Evaluating the efficiency and temporal variation of pilot-scale hybrid and integrated constructed wetlands for treating high BOD and P concentrated dairy effluent

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Abstract: The performance and temporal variation of 3 hybrid and 3 integrated, saturated flow, pilot-scale constructed wetlands (CW) were tested for treating dairy-farm effluent. The 3 hybrid systems each consisted of 2 CWs in series; either vertical flow (VF) followed by horizontal flow (HF) or HF followed by HF. The integrated systems consist of a CW (either VF or HF) followed by an electric arc furnace (EAF) steel slag filter for removing phosphorus (P). The CWs began operating in August 2007. Each system received a daily pulse of wastewater resulting in a hydraulic loading rate (HLR) of 0.038 m/day with a nominal residence time of ~5 days. In April of 2008, the CWs mode of operation was changed from pulse to continuous flow, resulting in a HLR of 0.081 m/day. Weekly monitoring was carried out for five-day biochemical oxygen demand (BOD_5), total suspended solids (TSS), ammonium (NH_4^+), dissolved reactive phosphorus (DRP), and pH. The CWs treatment performance was evaluated for the fall of 2007 and 2008 operation periods. A time series analysis, for 2008, show that DRP, BOD_5, and water temperature are auto-correlated for 35 days. Integrated CWs remove significantly more DRP than hybrid CWs ($p < 0.05$). Geochemical modeling of the minerals that form on EAF steel slag was implemented to describe the processes of P removal. During the late summer of 2008, the integrated CWs removed a significantly higher amount of NH_4^+. Hybrid CWs appeared to be more efficient then integrated systems for removing BOD_5, but hybrid systems were only significantly more efficient at removing BOD_5 in late summer of 2008.

Key Words: constructed wetlands, phosphorus, steel slag, hybrid, dairy wastewater, temporal variation

1. Introduction

Research for improving constructed wetland (CW) nutrient removal capabilities is motivated by the increasingly stringent worldwide water quality regulations and the often erratic performance of existing CWs for treating nutrient rich wastewater. Treating livestock wastewater with CWs have become recognized as a viable treatment technology, however, data on the performance of systems treating dairy effluents, especially in cold climates, are fairly limited (Knight et al., 2000; Newman et al., 2000; Schaafsma et al., 2000). Of the 700 CWs operating in North America, the Livestock Wastewater Treatment Database (LWDB), known as the most comprehensive CW database to date, provides data for only 38 CWs treating dairy waste (Knight et al., 2000). While CWs are effective in organic matter and total suspended solids (TSS) removal, nutrient removal needs to be improved, especially in cold climates where a decrease in treatment efficiency is frequently observed during winter months (Kadlec et al., 2000; Hunt and Poach, 2001).

CWs have relatively low start-up costs as compared to other types of wastewater treatment systems, and less maintenance requirements, making them more applicable for small and medium-scale farms; however, their limited ability to remove P and the variable nutrient concentrations typical of agricultural wastewater, have created concerns over the efficacy and longevity of these systems (IWA, 2006). There is a need for additional research to improve the nutrient treatment performance of dairy wetlands and to expand their longevity in cold climates.

The design of CWs has evolved to accommodate the treatment needs for various types of wastewater and systems applications. Vymazal (2007) provides a comprehensive overview of multiple system designs. Over the past decade, hybrid CW systems (multiple CWs, employing surface, subsurface or vertical flow and operating in series) have been researched with the aim to improve CWs treatment efficacy, especially for nutrient reduction (Vymazal, 2007). Artificial aeration of horizontal flow systems and vertical flow systems was developed to facilitate O_2 mass transfer thereby enhancing nitrogen (N) and organic matter removal. To improve phosphorus (P) removal, various natural and industrial waste materials have been tested (Mann, 1997; Arias et al., 2001; Drizo et al., 2008). For example Weber et al. (2007) recently showed in column scale studies using electric arc furnace (EAF) steel slag filters at the outlet of CWs improved dissolved reactive phosphorus (DRP) removal efficiency from dairy farm effluent by 74% with a P capacity of ~1.5 g-P/ kg-slag. Despite these research efforts, P removal in constructed wetlands remains largely unresolved and is an important issue for investigation (IWA, 2008).

Hybrid constructed wetlands are well-established systems that are known to be efficient at removing organic matter, suspended solids, and nitrogen species when properly designed (Vymazal, 2007). The use of an EAF steel slag filter for P removal in combination with a CW is not well studied to date; most previous studies are lab-scale, batch reactions (REF), or column scale flow through reactors (Weber et al., 2007). The EAF slag filters contain the chemical oxides ideal for phosphorus precipitation; Fe_2O_3 (35%), CaO (30%), and Al_2O_3 (5%) (Drizzo et al., 2006). The adsorption and precipitation reactions that occur on slag are controlled by the adsorptive capacity of the slag and the kinetics of the reaction. Slag filters operate by adsorbing inorganic ions such as PO_4^{3-}, through mechanisms such as physical adsorption, chemisorption, and ion exchange with oxides that exist on the surface of the slag (Pratt et al., 2007). Phosphorus reacting with Fe_2O_3 or CaO reaches an equilibrium quickly (Spiteri et al., 2007); laboratory batch reactions show that slag reaches an equilibrium with soluble P within 13 hours (Rosolen, 2000).

This research moves forward the study of CWs integrated with slag phosphorus filters (integrated systems), by analyzing the significant treatment differences that exist between the pilot-scale hybrid and integrated CW systems, built and employed for this research, while considering temporal variation. For the pilot scale CWs, the inflow was controlled but the outflow was variable due to changing climatic conditions. An adjusted hydraulic loading rate was used, along with the corresponding concentration at a sampling location, to determine CW performance. One-way ANOVA was performed to compare the differences in DRP, BOD_5, TSS, and NH_4^+ between sampling locations.

Time series analysis, using geostatistical semi-variograms, was used to help describe how CW performance changes temporally.

