted with river bulrush (*Schoenoplectus fluviatilis*). The three slag filters (CWs 10–12) designed for P removal were filled with EAF steel slag from Quebec, Canada which packs to a measured porosity of 44 ± 2% error (Drizo et al., 2006).

The inlet of the VF CWs is centrally located along the top wall opposite the centrally located outlet sampling pipe (Fig. 1c). The VF CW wastewater was maintained at a constant head, approximately 3 cm below the gravel surface, allowing downward vertical flow to the perforated outlet pipes along the bottom of the wetland (Fig. 1c). The inlet pipes for the HF CWs provided an even distribution of influent across the width of the cell (Fig. 1f). The CW flows were modeled using the program SEEP/W° (GEO-SLOPE©, 1995–2010), which is a finite element analysis program designed to model a variety of groundwater flow environments. The ideal flow (modeled) patterns through the VF and HF CWs are presented in Fig. 1e and d, respectively.

The CWs were operated from August to December in 2007, and from May to September in 2008 for a total of 30 weeks. During the 2007 operation, the influent dairy wastewater was pulsed daily with a hydraulic loading rate of 1.9 cm/day to the wetland cells, as this more closely resembles flow from milk house operations. In 2008, the system was changed to a continuous flow, with a hydraulic loading rate of 3.9 cm/day, using a constant head reservoir to conduct tracer studies and to investigate hydraulic characteristics of the systems. Constant head was maintained using a pump triggered by float switches connected to an electromagnetic relay. The CW influent flow rate was calibrated with needle valves.

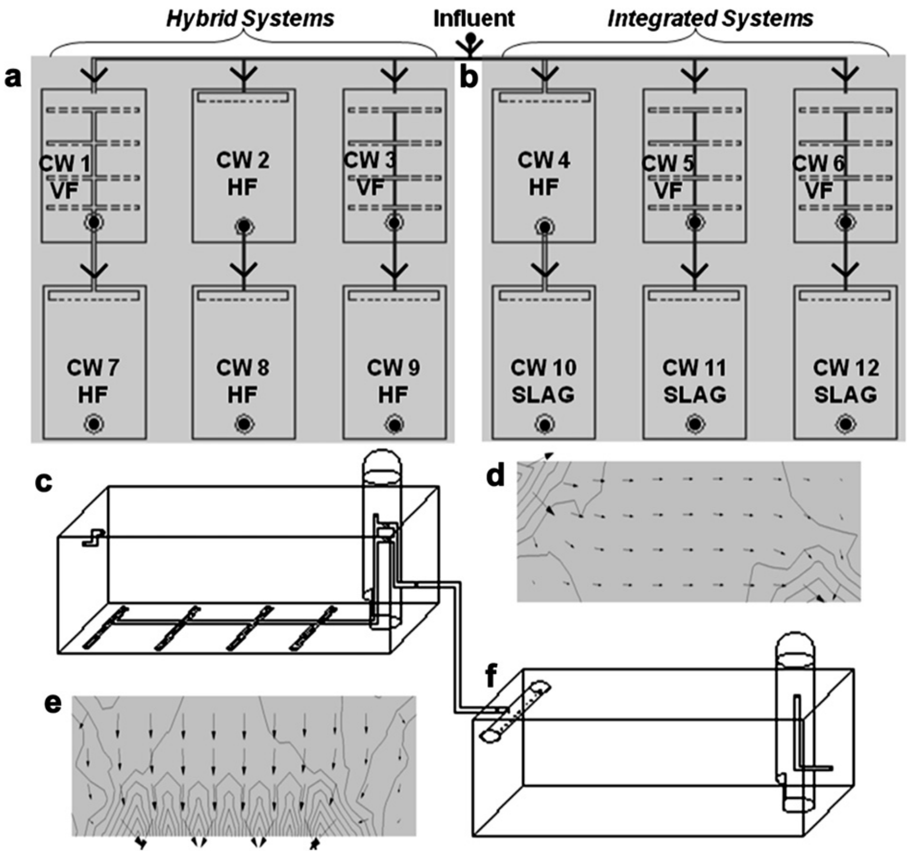

Fig. 1 – Experimental layout of the 6 CWs of the (a) hybrid systems in plan view, and (b) integrated systems in plan view. (c) Cross-section of a VF CW showing the inlet pipe (upper left) and the outlet pipe (bottom), (d) cross-section of the SEEP/W° modeled flow through a HF CW, (e) cross-section of the SEEP/W° modeled flow through a VF CW, and (f) the plumbing for a HF CW.

2.2. *Constructed wetland hydraulics*

2.2.1. *Nominal hydraulic retention time*

Although the CW influent flow rate was controlled and known in this research, the outflow was influenced by rainfall and evapotranspiration. The outlet flows were not measured. An adjusted flow rate for the effluent of the CWs was calculated using the measured inflow, measured precipitation (PT) data, and calculated evapotranspiration (ET) from the Penman method (Ward and Trimble, 2004). The calculated nominal hydraulic retention time (nHRT) for each CW with the daily pulse flows associated with the 2007 operating season was ~5 days (10.4 days ± 21% error for the 2 CWs in-series); while the continuous flow of 2008 resulted in a nHRT of ~2.5 days for each CW (5.6 days ± 16% error for the 2 CWs in-series). Two bromide tracer studies, performed on different dates during the 2008 continuous flow operation, indicated residence times falling within the range of calculated nHRTs (Lee, 2009).

