USING FREE WATER SURFACE CONSTRUCTED WETLAND FOR THE MITIGATION OF HIGH PH SECONDARY EFFLUENT FROM MUNICIPAL WASTEWATER TREATMENT PLANT

by

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Abstract

Wastewater stabilization ponds (WSPs) are considered to be the most sustainable technology for small, rural and remote communities in North America. However, due to the configuration of WSPs and limited control over these systems, performance concerns during certain parts of the year may arise, as elevated temperature and extended hydraulic retention time (HRT) could stimulate excessive algal growth that results in sustained high pH levels in the system and effluent. Amherstview Water Pollution Control Plant (WPCP) in Amherstview, Ontario frequently experiences high pH effluent during the summer and is assessing the potential of a constructed wetland (CW) system to mitigate these operational issues.

In order to design a CW, a bench-scale experiment was conducted to identify the best available substrates and operational conditions in the laboratory. A short-term assessment of four substrates followed by long-term monitoring of the two most promising substrates was undertaken under different HRTs and organic loading rates (OLRs). The results showed that peat exhibited the best pH attenuation capacity, and the pH attenuation performance could be substantially improved when the OLR was increased over 70 mg/L COD with a HRT longer than 4 days.

The feasibility of this CW system was further tested in the field over the span of a year to investigate the nutrients removal efficiencies, as well as to evaluate the effects of substrate and vegetation on the wetland system using authentic secondary effluents from the Amherstview WPCP. The results showed that all treatment systems could attenuate

the pH level during both the start-up and operational periods, while significant nutrient removal performance could only be observed during the operational period.

The results of the bench-scale and small-scale studies provided useful information for the design of the pilot-scale CW. The pilot-scale CW was successfully designed and established at the Amherstview WPCP. Overall, this newly designed free water surface (FWS) CW was highly effective at retaining phosphate (PO_4-P) and total phosphorus (TP), and fairly effective at removing nitrate (NO_3-N) and total nitrogen (TN). It is anticipated that the treatment performance of this CW could further improve when the CW becomes more mature.

Co-Authorship

Chapter 2 through 6 of this thesis have been accepted or will be submitted for publication in peer-reviewed scientific journals. The presented work was carried out by Meng Jin, with the assistance of the indicated co-authors who provided valuable comments, suggestions and revisions to the manuscripts.

CHAPTER 2

Factors affect the Algal Bloom in Wastewater Stabilization Ponds and Potential Mitigation Methods

Meng Jin, Pascale Champagne, Geof Hall

Manuscript will be submitted to *Water Science and Technology*.

CHAPTER 3

Substrates Applied in Constructed Wetland Systems for Wastewater Treatment: A Review (2008-2017)

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CHAPTER 4

Effects of Different Substrates in the Mitigation of Algae-induced High pH Wastewater in a Pilot-scale Free Water Surface Wetland Systems

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CHAPTER 5

Peat as Substrate for Small-scale Constructed Wetlands Polishing Secondary Effluents from Municipal Wastewater Treatment Plant

Meng Jin, Jacob Carlos, Rachel McConnell, Geof Hall, Pascale Champagne

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CHAPTER 6

Treatment Performances of a Pilot-scale Free Water Surface Constructed Wetland System for Secondary Effluents

Meng Jin, Pascale Champagne, Rachel McConnell, Geof Hall

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AC-MC	Aluminum Chloride Modified Clay
ANAMMOX	Anaerobic Ammonium Oxidation
ANOVA	Analysis of Variance
AS-MC	Aluminium Sulfate Modified Clay
BOD	Biological Oxygen Demand (mg/L)
CAPB	Cocamidopropyl Betaine
Chl-*a*	Chlorophyll- *a*
COD	Chemical Oxygen Demand (mg/L)
CRCA	Cataraqui Region Conservation Authority
CS	Corn Starch
CW	Constructed Wetland
DO	Dissolved Oxygen (mg/L)
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
E_h	Redox Potential
FWS	Free Water Surface
HRT	Hydraulic Retention Time (d^{-1})
HSSF	Horizontal Subsurface Flow
MOECC	Ministry of the Environment and Climate Control
NH_4-N	Ammonium (mg/L)
NO_3-N	Nitrate (mg/L)
NO_2-N	Nitrite (mg/L)