2. Methods

2.1 Experimental Setup

The CW pilot-scale systems, built for this research study, exist at the CW facility on the Paul Miller Dairy Farm in Burlington, Vermont. There were two distinct system classifications. The first three CW systems (hybrid CW systems) shown in Figure 1 are a combination of two CWs in series, and the last three systems (integrated CW systems) are a combination of a CW followed by an electric arc furnace steel slag filter for removing phosphorus, henceforth called the slag filter. Within these two system classifications (hybrid and integrated) different flow regimes existed; two of the first in series CWs were vertical flow (VF), and one was horizontal flow (HF) for both the hybrid and integrated systems. Water samples were collected weekly at the outlet of all twelve CWs. One sample of the influent wastewater was collected weekly entering the first-in-series CWs (CWs 1-6), the 13 sampling locations are identified by solid circles in Figure 1.

The twelve individual CWs were constructed with a length, width, and height of 1.7m, 1.1m, and 0.5m, respectively. Nine of the CWs (CWs 1-9) were packed with gravel having a porosity of 0.4. The top 3 cm of these CWs were layered with organic soil and planted with river bulrush (*Schoenoplectus fluviatilis* (Torr.)). Three P filters (CWs 10-12) were filled with EAF steel slag (20-50 mm diameter) from Quebec having a porosity of 0.42 (Drizo et al., 2006).

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

The CWs were operated from August to December in 2007, and from May to September in 2008. During the 2007 CW operation, the influent wastewater was supplied to the wetland cells once daily as a pulse flow. In 2008, the flow was modified to operate as a continuous flow through system. A constant head reservoir of dairy wastewater was maintained using a pump that was triggered by float switches connected to an electromagnetic relay. The CW influent flow-rate was calibrated with needle valves. The nominal hydraulic retention time (HRT) for the daily pulse flow associated with the 2007 operating season was ~5 days. Whereas, the continuous flow of 2008 resulted in a nominal HRT of ~2.5 days.

The wastewater in this research is generated from a combination of feed lot runoff and milk parlor washwater as described in Munoz's Thesis (200_). The feedlot runoff has a watershed of approximately 1750 m^2, and the concentration and flow from this wastewater source depends mostly on precipitation. Wastewater from the milk parlor and milk house is generated during two or three periods each day: two milkings and one laundry event. On average the CWRC wastewater is influent receives 66 to 132 kg of milk per day (Munoz, 200_). The wastewater used in this research was tapped from this wastewater source.

2.2 Sample Collection and Laboratory Analysis

During the 2007 operation period, all water samples were collected weekly from the one influent wastewater sampling port and outlets of each of the 12 CWs. Five-day biochemical oxygen demand (BOD_5) and total suspended solids (TSS) tests were performed weekly following the Standard Methods (Eaton et al., 2005). Inorganic nitrogen species, nitrate (NO_3^-) and ammonium (NH_4^+), were analyzed on a weekly basis using a flow-through Lachat (Quik Chem FIA+ 8000 series). Weekly analysis of DRP was performed using the stannous chloride method (Eaton et al., 2005). Temperature and pH of the water samples were recorded weekly *in situ* using a field pH probe (Fisher Scientific Accumet waterproof AP71). Separate samples were collected in 5 ml bottles with no air space for lab analysis of redox reactive species using electrovoltametry techniques according to Luther et al. (2008). The samples were analyzed for Total P, Ca and metals approximately once a month using the persulfate digestion method (Eaton et al., 2005), 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. However, dissolved oxygen (DO) was also measured *in situ* using a field DO meter (HACH LDO®).

2.3 Adjusted Hydraulic Loading Rate

An adjusted hydraulic loading rate was calculated using the measured inflow, measured precipitation (PT) data, and calculated evapotranspiration (ET) from the Penman method (Ward and Trimble, 2004). On-site hourly temperature data, local National Oceanic and Atmospheric Administration (NOAA) hourly records for relative humidity, and a latitudinal estimate for average monthly solar radiation (Ward and Trimble, 2004) were used in the calculation of potential evapotranspiration. The on-site hourly PT data, the calculated ET, and the known influent flow of wastewater (Q_{in}) were used to estimate the flow out (Q_{out}), using a simplified dynamic water budget from Kadlec and Knight (1996):

$$Q_{out} = PT(A) + ET(A) + Q_{in}$$

where; PT and ET are multiplied by the surface area (A) of the CW to obtain a flow rate. For this study, the influent was assumed to be a constant and the flow out is an average calculated for each day. All of the flows were converted to hydraulic loading rates (m^3/m^2/day or m/day) by dividing the flow by the surface area of the CW systems in this study. The hydraulic loading rates were multiplied by the measured chemical constituents to calculate mass loading rates (eg. mg BOD_5/m^2/day). These adjusted loading rates were used in the data analysis.

2.4 Data Analysis

A time series analysis with the use of temporal semivariograms was performed to determine the extent of auto-correlation for measured time series data, and allowed for seasonal effects to be quantified. Temporal semivariograms were created for every measured parameter for each categorized CW system, using methodology adapted from Isaaks and Srivastava (1989). The time series analysis showed that significantly different time periods existed. Data were split according to these significantly different time periods of operation before conducting an ANOVA. One-way ANOVA was performed using SAS statistical software to determine if significant differences exist between the treatment systems. The categories used (Table 1) in the one-way ANOVA combined discrete sampling locations into the minimum number of unique CW systems. CW systems were then allocated into significantly different groups using Fisher's least-significant-difference multiple comparison test.

The performance, or efficiency, of the CWs was calculated as a percent reduction of the adjusted mass loading rate from the inlet to the outlet of a CW system:

$$((\text{mass loading rate in} - \text{mass loading rate out}) / \text{mass loading rate in}) * 100$$

The efficiencies of the CW categories, from Table 1, were calculated for the duration of the sampling period using a 15 day, overlapping moving window average.