2.3. *Water quality monitoring*

During the 2007 operation period, all water samples were collected weekly from the influent wastewater sampling port and the 12 CW outlets. The 5-day biochemical oxygen demand (BOD_5) and total suspended solids (TSS) concentrations were determined according to the standard methods (APHA, 1989). Ammonium (NH_4^+) was analyzed using a flow through Lachat (Quik Chem FIA+ 8000 series) (APHA, 1989). Dissolved reactive phosphorus (DRP) analysis was performed using the stannous chloride method (APHA, 1989). Temperature and pH were recorded *in situ* using a field pH probe (Fisher Scientific Accumet waterproof AP71) at the locations where samples were collected (Fig. 1). Additional samples were collected in 5 ml bottles with no headspace for voltammetric lab analysis of redox reactive species (O_2, Fe^{2+}, Fe^{3+}, Mn^{2+}, H_2S) using a hanging drop mercury electrode (a Princeton Applied Research Model 301 HDME with an Analytical Instrument Systems DLK-100A potentiostat). The samples were analyzed approximately once a month for Total P, Ca^{2+}, and metals using the persulfate digestion method (APHA, 1989), and measured using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Perkin Elmer 3000 DV). The same sampling and analysis techniques were used over the 2008 field season. In addition, dissolved oxygen (DO) was also measured *in situ* at the sampling locations using a field DO meter (HACH LDO®).

2.4. *Data analyses*

2.4.1. *Constructed wetland treatment efficiency*

The efficiency of the CWs was calculated as a percent reduction of the adjusted mass flux rate from the inlet to the outlet of a CW system. Table 1 shows the efficiencies of the CWs for

Table 1 – Average percent reduction of measured parameters.

Category	CWs included	BOD_5 [%]	DRP [%]	TSS [%]	Ammonia [%]
Period 1					
Upper VF	(Outlets of CWs 1, 3, 5, and 6)	80	59	42	52
Upper HF	(Outlets of CWs 2 and 4)	77	65	87	48
VF–HF	(Outlets of CWs 7 and 9)	89	68	94	61
HF–HF	(Outlet of CW 8)	86	75	95	64
VF–slag	(Outlets of CWs 11 and 12)	90	>99	93	68
HF–slag	(Outlet of CW 10)	83	>99	93	62
Period 2					
Upper VF	(Outlets of CWs 1, 3, 5, and 6)	78	56	81	
Upper HF	(Outlets of CWs 2 and 4)	73	58	87	
VF–HF	(Outlets of CWs 7 and 9)	87	67	92	
HF–HF	(Outlet of CW 8)	82	68	92	
VF–slag	(Outlets of CWs 11 and 12)	83	>99	92	
HF–slag	(Outlet of CW 10)	83	>99	83	
Period 3					
Upper VF	(Outlets of CWs 1, 3, 5, and 6)	91	50	95	53
Upper HF	(Outlets of CWs 2 and 4)	91	55	94	54
VF–HF	(Outlets of CWs 7 and 9)	95	63	97	67
HF–HF	(Outlet of CW 8)	96	63	97	63
VF–slag	(Outlets of CWs 11 and 12)	92	>99	97	79
HF–slag	(Outlet of CW 10)	92	>99	95	73

the fall of 2007 (Period 1), early summer 2008 (Period 2), and late summer 2008 (Period 3). The efficiencies of the 6 CW categories (see Table 1 for category labels) were calculated for the duration of the sampling period using a 15-day, moving window average. Given the nHRTs, samples collected at the outlets do not correspond to the influent samples collected on the same day. To account for this, treatment efficiency was calculated using a 15-day period to capture an average representative mass flux rate for a particular day.

2.4.2. *Time series analysis*

A time series analysis using temporal semivariograms was performed to determine the extent of autocorrelation for measured time series data. It also allowed seasonal effects to be quantified. A semivariogram is a basic geostatistical tool that is useful in describing temporal trends in environmental data sets (Goovaerts, 1998). Temporal semivariograms were created for every measured parameter for each categorized CW system using methodology adapted from Isaaks and Srivastava (1989). Semivariance is a type of non-normalized correlation coefficient, and semivariograms were created for each parameter in this study. For example, BOD_5 was measured at one sampling location at distinct time intervals over the course of the CW operation period and a semivariogram was created from the data. This time series analysis showed distinct differences in the CW's temporal correlation and performance over the operation period, and as a result, the data were divided into these significantly different time periods (Fall 2007, Early Summer 2008, and Late Summer 2008) before conducting an ANOVA.

2.4.3. *ANOVA*

One-way ANOVA was performed using SAS statistical software (SAS 9.1, 2002–2003) to determine if significant differences exist between the treatment systems. The categories used in the one-way ANOVA combined discrete sampling locations into the minimum number of unique CW systems (e.g. Table 1). CW systems were then allocated into significantly different groups using Fisher's least significant difference multiple comparison test.

2.5. *Geochemical modeling*

The Geochemist's Workbench® modeling software (Version 6.0.3, thermo.dat database) was utilized to simulate a batch reaction of the chemical oxide constituents of slag mixed with the wastewater chemistry from the outlet of CW 6. The EAF slag material contains the chemical oxides known to stimulate P precipitation; Fe_2O_3 (35%), CaO (30%), and Al_2O_3 (5%) (Drizo et al., 2006). This model is an equilibrium model and does not consider kinetics. Sorption reactions and phosphate mineralization occurs at a much faster rate than flow through the slag filters so only thermodynamics models were considered. The assumption of equilibrium may be reasonable in the slag filters because it is known that the primary slag oxides (Fe_2O_3 and CaO) immobilize P from solution quickly (e.g. Inskeep and Silvertooth, 1988; Spiteri et al., 2007) and are thus unlikely to be kinetically controlled. The simulation is analogous to a titration of slag material into P rich wastewater; in the model, EAF steel slag oxides were added incrementally to the simulated wastewater solution. The software calculates the chemical speciation and mineral precipitation reactions occurring in the wastewater using values of chemical concentrations, temperature, redox state, and pH measured at the effluent of CW 6.