OLR	Organic Loading Rate
PAC-MC	Polyaluminum Chloride Modified Clay
PO_4-P	Phosphate (mg/L)
R	Removal Efficiency
RR	Removal Rate
SFCW	Surface Flow Constructed Wetland
TCAP	Thermally-treated Calcium-rich Attapulgite
TN	Total Nitrogen (mg/L)
TP	Total Phosphorous (mg/L)
TSS	Total Suspended Solids
VSSF	Vertical Subsurface Flow
V_v	The volume of void space in substrate (L)
V_T	The total or bulk volume of substrate (L)
WSP	Wastewater Stabilization Pond
WPCP	Water Pollution Control Plant
WWTP	Wastewater Treatment Plant
Ø:	Porosity (dimensionless)

Chapter 1

Introduction

1.1 Background overview

In Canada, there are more than 3,500 wastewater treatment facilities. Many of these wastewater treatment facilities employ biological wastewater treatment technologies such as the activated sludge process (Lotito et al., 2014); biofilm-based technologies such as trickling filters (Daigger & Boltz, 2011), vegetation filters (Miguel et al., 2014); as well as pond systems, such as oxidation ditches and waste stabilization ponds (WSPs) (Hosetti & Frost, 1998). In Ontario, for instance, there are approximately 137 municipal wastewater treatment facilities that employ WSPs ranging from completely passive to active treatment systems (Crites & Technobanoglous, 1998; Hosetti & Frost, 1998; Mara, 1996).

WSPs are considered to be the most sustainable technology for small, rural and remote communities. WSP systems requires little to no energy to operate and low-cost to build and implement compared to conventional technologies. They can effectively remove a large fraction of influent organic and nutrient constituents as well as attenuate bacteria and pathogen levels in municipal wastewater (Maynard et al., 1999; Reinoso et al., 2008; Senzia et al., 2003). However, due to the configuration of WSPs and limited control over these systems, performance concerns during certain parts of the year may arise. Elevated temperatures and high levels of solar radiation can lead to the discharge of a deteriorated effluent from the facility during certain periods of the treatment season. Shallow WSP basins encourage sunlight penetration, which, along with the increased temperature, could provide a favorable environment for algae to thrive during the summer treatment season. This could potentially stimulate excessive algae growth in these WSPs. At the same time, the extensive consumption of dissolved CO_2 can result in sustained high pH levels in the system and effluent.

There are quite a few factors that affect algal growth or algal bloom events in WSP systems. Climatic conditions are the most critical as described above. The synergy between algae and heterotrophic microorganisms is an important feature of WSP systems. However, both of them require same nutrients (e.g. nitrogen, phosphorous) and other essential elements for their growth, for which they compete within WSP system. A study conducted by Currie and Kalff (1984) showed that heterotrophic bacteria were stronger competitors for nutrients, particularly for phosphorus and should outcompete algae easily under phosphorus-limited environments. However, another rationale provided by Klug (2005) was that algae are nutrient-limited and bacteria are energy-limited (carbon-limited) in many cases. Under energy-limited conditions, bacteria depend on the extracellular release of organic carbon by algae, which further stimulate the growth of algae (Cole et al., 1982). As a photoautotrophic microorganism, algae uses inorganic carbon source to support its growth, and the availability and quantity of inorganic carbon could also affect their growth. Schippers et al. (2004) conducted a study to investigate the relationship between atmospheric CO_2 and algal growth in eutrophic freshwater, and their results indicated that algal growth doubled with the doubling of atmospheric CO_2 concentration.