2.5 Geochemical Modeling

The Geochemist's Workbench® modeling software 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 software was used to calculate chemical speciation in the wastewater using values of chemical concentrations, temperature, redox sate, and pH measured at the effluent of CW 6. The EAF steel slag oxides were then added incrementally to the wastewater solution. This model is an equilibrium model; the simulation is analogous to a titration, with slag being titrated into a P rich wastewater.

3. Results and Discussion

3.1 Time Series Analysis

The loading rates of BOD_5, DRP, and TSS over the course of the 2007 and 2008 operation periods are displayed in Figure 2. Note that mass loading rates are on a log scale. Concentrations varied during the sampling periods but the average influent concentrations for BOD_5, DRP, TSS, and NH_4^+ were: 2,500 mg/l (standard deviation = 824 mg/l), 46 mg/l (standard deviation = 11 mg/l), 740 mg/l (standard deviation = 246 mg/l), and 260 mg/l (standard deviation = 100 mg/l) respectively.

A time-series analysis performed on the 2007 and 2008 CW data showed the extent to which the discrete CW systems were auto-correlated over time. A detectable change in treatment efficiency over time was detected for the 2008 operating period. An example of the semivariogram produced for BOD_5 sampled in 2008 at the outlet of the upper HF CWs is shown in Figure 3. This semivariogram is generally representative of the BOD_5 semivariograms for each of the other CW categories (Table 1) in 2008, but the influent semivariogram did not show a detectable change over the course of the season (Figure 4). Note that samples collected one week apart are more correlated than measurements separated by 2 weeks or more, in Figure 3. After 2 weeks, the semivariance remains constant for an additional 3 weeks. After 5 weeks, the semivariance begins to increase again, and does not become steady until approximately 9 weeks. The increasing temporal semivariance indicates a significant difference occurs in the treatment performance of the CWs over the course of the 2008 operation period. TSS, and temperature also have a second time period where semivariance increases (auto-correlation decreases); with the second increase occurring at anywhere from 6 to 10 weeks separation. The semivariogram analysis showed that the CWs performed significantly different in the beginning of the summer compared to the end of the summer in 2008. Therefore, the 2008 data were partitioned into early summer (May 7th to June 25th) and late summer (July 15th to September 10th) (Figure 2), before performing the ANOVA.

An underlying assumption of ANOVA (and most parametric statistical procedures) is that the data are independent. In a wetland, observations are not necessarily independent, because point observations are auto-correlated, meaning that measurements taken spatially or temporally close to each other are more similar than those taken farther apart. The time series analysis clearly indicated that the data in this study are not completely independent.

The semivariograms proved to have wide 95% confidence bands, and this is probably due to the stochastic behavior of environmental samples. The large variances associated with calculated semivariograms may be caused by temporal sources of variation from a time scale that is smaller then the shortest difference in time between samplings (Goovaerts, 1998). Many of the semivariograms had a discontinuity at the origin, called the nugget effect (Goovaerts, 1998), and given the HRT of the CW systems it is apparent that weekly sampling did not provide enough resolution to capture a more accurate temporal correlation of the measured parameters. An example of a small scale temporal change that could affect CW mass loading rates is the dilution of chemical constituents and the increase of flow from a rain event. This time series analysis was more accurate at detecting temporal changes that took place over the course of a season.

Temperature, BOD_5, and TSS had two distinct periods in 2008 where the CW systems operated differently. The time-series analysis showed no detectible difference in the influent mass loading rate during 2008, so it can be inferred that difference in the mass loading of BOD_5 and TSS are due to changes in the performance of the CWs. The CWs experienced an increased removal efficiency of BOD_5 and TSS during late summer of 2008 (Figure 5). Other parameters that changed from early summer to late summer were temperature and plant biomass, and these factors may have directly influenced the changes in CW treatment performance. It is difficult to quantify what factors affect change in wetland treatment performance, because it is probably a combination of many chemical, physical, and biological processes (Kadlec, 1999).

3.2 Constructed Wetland Calculated Treatment Efficiency

The efficiencies (Figure 5) of the CW categories (Table 1) for 2007 and 2008 were calculated for the duration of the sampling periods using overlapping moving window averages of 15 day intervals, in an attempt of removing stochastic variability while maintaining long-term temporal variation. The removal of DRP by the slag systems is shown to be 100% during 2007 and 2008. It is noticeable that the CWs during the summer of 2008 have two periods that are marked by distinctly different removal efficiencies; these changes in BOD_5 and TSS treatment efficiencies were quantified with the time-series semivariogram analysis, as previously mentioned.

3.3 ANOVA

When interpreting time series field data and analyzing CW pollutant removal efficiency, one ought to take into account that the CW outlet samples do not reflect the influent wastewater for that same snapshot in time, but rather a few days prior. Moreover, a direct comparison of inlet to outlet concentrations, over short time periods, is further complicated because the hydraulic flow through a wetland may include multiple paths with different retention times and rate constants (Kadlec, 2000). To avoid the stochastic variability associated with inlet and outlet measurements, a long-term sampling period is useful to provide average values that can be correlated with a model (Kadlec, 2000). In this research, data from 2007 was averaged over the operation period to provide an adequate sample size for doing a one-way ANOVA. Data were partitioned into two periods for 2008 (early and late summer as determined by the time-series analysis), and the number of data points for each period in 2008 is adequate for an ANOVA.

ANOVA for 2007 and 2008 concluded that there were significant differences (p-value < 0.5) that existed in all of the measured parameters for each sampling period. In all cases, as expected, the influent BOD_5, DRP, TSS, and NH_4^+ mass loading rates were significantly different from the effluent of all CW categories (Table 1). In terms of the integrated CW systems, also as expected, DRP mass loading out was found to be significantly lower then the DRP mass loading of all other CW categories.