3. Results and discussion

3.1. *Constructed wetland treatment efficiency*

Because of long retention times, one of the difficulties with CWs is that outlet samples do not correspond to the influent wastewater when sampling is done at the same time, but rather the outlet sample corresponds to the inlet sample of a few days prior. Moreover, a direct comparison of inlet to outlet concentrations, over short-time periods, is further complicated by the variability of ecological zones within the wetland. Travel of the wastewater may include multiple pathways with different hydraulic retention times and degradation rates (Kadlec, 2000). To avoid the stochastic variability associated with inlet and outlet measurements, a long-term sampling period is often used and provides mean values that are more representative of the average behavior of a distinct CW (Kadlec, 2000). The results of this experiment (Fig. 2) are an example of stochastic variability. Fig. 2 shows the mass flux rates of BOD_5, DRP, and TSS over the course of the 2007 and 2008 operation periods; a log scale is necessary to accommodate these highly variable values. Concentrations varied during the sampling periods, but the average influent concentrations for

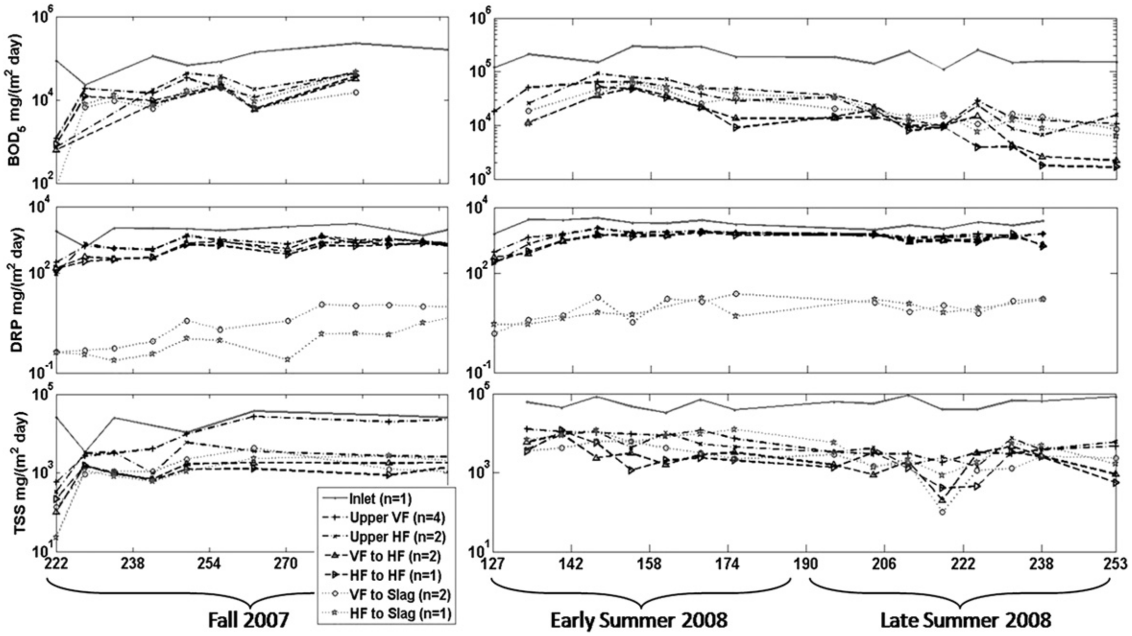

Fig. 2 – Semi-log plots showing the difference for the wastewater influent and effluent mass flux rates for the six CW systems over the 2007 and 2008 operating period. The *x*-axis is in units of year days.

BOD_5, DRP, TSS, and NH_4^+ were: 2,500 ± 33% mg/l, 46 ± 24% mg/l, 740 ± 33% mg/l, and 260 ± 38% mg/l, respectively.

During the 2007 operation period (pulse feeding), both VF–VF and HF–HF achieved high treatment efficiencies in BOD_5 (89 and 86%) and TSS (94 and 95%), respectively. HF–HF exhibited higher DRP (75%) and NH_4^+ (64%) removal efficiencies when compared to the VF–HF systems which removed 68% (DRP) and 64% (NH_4^+), however, these differences were not significant (Table 1). Integrated systems achieved the highest DRP efficiency (nearly 100%), being consistently below 0.5 mg/L (Table 1). Integrated VF–slag systems also achieved high performances in NH_4^+ (68%) and BOD_5 (90%) when compared to HF–slag and hybrid systems (Table 1).

The CWs performance during the summer of 2008 was marked by two distinct periods of different removal efficiencies. These changes were apparent in the treatment efficiencies of BOD_5 and TSS, and were quantified using a time series analysis. The removal efficiency of DRP by the slag systems showed nearly 100% efficiency during both periods (Table 1). It is notable that the CWs performance during the summer of 2008 was marked by two distinct periods of different removal efficiencies. These changes were apparent in the treatment efficiencies of BOD_5 and TSS, and were quantified using a time series analysis.

3.1.1. *Temporal variation*

Temperature and plant biomass changed from early summer to late summer and these factors may have directly influenced CW treatment performance. It is difficult to quantify what single factors affect change in wetland treatment performance due to the simultaneous interaction of many chemical, physical, and biological processes at work (Kadlec, 1999), however, quantifying temporal differences is important for subsequent analysis. Temporal semivariogram analyses were performed for all investigated pollutants and on all systems, to quantify the seasonal (temporal) variation on the systems' performances. A time series analysis is useful for determining the temporal changes that occur in data and justifies splitting up the data before it is analyzed. A time series analysis performed on the 2007 and 2008 CW data showed the extent to which the discrete CW systems were autocorrelated in time. A change in treatment efficiency over time was detected for the 2008 operating period for BOD_5 and TSS in all systems, and in 2007 there were no distinguished trends. An example semivariogram for BOD_5, measured in 2008 at the outlet of the upper HF CWs, is shown in Fig. 3b. It is representative of the BOD_5 semivariograms for each of the other CW categories in 2008. Interestingly the influent semivariogram did not show a detectable change over the course of the season (Fig. 3a). The increasing temporal semivariance indicates strong autocorrelation and a difference in the treatment performance over the course of the 2008 operation period. Note that samples collected between 7 and 14 days apart are more correlated than measurements separated by 14 days or more (Fig. 3b). After 14 days, the semivariance plateaus for an additional 21 days. After 35 days, the data again become autocorrelated, and does not level off until approximately 60 days. The semivariograms have wide 95% confidence bands (Fig. 3), and many of the semivariograms had a discontinuity at the origin, called the nugget effect (Goovaerts, 1998).