A reasonable amount of algal activity is expected in WSPs and is essential to sustain the ecological equilibrium of these systems. However, when there are higher concentrations of nutrients available as well as sufficient light, the environment will favor the growth of algae, which can also be correlated with the occurrence of algal blooms (Barsanti & Gualtieri, 2014). Consequences of these algal blooms are notable increases in effluent pH, biological oxygen demand (BOD), and total suspended solids (TSS). The rapid growth of algae leads to the consumption of large amounts of CO_2, which cannot be replenished immediately by heterotrophic microorganisms or through direct mass transfer from the atmosphere. When this occurs, large amounts of algae released in the secondary effluent could increase decay rates and potentially consume large quantities of dissolved oxygen (DO), leading to unacceptably high BOD levels in downstream receiving environments (Maynard et al., 1999). These conditions will also inevitability lead to increases in effluent pH levels due to the high consumption of CO_2 (Pipes, 1962).

In order to mitigate the elevated pH and deteriorated water quality in secondary effluents from WSP systems, a number of methods have been proposed by either removing excessive algae in WSP system or directly neutralizing the elevated pH level in the downstream processes (Roadcap et al., 2005; Rodríguez et al., 2007; Shen et al., 2011). Among those methods, the use of constructed wetlands (CW) has emerged as a more cost-effective and environmental friendly technology to tackle the issue. CWs are engineered man-made systems that take advantage of many of the same processes that occur in natural wetlands, but do so in a more controlled system. These processes, which include infiltration, sedimentation, and microbial degradation, contribute to treatment of wastewater (Abou-Elela et al., 2013; Kadlec & Wallace, 2008; Vymazal, 2005). In comparison to the other treatment methods noted above, CWs do not require sustained chemical and energy inputs. CWs utilize the naturally occurring interactive reactions between the biotic and abiotic environment within the system in order to stimulate wastewater mitigation. One of the most distinctive merits of these systems is that they have been noted to be more resilient to ambient environmental changes due to the complexity of the ecosystem (Kadlec & Wallace, 2008). Therefore, temporarily elevated temperatures and high solar radiation may not as significantly affect the overall performance of CWs as they would in a WSP systems.

There are two main types of construct wetlands, surface flow CWs and subsurface flow CWs. Surface flow CWs are defined as wetland systems where the water surface is exposed to the atmosphere. Subsurface flow CWs are typically constructed as a bed or channel containing appropriate media, such as coarse rock, gravel, sand and other soils. In terms of subsurface CWs, there are horizontal subsurface flow (HSSF) and vertical subsurface flow (VSSF) CWs. Generally speaking, the HSSF CWs encourage the anaerobic biological processes, whereas the VSSF CWs promote the aerobic biological processes. Surface flow CWs are ideal for small communities with low strength of raw wastewater as the construction cost per capital is typically lower than subsurface flow CW. Subsurface flow CWs tend to provide better treatment performance as water flow through the substrate materials enhances treatment. However, clogging is one of the big issues related to the subsurface flow CWs, and the cost of substrate replacement is expensive. Hybrid CW systems were developed in the 1960s, and their recent use has increased with the establishment of more stringent discharge limits for nitrogen. The early hybrid CWs consisted of multiple stages of VSSF CWs followed by multiple stages of HSSF CWs. In 1990s, HSSF-VSSF and VSSF-HSSF hybrid systems were developed. In order to achieve higher removal of total nitrogen, surface flow CWs were also added to the hybrid system as well. VSSF-HSSF is the most commonly used hybrid system for the removal of nitrogenous compounds, and are usually more efficient than HSSF-VSSF.