ANOVA of BOD_5, DRP, TSS, and NH_4^+ mass loading rates for all of the other CW categories were more complicated and harder to draw definitive conclusions from. Multiple comparison tests of each CW category for four different measured parameters are shown in Figure 6. For example, in 2007, DRP effluent mass loading rates from the HF-HF system were found to be significantly lower then the DRP mass loading rates from the upper VF systems (Figure 6). Two CWs in-series uptaking more DRP then one CW in-series seems intuitive, but this significant difference was not found for the sampling periods in 2008. 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 can not be biodegraded and off-gassed in the same manner as Nitrogen because no valency changes occur during microbial assimilation of P (Vymazal, 2007), and the main mechanisms of P removal in wetlands are generally attributed to P adsorption and precipitation from solution (Vymazal, 2007; Rustige et al., 2003).

In late summer of 2008 BOD_5 removal was found to be significantly different in the effluent of the hybrid CWs (VF-HF and HF-HF) compared to the effluent of the upper VF and upper HF systems. BOD_5 kinetics are commonly modeled with a first order reduction model (Davis and Cornwell, 1998; Kadlec and Knight, 1996), so it is clear that the hybrid systems, with a two fold higher retention time, would have a more complete removal of BOD_5. It is unclear why this significant difference was not detected in 2007 and early summer of 2008. It is important to note that the VF-slag systems had a significantly lower removal of BOD_5 then the HF-HF system; this may imply that the environment of a CW is more conducive for organic matter removal then a slag filter.

Late summer of 2008 shows that NH_4^+ loading rates have three different multiple comparison groups (Figure 6); the outlet of the integrated systems have a significantly lower loading rate then the upper CW systems. This significant difference was not found in 2007 and NH_4^+ data does not exist for early summer 2008.

It is important to note, that apart from changes in the flow regime between the 2007 and 2008 sampling periods, differences in the performances may have been affected by the higher temperatures and vegetation growth in 2008. The 2008 CW operating period had a different hydraulic loading rate, and different climatological conditions from the 2007 CW operating period. The 2008 CW operating period was carried out over the course of the growing season. It is well established that temperature plays an important role in CW treatment performances (Kadlec, 2000; Kadlec and Knight, 1996).

3.4 Constructed Wetland Geochemistry

Redox analysis of the CW wastewater indicate reducing conditions. The 2007 and 2008 redox analysis with electroanalytical microelectrodes showed that the influent wastewater was rich with sulfide, implying a sulfur reducing environment. As the wastewater flowed through the CWs, the environment became less reduced. The outlet measurements generally showed an iron and manganese reducing environment typical of most CWs that are not mechanically aerated. The transfer of oxygen to the CW water through plant roots and diffusion at the air water interface is not sufficient to sustain aerobic degradation for heterotrophic bacteria (Vymazal, 2005).

3.5 Slag Geochemical Modeling

The impressive removal of P from solution by the EAF steel slag phosphorus filters is due to the chemical constituents that comprise the slag material. The model of the P rich solution reacting with slag (Figure 7) is a testament to how essentially all P was removed from solution in the integrated CW systems. This model is also useful for predicting that hydroxyapatite and vivianite are phosphorus compounds that are potentially forming on or around the slag. In the pilot scale slag filters used for this study the P removal capability does not drastically diminish, but eventually, when enough P is loaded into the filters they will stop removing P from solution. Further modeling can be used to demonstrate how P could be released from the slag for possible slag rejuvenation.

The effluent from the integrated CWs showed elevated pH measurements (ranging from 10 to 12), which is representative of orthophosphate reacting with calcium oxides, and was verified by the geochemical equilibrium model. Weber et al. (2007) and Drizo et al. (2008) recently showed that at shorter HRTs (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 HRT (5 days and 2.5 days) employed in this study shows that the EAF steel slag filters can cause elevated pH (11 average) for a much longer time period.

4. Conclusions

The geostatistical temporal semivariogram analysis quantified the extent of temporal correlation of the measured parameters over the field season. This analysis for 2008 suggested that measurement points were not completely independent and should be separated into two groups (May-June and July-September). The temporal semivariograms also showed that TSS and BOD_5 have a similar range of correlation to temperature, so changes in temperature may affect the performance of the CWs.

ANOVA results provided significant differences that existed between the categorized CW systems, and it was apparent that the late summer of 2008, when there was the most macrophyte biomass, had the highest rate of nutrient removal. The hybrid CWs seemed to outperform the other CW systems in terms of organics removal, and this was significant during the late summer of 2008. The integrated CW systems consistently outperformed the other CW systems with regard to P removal. The geochemical modeling of P removal illustrated that hydroxyapatite and vivianite are the potential minerals forming to remove P from solution. The problem of high pH effluent that can occur at the effluent of the slag P removing filters needs to be taken into account, if slag is to be considered as a component of wastewater treatment. Overall this research shows that EAF steel slag P removing filters can be incorporated with CWs to achieve a high P removal to supplement the BOD_5 and TSS removal that is intrinsic to CWs.

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6. References

Arias CA, Del Bubba M , Brix H. Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. Water Research 2001; 35: 1159-1168.

Cooper P. (2008). Constructed Wetlands for Pollution Control. International Water Association, Indore, India.

Davis M, Cornwell D. Introduction to Enviornmental Engineering, Third Edition. USA: McGraw-Hill; 1998. pp.

Drizo A, Forget C, Chapuis R, Comeau Y. P removal by electric arc furnace steel slag and serpentine. Water Research 2006; 40: 1547-1554.

Drizo (2008)

Standard Methods for the Examination of Water and Wastewater, 21st ed. American Public Health Association, American Water Works Association, and the Water Environment Federation. 2005; Eaton AD, Clesceri L S, Rice E W, Greenberg AE (Eds). pp.

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

Hunt PG, Poach ME. State of the art for animal wastewater treatment in constructed wetlands. Water Sci Technol 2001; 44 (11-12): 19-25.

International Water Association (2006). Wetland Systems for Water Pollution Control. Proceedings from the 10th International Conference on Wetland Systems for water Pollution Control, held in Lisbon, Portugal, 23-29th September 2006.