The time series analysis found that TSS, and temperature also have a second time period where semivariance increases (indicative of autocorrelation), with the second increase occurring anywhere between 40 and 60 days of separation indicating a difference in CW performance between the beginning and end of the summer in 2008. The statistical significance was further validated by averaging the early summer measured parameters (BOD_5 and TSS) and comparing

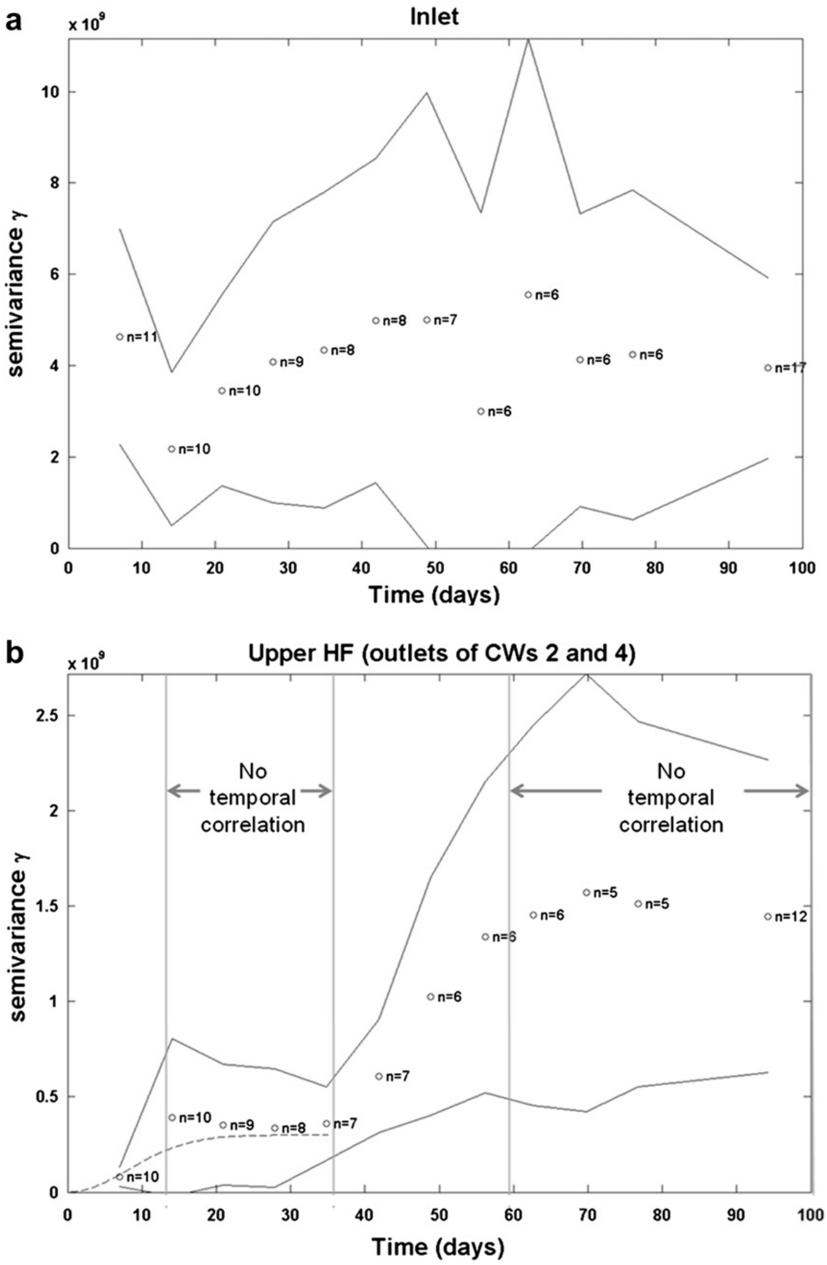

Fig. 3 – Temporal semivariograms for 2008 BOD_5 mass flux rates at the (a) the influent, and (b) outlet of the upper HF CWs. The solid lines represent the 95% confidence intervals, the dotted line is a best fit model, and the circles represent the binned semivariances with a corresponding number of data points used to find the average semivariance in the bin.

to an average of late summer; there was a significant difference ($p < 0.0001$). Therefore, the 2008 data (Fig. 2) were divided into early summer (May 7th–June 25t^{h}) and late summer (July 15th–September 10th) in order to compare the CW systems' treatment performances using ANOVA.

Temperature, BOD_5, and TSS had two distinct periods in 2008 when the CW systems operated differently. Time series analysis showed no detectible difference in the influent mass flux rate during 2008, so it was inferred that the differences in mass flux of BOD_5 and TSS at the CW outlets were due to changes in performance of the CWs. The CWs experienced an increased removal efficiency of BOD_5 and TSS during late summer of 2008 (Table 1). Although plant biomass was not measured in this research, there was a notable change in the plant density from early to late summer of 2008. In early summer the plants were sparse and less than 0.25 m tall, and by late summer the plants covered the entire CW area and were greater than 1.0 meter tall.

3.1.2. *ANOVA results*

In this research, data from 2007 were averaged over the operation period to provide an adequate sample size for performing a one-way ANOVA. An underlying assumption of ANOVA (and most parametric statistical procedures) is that the data are independent. However, the time series analysis showed the 2008 data to be autocorrelated over a time period

Table 2 – BOD_5 (mg/(m^2 day)) for Fisher's LSD multiple comparisons test, late summer 2008.