A number of studies have been undertaken to evaluate the performance of both surface and subsurface flow CWs (Abou-Elela et al., 2013; Aguirre et al., 2005; García et al., 2005). Most of these studies have focused primarily on attenuating TSS, BOD, chemical oxygen demand (COD), and nutrient levels and the treatment of raw municipal wastewater. There is very little information regarding the application of CWs to attenuate municipal wastewaters exhibiting extreme pH conditions. Although, subsurface flow wetlands are considered more attractive because of their demonstrated ability to effectively attenuate a number of chemical and biological constituents, they remain more costly to build and are subject to higher maintenance costs compared to surface flow wetlands (Vymazal, 2008). In addition, clogging is often an issue associated with subsurface flow wetlands, due to their similarity to filter beds, requiring continuous monitoring and maintenance to ensure optimal performance (Knowles et al., 2011; Nivala et al., 2012). Surface flow CWs, on the other hand, have low energy and maintenance requirements and are more attractive to fiscally constrained municipalities across Canada.

Substrates, an important part of the CW, are employed to not only provide the direct treatment, but also to facilitate the biochemical processes that occur within the CWs. To date, a variety of materials have been tested on a laboratory scale or utilized in the field as substrate in both surface flow and subsurface flow CW systems. There are mainly two types of substrates in CWs: mineral-based substrates (e.g. gravel, limestone, zeolite) and organic-based substrates (e.g. peat, sludge, rice straw) (Babatunde et al., 2011; Cao et al., 2016; Li et al., 2008; Stefanakis et al., 2009; Tao & Wang, 2009), which are currently studied by researchers. Different substrates have different effects on CW systems, and they are strategically employed to achieve specific treatment goals. As such, identifying suitable substrates, as well as feasibility studies are typically required before the selection of substrates can be made and applied in a pilot-scale or full-scale CW systems.

The Corporation of Loyalist Township Utilities Division (LTU) currently manages the Amherstview Water Pollution Control Plant (WPCP) in Eastern Ontario. They are one of the wastewater treatment plants in Ontario that employs WSPs as part of their wastewater treatment strategy. Since 2003, they have regularly experienced extreme high pH effluent events during the summer months. The regulatory effluent limits are listed in Table 1.1, with the typical discharge range of pH at the Amherstview WPCP being from 6.0 to 9.5. However, historical data from the plant show that the final effluent of the Amherstview WPCP has frequently been above 10 during summer months. The discharged wastewater enters the Bayview bog, a natural wetland with large populations of cattails. Long-term monitoring of the water in the wetland showed that pH levels consistently met the discharge limits for at the Amherstview WPCP. Therefore, establishing a free water surface (FWS) CW at the Amherstview WPCP was proposed to solve the periodic high pH issue.

Through an ongoing collaboration (2010 - present), Queen's University has been assisting Loyalist Township in the design, implementation and evaluation of the performance of a FWS CW implemented with the aim of attenuating these high pH effluent events. The FWS CW is expected to provide a low-cost, low-maintenance downstream process for attenuating the high pH levels and the associated increase in suspended solids due to algal growth and decay (Steinmann et al., 2003). This solution is currently being developed in cooperation with the Ministry of the Environment Ontario and Climate Change (MOECC), Cataraqui Region Conservation Authority (CRCA), and in collaboration with Loyalist Township to establish a demonstration site at the Amherstview WPCP such that other small municipalities who struggle with the similar operational issues can benefit from this study.

Table 1.1 Amherstview WPCP Certificate of Approval No. 4210-7F3TMW (Issued June 5, 2008)

Regulatory discharge limit at the Amherstview WPCP		
Parameters	Objective	Discharge limit
pH	N/A	6.0 - 9.5
cBOD5	10 mg/L	15 mg/L
TSS	15 mg/L	25 mg/L
NH_4-N	2.0 mg/L	3.0 mg/L
TP	0.7 mg/L	0.9 mg/L
E. coli	N/A	100 cfu/100ml

The main objective of this doctoral research project is to provide valuable information for the upgrades anticipated at the Loyalist Township Amherstview WPCP. The outcomes of this study described below will not only serve as a demonstration project for other small municipalities in Ontario, but will also provide valuable insight into the water chemistry and biological conditions leading to the high pH effluent and associated excessive algal growth in WSPs. The knowledge gained would also be very useful in terms of controlling the excessive growth of algae in WSPs.