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

Kadlec R, Knight R. Treatment Wetlands. Boca Raton: CRC Press; 1996. pp.

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

Kadlec RH. The inadequacy of first-order treatment wetland models. Ecological Engineering 2000;15:105-119.

Kadlec RH, Knight R, Vymazal J, Brix H, Cooper P, Haberl R (2000b). Constructed Wetlands for Pollution Control. International Water Association, London, UK.

Knight R, Payne V, Borer E, Clarke R, Pries J. Constructed wetlands for livestock wastewater management. Ecological Engineering 2000;15:41-55.

Luther GW, Glazer BT, Ma S, Toouwborst RE, Moore TS, Metzger E, Kraiya C, Waite T J, Druschel G, Sundby B, Taillefert M, Nuzzio D B, Shank TM, Lewis BL, Brendel PJ. Use of voltammetric solid-state (micro)electrodes for studying biogeochemical processes: Laboratory measurements to real time measurements with an *in situ* electrochemical analyzer (ISEA). Maine Chemistry 2008;108:221-235.

Mann RA. Phosphorus adsorption and desorption characteristics of constructed wetland gravels and steelworks by-products. Austr J Soil Res 1997;35:375-384.

Newman J, Clausen J, Neafsey J. Seasonal performance of a wetland constructed to process dairy milkhouse wastewater in Connecticut. Ecological Engineering 2000;14:181-198.

Pratt C, Shilton A, Pratt S, Haverkamp RG, Bolan NS. Phosphorus removal mechanisms in active slag filters treating waste stabilization pond effluent. Environ Sci Technol 2007;41:3296-3301.

Rosolen (2000)

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

Schaafsma J, Baldwin A, Streb C. An evaluation of a constructed wetland to treat wastewater from a dairy farm in Maryland, USA. Ecological Engineering 2000;14:199206.

Spiteri C, Slomp C, Regnier P, Meile C, Van Cappelen P. Modelling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems. Journal of Contaminant Hydrology 2007;92:87-108.

Vymazal J. Removal of nutrients in various types of constructed wetlands. Science of the Total Environment 2007;380:48-65.

Ward A, Trimble S. Environmental Hydrology, Second Edition. USA: Lewis Publishers; 2004. pp.

Weber D, Drizo A, Twohig E, Bird S, Ross D. Upgrading constructed wetlands phosphorus reduction from a dairy effluent using EAF steel slag filters. Water Science and Technology 2007;56(3):135-143.

Table 1: List of unique CW categories used for one-way ANOVA

Inlet
upper VF (outlets of CWs 1, 3, 5, and 6)
upper HF (outlets of CWs 2 and 4)
VF-HF (outlets of CWs 7 and 9)
HF-HF (outlet of CW 8)
VF-Slag (outlets of CWs 11 and 12)
HF-Slag (outlet of CW 10)