LSD grouping		Mean	Percent variation	N	Location
	A	173,491	±29	8	Inlet
	B	17,104	±51	8	Upper VF (outlets of CWs 1, 3, 5, and 6)
	B	16,463	±63	8	Upper HF (outlets of CWs 2 and 4)
	B	14,716	±27	8	VF–slag (outlets of CWs 11 and 12)
C	B	14,439	±58	8	HF–slag (outlet of CW 10)
C	D	8994	±59	8	VF–HF (outlets of CWs 7 and 9)
	D	7875	±83	8	HF–HF (outlet of CW 8)

of 14 days and therefore not completely independent over the summer operation periods. As a result, the 2008 data were divided into two periods as determined by the time series analysis: early and late summer. The number of data points for each period was adequate for an ANOVA.

ANOVA for 2007 and 2008 periods showed significant differences ($p < 0.05$) in all of the measured parameters for the different sampling periods. As expected, the influent BOD_5, DRP, TSS, and NH_4^+ mass flux rates were significantly different from the effluent of all CW categories (listed in Table 1). DRP mass flux from the integrated CW systems effluent was found to be significantly lower ($p < 0.05$) than the DRP mass flux of all other CW categories, which was expected due to steel slag's high affinity for P.

ANOVA results of the treatment for BOD_5, DRP, TSS, and NH_4^+ removal efficiencies for all of the other CW categories were more complex. Comparisons of the four measured parameters for each CW category are shown in Tables 2–5. For example, in late summer of 2008 BOD_5 mass flux was found to be significantly different for the hybrid CWs (VF–HF and HF–HF) as compared to the upper VF and upper HF systems (Table 2). It is clear that the hybrid systems, with a two-fold higher retention time, would achieve more BOD_5 removal as BOD_5 kinetics are commonly modeled with a first-order reduction model (Davis and Cornwell, 1998; Kadlec and Knight, 1996). The VF–slag systems did not remove as much BOD_5 as the HF–HF system in late summer of 2008 ($p < 0.05$). It has been observed that slag does not substantially reduce organic matter from wastewater (Drizo et al., 2002); but in this study, slag did remove some BOD_5. Slag contributed as much as 10% of BOD_5 removal (Table 1: Fall 2007 and Early Summer 2008) and ranged to as little as 1% of BOD_5 removal (Table 1: Late summer 2008). In contrast, the CWs that were second in-series consistently removed 9% of BOD_5 in fall of 2007 and early summer of 2008, and the lowest percent removal of 4% occurred in late summer of 2008 (Table 1). It is apparent that most BOD_5 removal occurs within CWs that are first in-series.

Table 3 – TSS (mg/(m^2 day)) for Fisher's LSD multiple comparisons test, Fall 2007.

LSD grouping	Mean	Percent variation	N	Location
A	22,307	±109	7	Inlet
B	11,332	±93	8	Upper VF (outlets of CWs 1, 3, 5, and 6)
C	2803	±60	8	Upper HF (outlets of CWs 2 and 4)
C	1501	±84	8	VF–slag (outlets of CWs 11 and 12)
C	1340	±69	8	HF–slag (outlet of CW 10)
C	1296	±50	8	VF–HF (outlets of CWs 7 and 9)
C	1027	±43	8	HF–HF (outlet of CW 8)

Apart from changes in the flow regime between the 2007 and 2008 sampling periods, differences in performance may have been affected by the higher temperatures and vegetation growth in 2008. The 2007 operation period lasted from August to December, while the 2008 CW operating period was carried out over the course of the growing season (May–September). It is well established that temperature plays an important role in CW treatment performances (Kadlec and Knight, 1996; Kadlec, 1999). The heterotrophic bacteria responsible for organic consumption are most likely microorganisms with low to midrange temperature optima (Madigan and Martinko, 2006). Consistent with this idea, BOD_5 rate constants are considered to increase with temperature, for applications of wastewater treatment (Davis and Cornwell, 1998).

Redox analysis of the CW wastewater indicated anoxic conditions as the 2007 and 2008 redox analysis of the influent wastewater contained dissolved sulfide. As the wastewater flowed through the CWs, the environment became less reduced. The outlet measurements generally indicated the presence of dissolved iron (II) and manganese (II) (but not dissolved sulfide), suggesting an anaerobic reducing environment typical of most CWs that are not mechanically aerated (Vymazal, 2005). Transfer of oxygen to CW water through plant roots and diffusion at the air water interface provides a limited capacity for aerobic degradation by heterotrophic bacteria in a system of high BOD_5 (Vymazal, 2005). Without air diffusion pumps, improved aerobic conditions could be achieved by utilizing vertical flow CWs where pulse flow is interspersed with periods of air filling the void space (e.g. Brix and Arias, 2005). Unsaturated VF CWs require pumps to provide a pulse flow of wastewater to the CW. Ultimately, aeration of wastewater in CWs requires the addition of pumps. It may be more economical in agricultural settings to use more land for a larger wetland to treat wastewater rather than spending money on pumps and the energy to supply them.

Total suspended solids removal was generally greater than 80% (Table 1) for all of the CW categories. During 2007, the VF CW systems had a significantly lower (Table 3) TSS removal efficiency of 46%. In 2007, the CWs operated with a pulse flow of wastewater, and this pulse flow may have introduced turbulence disturbing the sediments bound to the media in the CWs. Furthermore, compost was layered on the CWs immediately prior to operation in 2007, and this may have contributed to increased suspended solids. The outlet pipes of the VF CWs are on the bottom of the CW, so sediments settling in solution may easily flow into the outlet ports proximal to sampling locations. Suspended solids may lead to eventual

Table 4 – Ammonia (mg/(m^2 day)) for Fisher's LSD multiple comparisons test, late summer 2008.