1.2 Research objectives

The main objectives will be achieved through the following sub-objectives:

1) Investigate the factors that affect algal growth or algal bloom events.
2) Review available materials both mineral-based and organic-based that have been tested in the laboratory or employed in the field as substrate in CW systems.
3) Identify and test suitable substrates (e.g. peat, organic mulch, gravel, topsoil) on a bench-scale continuous flow wetland reactor for attenuating elevated pH synthetic wastewater that mimic the characteristic of secondary effluent at the Amherstview WPCP.
4) Establish a field-scale feasibility study of three small-scale on-site surface flow CWs with different combination of substrate peat and wetland vegetation *Typha latifolia* (*T. latifolia*) for treating secondary effluent at the Amherstview WPCP. and compare the treatment performance of these systems.
5) Design and implement a pilot-scale FWS CW to replace a WSP at the Amherstview WPCP with different configurations for mitigating high pH effluent.

1.3 Thesis organization

This thesis is composed of seven chapters. Chapter 1 is a general introduction that presents the background information, objectives and the organization of the thesis. In order to achieve the abovementioned objectives, a series of studies and experiments were conducted and designed based on the latest literature in the field. Literature review studies are conducted and presented in Chapter 2 and Chapter 3. Experimental studies, their analyses and discussions are presented in Chapters 4, 5, and 6. The relationship between Chapters 2 to 6 are illustrated in Figure 1.1. These five separate chapters (manuscripts) have been published, accepted or will be submitted for publication in peer-reviewed scientific journals. Chapter 7 concludes the entire thesis with recommendations for future work. Both scientific and community contributions are listed in Chapter 7 as well.

Chapter 2 is a literature review on the factors that have been demonstrated to affect the algal growth in WSP systems. The potential mitigation methods were reviewed and discussed in detail.

Chapter 3 presents a comprehensive review on the CW system and substrate materials that been employed in CW systems. Available organic-based and mineral-based materials that have been or could be utilized as substrate in the past decade are critically reviewed.

Chapter 4 is an original research paper presenting a bench-scale laboratory test to identify the best available substrate for the design of subsequent pilot-scale FWS CW that will be employed at the Amherstview WPCP. Four locally available substrates (peat, organic mulch, gravel, topsoil) were evaluated based on their performance for attenuating high pH and nutrient levels. Different hydraulic retention time (HRT) and organic concentrations were used to assess their performance.

Chapter 5 is an original research paper primarily focusing on comparing the treatment performance of three small-scale on-site wetland systems with different vegetation and substrate combinations. The tests were originally conducted based on the information yielded by the review and research study described in Chapter 2 and Chapter 4. The effects of employing substrate and vegetation alone and in combination were assessed in the field for their respective ability to mitigate pH and nutrient concentrations. The investigations and findings aimed to derive further information and operational conditions for the subsequent pilot-scale FWS CW at the Amherstview WPCP.

Chapter 6 presents the design and the establishment of the newly designed FWS CW at the Amherstview WPCP for the purpose of mitigating elevated pH effluent from their secondary effluent. This FWS CW was designed based on the information and knowledge we derived and concluded from the previous study in this thesis (Chapter 2, 3, 4 and 5), as well as the USEPA manual of CW treatment of municipal wastewaters. The initial monitoring program and results were also included, and the data collected from the field were utilized to compare the treatment performance of each individual treatment train to determine the best approach.

Chapter 7 concludes the thesis with the contribution of this thesis and proposed recommendations for future works.