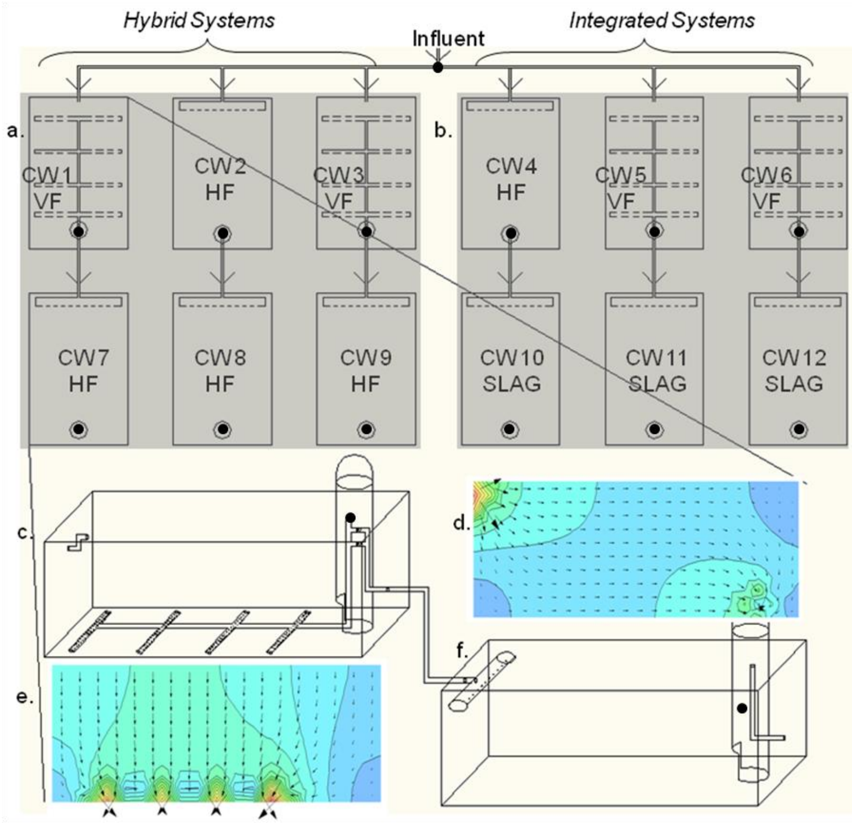


Figure 1

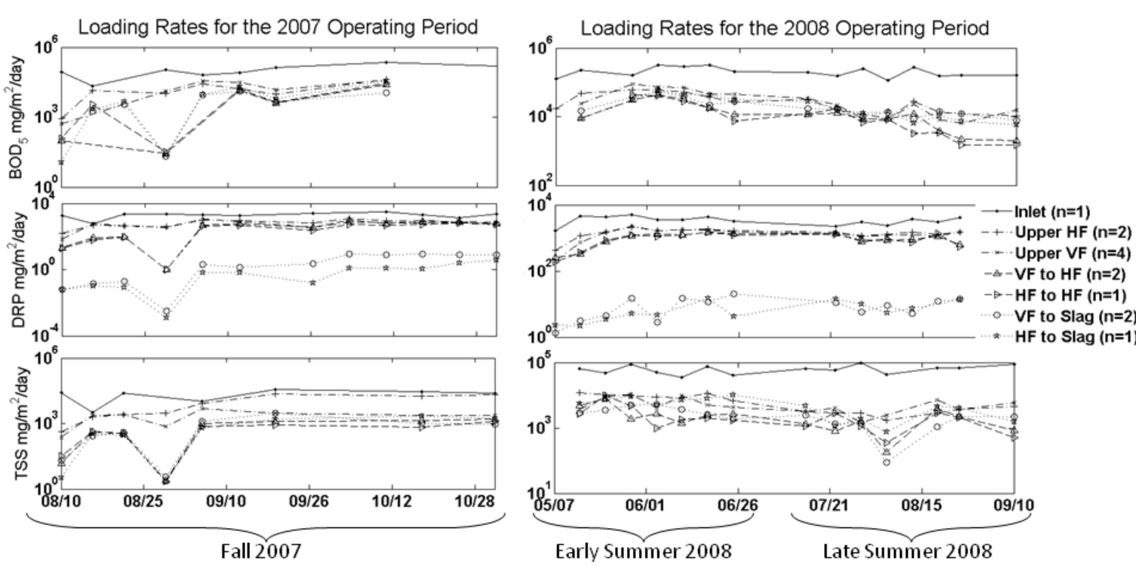
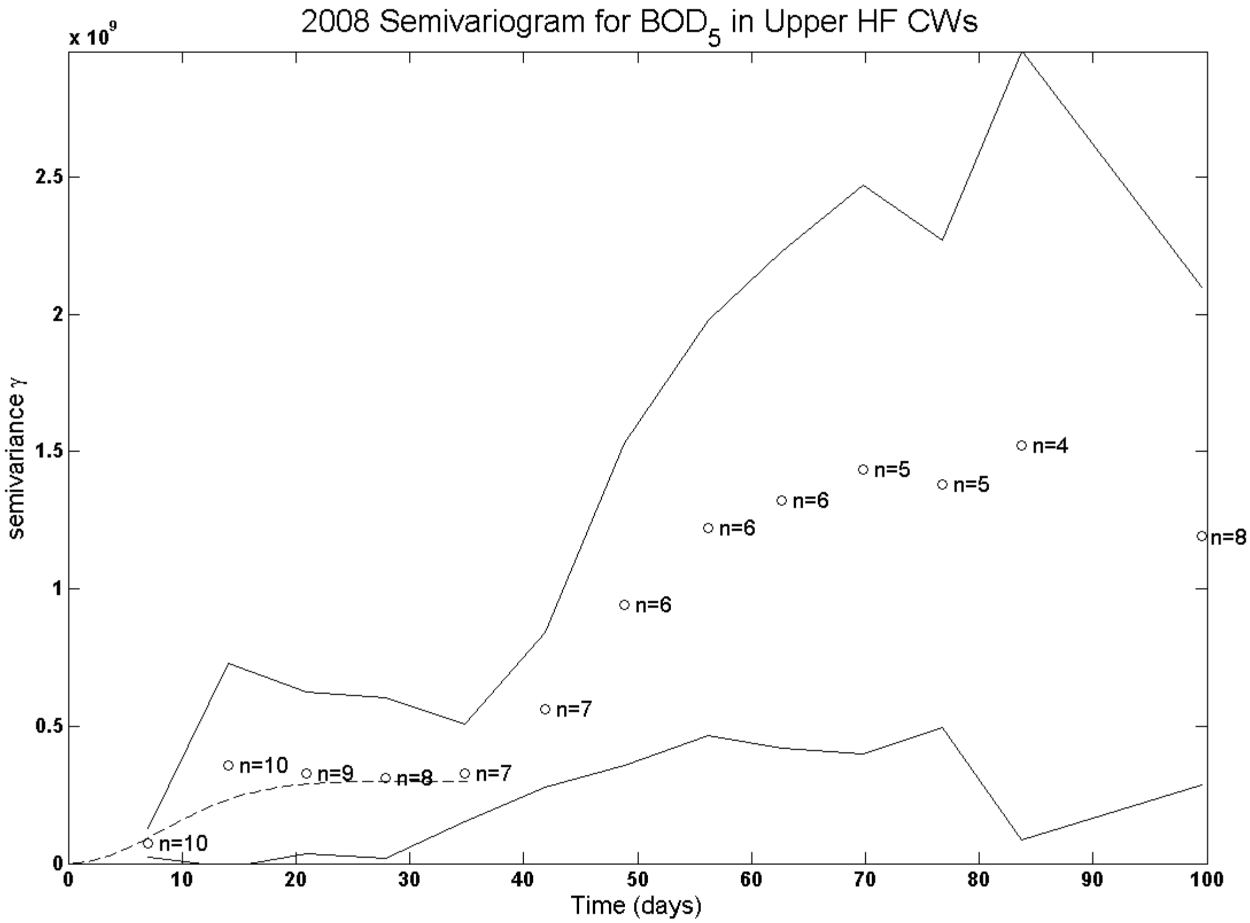