LSD grouping		Mean	Percent variation	N	Location
	A	17,299	±30	6	Inlet
	B	8067	±19	6	Upper VF (outlets of CWs 1, 3, 5, and 6)
	B	7942	±21	6	Upper HF (outlets of CWs 2 and 4)
C	B	6201	±15	6	HF–HF (outlet of CW 8)
C	B	5796	±39	6	VF–HF (outlets of CWs 7 and 9)
C	B	5002	±46	6	HF–slag (outlet of CW 10)
C		4246	±59	6	VF–slag (outlets of CWs 11 and 12)

clogging, so outlet structures should be properly designed to prevent clogging from potentially high sediment loads in dairy wastewater.

Ammonia mass flux rates in late summer of 2008 show three multiple comparison groups (Table 4); the outlet of the integrated systems has a significantly lower mass flux rate than the upper CW systems. This significant difference was not found in 2007; and ammonia was not measured in early summer 2008. Ammonia in wastewater has been found to adsorb to calcite (Seo et al., 2008). The elevated pH (>10) that is experienced in the slag filter environment shifts the activity of ammonia species toward unionized ammonia (pK_a for ammonium is 9.24; above that pH, NH_3 is the predominant form), which may be more readily volatilized, similar to results found by Renman et al. (2009). Removal of total nitrogen cannot be calculated for this study because total nitrogen was not measured; the removal rate of ammonia is uncertain because organic forms of nitrogen were likely contributing to the concentration of ammonia in parallel to mechanisms that were removing it from solution.

In 2007, DRP effluent mass flux rates from the HF–HF system were found to be significantly lower than the DRP mass flux rates from the upper VF systems (Table 5). Two CWs in-series removing more DRP than one CW in-series seems likely, however there was no significant difference observed during the 2008 sampling periods. DRP removal may not have been significantly different between the hybrid and upper CW systems in 2008, because the capacity of the wetland media may have reached a threshold for adsorbing P. Phosphorus cannot be biodegraded or off-gassed in the same manner as nitrogen because P occurs in a sedimentary cycle rather than a gaseous cycle (Mitsch and Gosselink, 1993); and the main mechanisms of P removal in wetlands are generally attributed to P adsorption and precipitation from solution (Mitsch and Gosselink, 1993; Rustige et al., 2003; Vymazal, 2007; Pratt et al., 2007).

Table 5 – DRP (mg/(m^2 day)) for Fisher's LSD multiple comparisons test, Fall 2007.

LSD grouping		Mean	Percent variation	N	Location
	A	2005	±31	11	Inlet
	B	827	±38	12	Upper VF (outlets of CWs 1, 3, 5, and 6)
C	B	706	±45	12	Upper HF (outlets of CWs 2 and 4)
C	B	654	±53	12	VF–HF (outlets of CWs 7 and 9)
C		504	±46	12	HF–HF (outlet of CW 8)
	D	5	±87	12	VF–slag (outlets of CWs 11 and 12)
	D	1	±101	12	HF–slag (outlet of CW 10)

3.2. *Geochemical modeling*

The very high removal efficiency of P from solution by the EAF steel slag filters is due to the chemical constituents that comprise the slag material and their reaction with the incoming wastewater. Geochemical modeling simulates the titration of a wastewater with oxides that comprise steel slag aggregates. This simulation is used to calculate the reactions occurring across different water:rock interface ratios. This simulation of a series of batch reactions may be interpreted as an ideal plug flow model, because a decreasing water:rock ratio (indicated by the reaction path in Fig. 4) might represent a water parcel that is interacting with the surface of more slag as it flows through the slag filter. Fig. 4 plots an example of these titration results on two different stability diagrams for $Fe–H_2O–P$ and $Ca–H_2O–P$ systems, showing different stability fields for mineral phases important in controlling P mobility. The model is initiated (left side of the reaction path in Fig. 4) with 374 l of wastewater, a neutral pH, and a P concentration of 30 mg/l. The model is completed (right side of reaction path in Fig. 4) with 374 l of wastewater, a pH equal to 10.5, and 0.0 mg/l of P. The model suggests that hydroxyapatite and vivianite are phosphate minerals that are potentially forming on or around the slag. Of particular importance is that at no point in this simulation are iron oxyhydroxide minerals (presented here as the phase $Fe(OH)_{3(ppd)}$) suggested as being a key part of P mobility in the system (through adsorption reactions). The reducing conditions observed in the wastewater are outside the conditions where $Fe(OH)_{3(ppd)}$ can form. Pratt et al. (2007) found the iron oxyhydroxide mineral to control P removal in melter slag; the reducing conditions in our systems suggest a different pathway for P removal in EAF steel slag. This model shows phosphate minerals that form and remain stable in reducing conditions. The high BOD_5 measurements coupled with the detection of hydrogen sulfide, iron(II), and manganese(II) in waters sampled from the filters support the maintenance of reducing conditions in much of the slag filters where P retention likely occurs. Modeling shows that even with elevated carbonate production associated with organic degradation, hydroxyapatite precipitates from the model solution first, removing almost all P from solution. Calcite begins to form after most P is removed from solution.

The effluent from the integrated CWs showed elevated pH in the field (ranging from 10 to 12), and this is a concern when releasing wastewater into the environment. This elevation of pH raises an important design consideration and suggests that the slag filters in this experiment have a water:rock ratio that

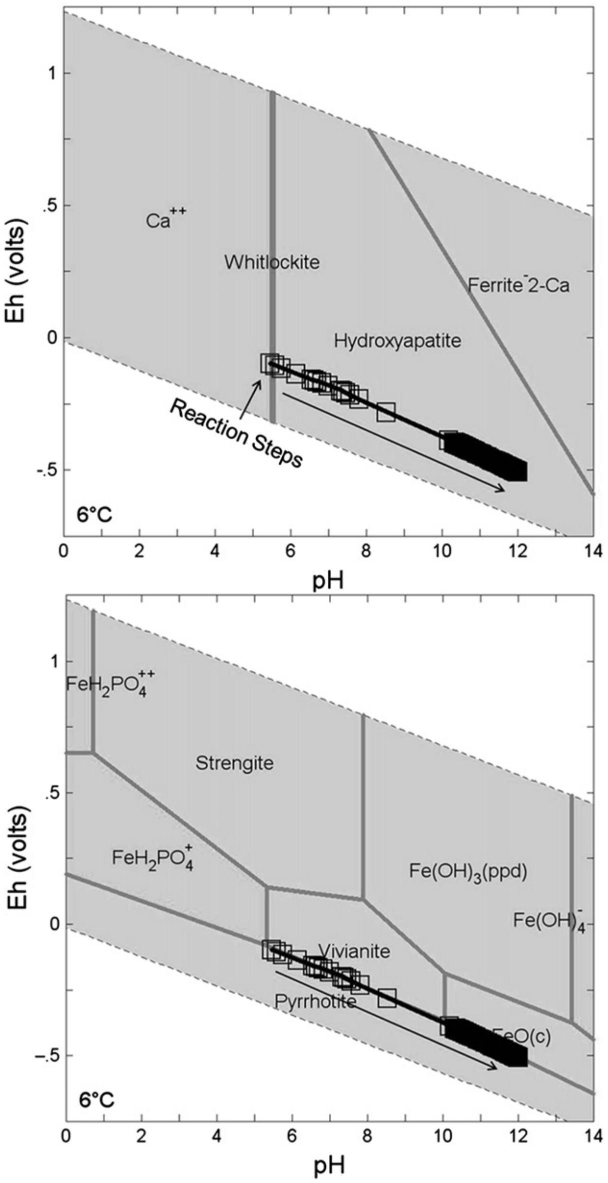

Fig. 4 – Geochemist's Workbench® activity diagrams for calcium and iron mineral species. The black squares represent the simulated addition of slag oxides to a P rich wastewater solution, and the solid line traces the reaction path from left to right as slag is incrementally added to the solution (e.g. the water:rock ratio decreases from left to right).

is too low and/or a reaction time that is too long. This finding at a pilot scale is useful; but would be disconcerting in application because improper sizing of slag filters can be detrimental. The elevated pH can be attributed to the dissolution of oxides present on the slag, which forms OH^- groups. A pH of 10–12 is approaching the alkalinity of a saturated solution of lime (Madigan and Martinko, 2006). According to the model as slag is incrementally added to the high P wastewater hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and vivianite ($Fe_3(PO_4)_2 8H_2O$) mineralizes, P is removed from solution, and pH gradually increases (Fig. 4). Each box along the titration line in Fig. 4 represents the addition of 3.8 g of slag oxides. In the simulation, after 99 g of slag reacts with 374 l of wastewater (water: rock = 3.78 kg/g); the concentration of P reduces from 30 mg/l to 0.1 mg/l and the pH is equal to 7.3. If we take the same simulated titration further, a total of 380 grams of slag was reacted with the 374 liters of wastewater (water: rock = 0.98 kg/g); the concentration of P is <0.001 mg/l and the pH is equal to 10.5. The model demonstrates that almost all P can be removed from the solution (mg/l of P <0.1), while the pH is still reasonable (pH < 8). The total mass of slag reacted in the model is an estimate based on the specific surface area of the slag in the filter and a prudent estimate of the thickness of slag reacted (on the order of microns). Geochemical modeling can help to optimize the performance of slag by modeling how much slag should be reacted for a given volume of wastewater, such that P is removed from solution, while pH remains close to neutral.

Weber et al. (2007) and Drizo et al. (2008) recently showed that at shorter nHRTs (1 day) EAF steel slag filters produce pH values that are elevated, only during the first 3 weeks of operation, and then stabilize below a pH of 9. The longer nHRTs(5 days and 2.5 days) for the flow through one slag filter employed in this study shows that the EAF steel slag filters can cause elevated pH (11 average) for a longer operation period. In practice, utilizing a slag filter before a CW might be useful so that alkalinity from the slag may be consumed in the CW as long as the pH is reasonable for nitrification. Nitrification is an acidifying process, so the addition of alkalinity may help to buffer this reaction.

4. Conclusions

Outcomes from this research may be useful for consideration in the design of CWs treating dairy wastewater, but care should be taken when scaling hydrologic systems up from pilot-scale to field-scale.

Geostatistical temporal semivariogram analyses indicate a temporal correlation in measured parameters over the summer field season. This analysis for 2008 suggested measurement points to be autocorrelated and should be separated into two groups (May–June and July–September). Different seasonal effects such as temperature and macrophyte biomass were likely responsible for the varying treatment performance in 2008. This time series analysis may be useful in other research to help separate data into significantly different groups before analysis is performed.

ANOVA results demonstrated significant differences between the categorized CW systems. Late summer of 2008, during the period of highest macrophyte biomass, had the highest rate of nutrient removal. Hybrid CWs seemed to outperform other CW systems in terms of organics removal, and this was significant during the late summer of 2008. The addition of inline slag filters to CW systems provides additional capability for removing substantial quantities of P from wastewater streams. In addition it improved ammonia reduction. Geochemical modeling of P removal illustrated that hydroxyapatite and vivianite are potentially important minerals controlling P removal from solution in these systems and that the maintenance of reducing conditions in much of these systems precludes formation of iron oxyhydroxide minerals that may sorb P species. The problem of high pH effluent that can occur at the outlet of the slag P removing filters needs to be taken into account, in order to become a viable practice for wastewater treatment. Overall this research shows that EAF steel slag P removing filters can be incorporated with CWs to achieve a high P and ammonia removal to supplement the BOD_5 and TSS removal that is intrinsic to CWs.

Acknowledgements

Funding for this research was supplied in part from the United States Department of Agriculture (USDA) as a research grant: "Constructed Wetlands Center for Research, Education, and Outreach at the University of Vermont: pollutant removal processes and mechanisms." The College of Engineering and Mathematical Sciences at the University of Vermont also provided funding for this research. We thank the 2009 University of Vermont Critical Writing Class for reviewing a draft of this paper.