Figure 2



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537 **Figure 3**

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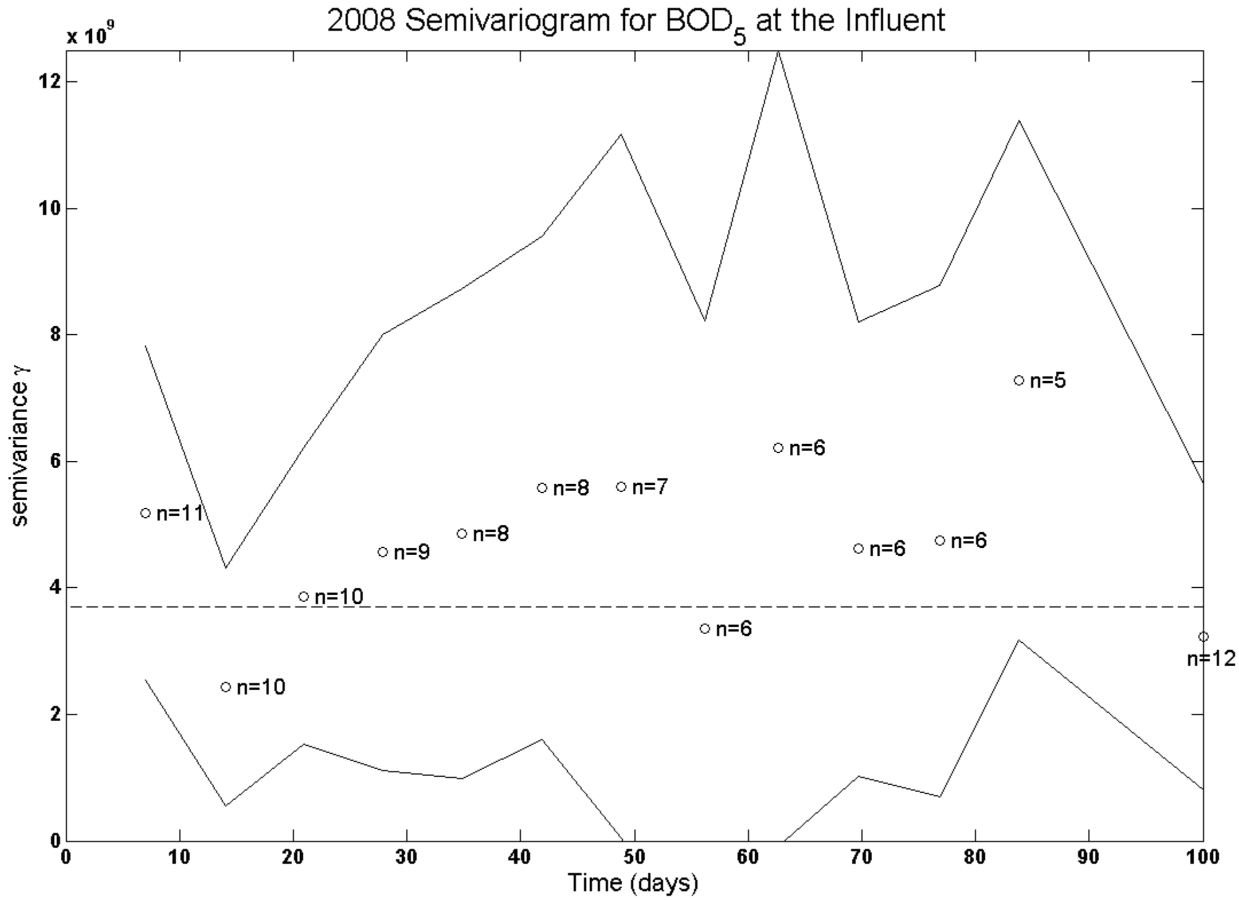
2008 Semivariogram for BOD_5 at the Influent
x 10^9
semivariance γ
Time (days)
0
2
4
6
8
10
12
0
10
20
30
40
50
60
70
80
90
100
n=11
n=10
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n=5
n=12