REFERENCES

APHA, 1989. Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Organization, Washington.

Arias, C.A., Del Bubba, M., Brix, H., 2001. Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. Water Res. 35 (5), 1159–1168.

Brix, H., Arias, C.A., 2005. The use of vertical flow constructed wetlands for on-site treatment of domestic wastewater: new Danish guidelines. Ecol. Eng. 25 (5), 491–500.

Davis, M., Cornwell, D., 1998. Introduction to Environmental Engineering, third ed. McGraw-Hill, New York, NY.

Drizo, A., Comeau, Y., Forget, C., Chapuis, R.P., 2002. Phosphorus saturation potential: a parameter for estimating the longevity of constructed wetland systems. Environ. Sci. Technol. 36, 4642–4648.

Drizo, A., Cummings, J., Weber, D., Twohig, E., Druschel, G., Bourke, B., 2008. New evidence for rejuvenation of phosphorus retention capacity in EAF steel slag. Environ. Sci. Technol. 42, 6191–6197.

Drizo, A., Forget, C., Chapuis, R., Comeau, Y., 2006. Phosphorus removal by electric arc furnace steel slag and serpentine. Water Res. 40, 1547–1554.

GEO-SLOPE International Ltd. All Rights Reserved. Copyright © 1995–2010.

Goovaerts, P., 1998. Geostatistical tools for characterizing the spatial variability of microbiological and physic-chemical soil properties. Biol. Fertil. Soils 27, 315–334.

Hunt, P.G., Poach, M.E., 2001. State of the art for animal wastewater treatment in constructed wetlands. Water Sci. Technol. 44 (11–12), 19–25.

Inskeep, W.P., Silvertooth, J.C., 1988. Kinetics of hydroxyapatite precipitation at pH 7.4 to 8.4. Geochim. Cosmochim. Acta 52, 1883–1893.

Isaaks, E., Srivastava, M., 1989. Introduction to Applied Geostatistics. Oxford University Press, New York, NY.

Johansson Westholm, L., 2006. Substrates for phosphorus removal – potential benefits for on-site wastewater treatment? Water Res. 40 (1), 23–36.

Kadlec, R., 1999. Chemical, physical, and biological cycles in treatment wetlands. Water Sci. Technol. 40 (3), 37–44.

Kadlec, R., 2000. The inadequacy of first-order treatment wetland models. Ecol. Eng. 15, 105–119.

Kadlec, R., Knight, R., 1996. Treatment Wetlands. CRC Press, Boca Raton, FL.

Knight, R., Payne, V., Borer, E., Clarke, R., Pries, J., 2000. Constructed wetlands for livestock wastewater management. Ecol. Eng. 15, 41–55.

Lee, M.S., 2009. Pilot-scale Constructed Wetlands Combined with Phosphorus Removing Slag Filters for Treating Dairy Wastewater. M.Sc. thesis, University of Vermont.

Madigan, M., Martinko, J., 2006. Brock Biology of Microorganisms. Prentice Hall, Upper Saddle River, NJ.

Mann, R.A., 1997. Phosphorus adsorption and desorption characteristics of constructed wetland gravels and steelworks by-products. Austr. J. Soil. Res. 35, 375–384.

Mitsch, W.J., Gosselink, J.G., 1993. Wetlands, second ed. Van Nostrand Reinhold, New York, NY.

Newman, J., Clausen, J., Neafsey, J., 2000. Seasonal performance of a wetland constructed to process dairy milkhouse wastewater in Connecticut. Ecol. Eng. 14, 181–198.

Pratt, C., Shilton, A., Pratt, S., Haverkamp, R.G., Bolan, N.S., 2007. Phosphorus removal mechanisms in active slag filters treating waste stabilization pond effluent. Environ. Sci. Technol. 41 (9), 3296–3301.

Renman, A., Hylander, L.D., Renman, G., 2009. Transformation and removal of nitrogen in reactive bed filter materials designed for on-site wastewater treatment. Ecol. Eng. 34 (3), 207–214.

Rustige, H., Tomac, I., Honer, G., 2003. Investigations on phosphorus retention in subsurface flow constructed wetlands. Water Sci. Technol. 48 (5), 67–74.

Schaafsma, J., Baldwin, A., Streb, C., 2000. An evaluation of a constructed wetland to treat wastewater from a dairy farm in Maryland, USA. Ecol. Eng. 14, 199–206.

Schindler, D.W., 1977. Evolution of phosphorus limitation in lakes. Science 195, 260–262.

Seo, C.S., Hwang, S.H., Kim, H.J., Cho, J.S., Lee, H.J., DeLaune, R.D., Jugsujinda, A., Lee, S.T., Seo, J.Y., Heo, J.S., 2008. Evaluation of 2- and 3-stage combinations of vertical and horizontal flow constructed wetlands for treating greenhouse wastewater. Ecol. Eng. 32, 121–132.

Spiteri, C., Slomp, C., Regnier, P., Meile, C., Van Cappelen, P., 2007. Modelling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems. J. Contam. Hydrol. 92, 87–108.

Vohla, C., Koiv, M., Bavor, H.J., Chazarenc, F., Mander, U., 2009. Filter materials for phosphorus removal from wastewater in treatment wetlands – a review. Ecol. Eng.. doi:10.1016/j.ecoleng.2009.08.003.

Vymazal, J., 2005. Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. Ecol. Eng. 25 (5), 478–490.

Vymazal, J., 2007. Removal of nutrients in various types of constructed wetlands. Sci. Tot. Environ. 380, 48–65.

Ward, A., Trimble, S., 2004. Environmental Hydrology, second ed. Lewis Publishers, New York, NY.

Weber, D., Drizo, A., Twohig, E., Bird, S., Ross, D., 2007. Upgrading constructed wetlands phosphorus reduction from a dairy effluent using EAF steel slag filters. Water Sci. Technol. 56 (3), 135–143.