Figure 4

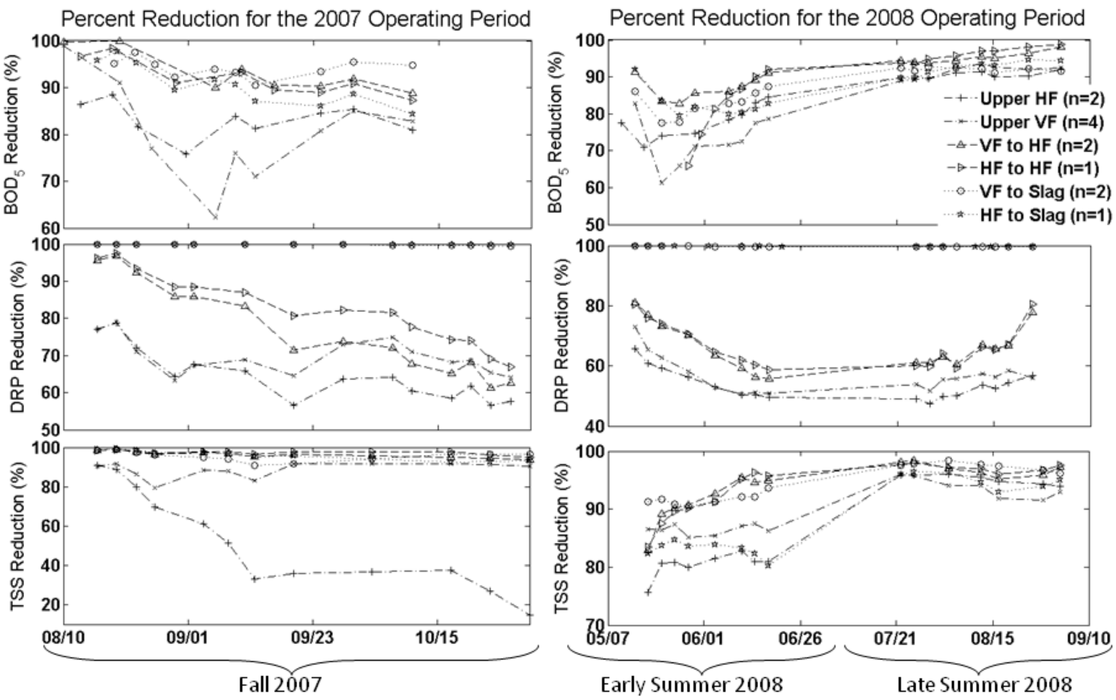

Figure 5

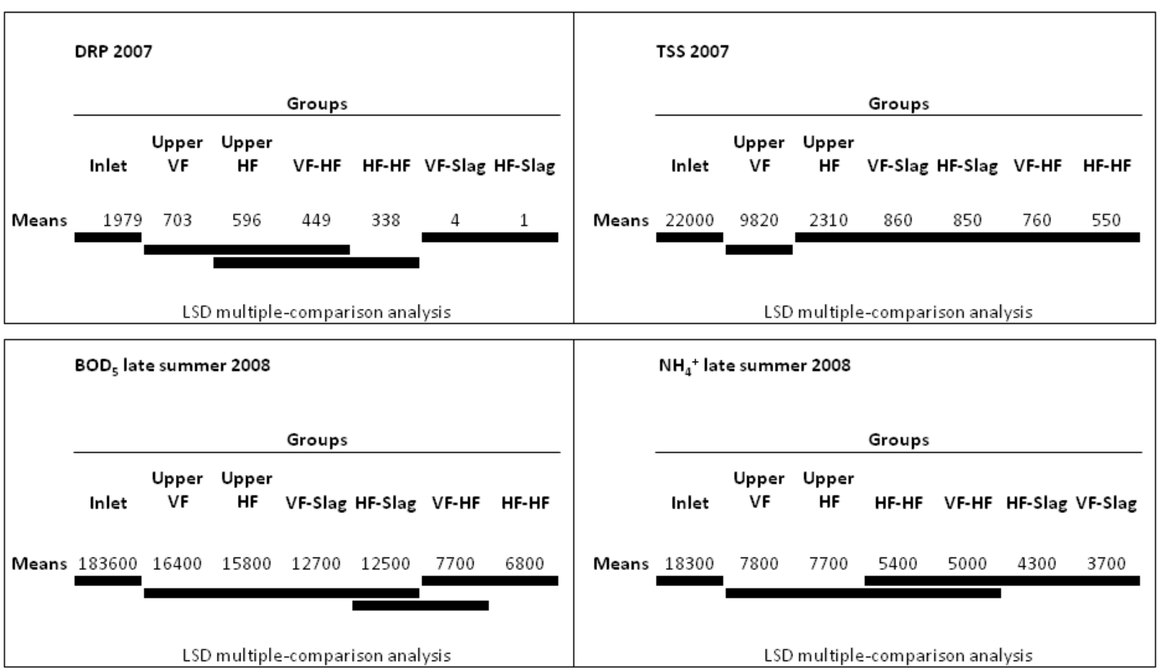

Figure 6

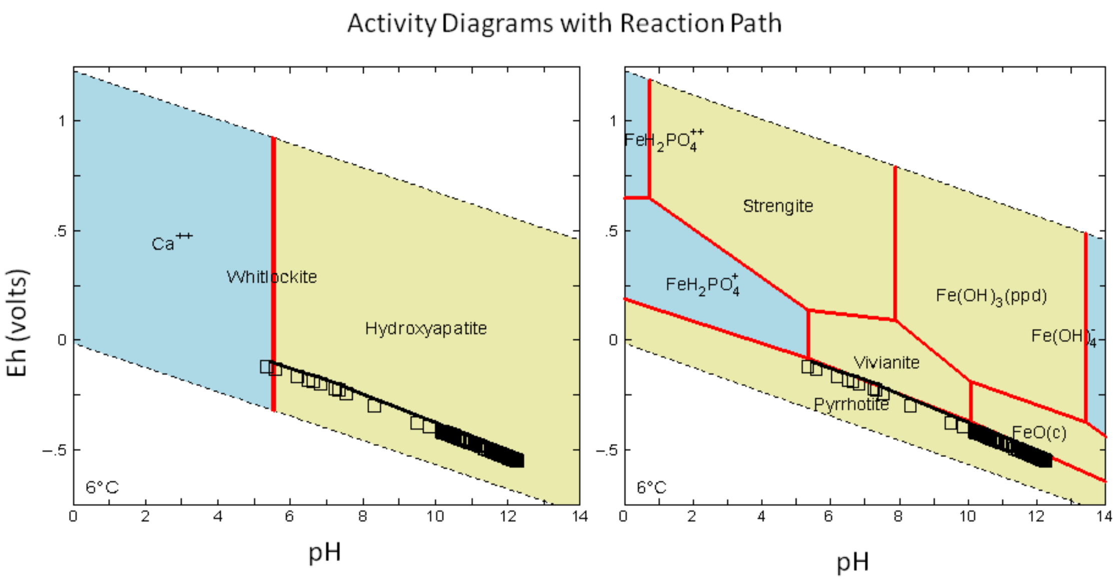

Figure 7

Figure 1: a. Experimental layout of the 6 CWs of the hybrid systems in plan view. b. Experimental layout of the 6 CWs of the 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 VF CW, e. cross-section of the SEEP/W° modeled flow through a HF CW, and f. the plumbing for a HF CW.

Figure 2: Semi-log plots showing the difference for the wastewater influent and effluent for the six CW systems over the 2007 and 2008 operating period.

Figure 3: Temporal semivariogram for 2008 BOD_5 loading rates. The solid lines represent the 95% confidence intervals, the dotted line is a best fit Gaussian model

(nugget=0; sill=3E9; range=20), and the circles represent the binned average semivariances with the corresponding number of data points (n) used to calculate the average semivariance.

Figure 4: Temporal Semivariogram for the BOD_5 loading rates in 2008, for the influent wastewater. The solid lines represent the 95% confidence bounds, the dotted line is a linear model (nugget=3.7E9; sill=3.7E9; range=100) to fit the trend of the semivariance, and the circles represent the binned semivariances with a corresponding number of data points used to find the average semivariance in the bin.

Figure 5: Removal efficiency of the different CW systems for the 2007 and 2008 CW operating periods. These plots were generated using moving window averages of the influent and effluent mass loading rates, with a window size of 15 days.

Figure 6: Selected results from the Fisher's least-significant-difference multiple comparison test. Groups with a common underscore are not significantly different ($p<0.05$). The means are loading rates in units of $mg/m^2/day$.

Figure 7: 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.