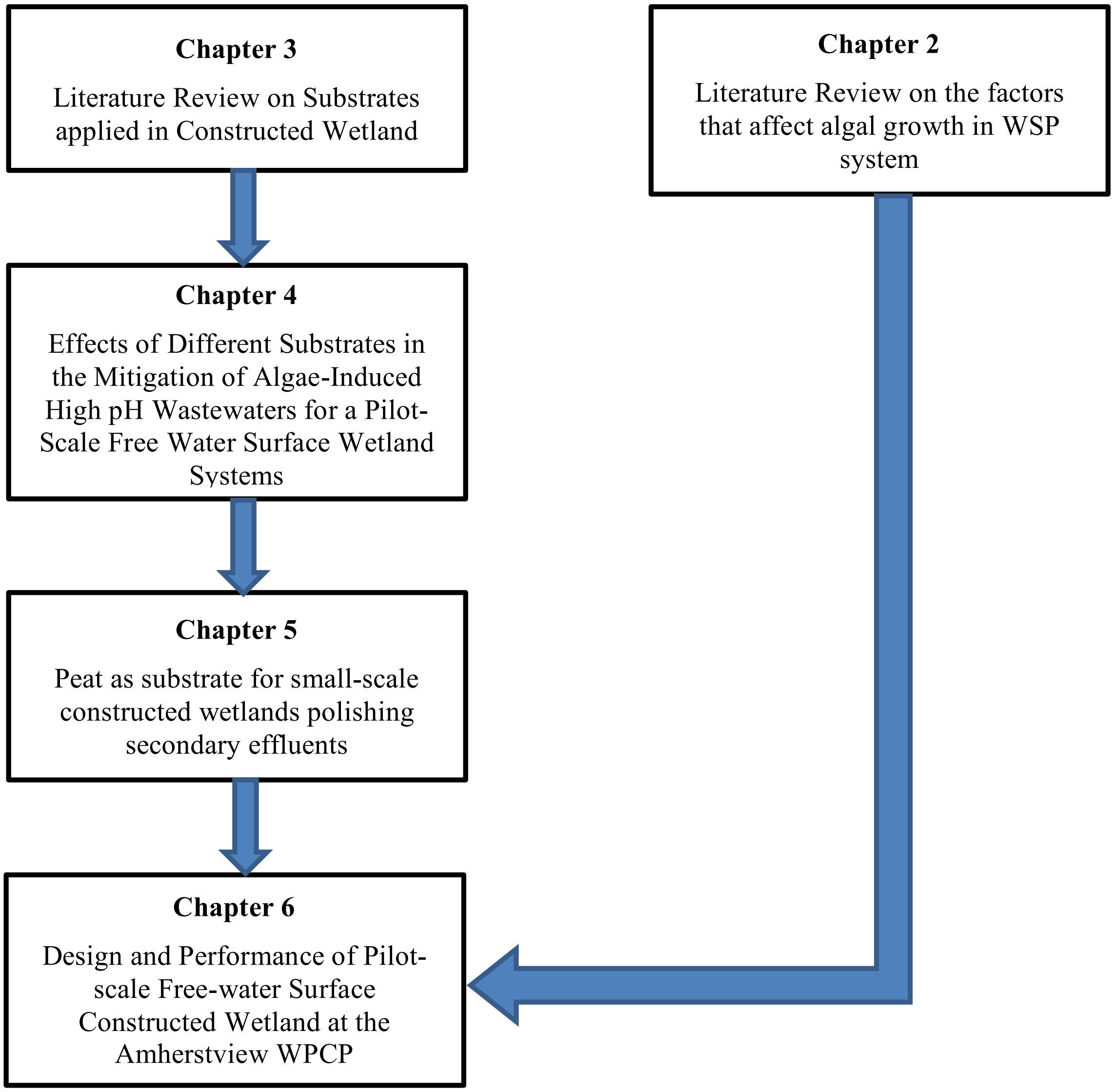


Figure 1.1 Relationship of the Chapters 2 to 6 and the project flowchart

1.4 Reference

Abou-Elela, S. I., Golinielli, G., Abou-Taleb, E. M., and Hellal, M. S. (2013). Municipal wastewater treatment in horizontal and vertical flows constructed wetlands. *Ecological Engineering, 61*, 460-468.

Aguirre, P., Ojeda, E., GarcÍa, J., BarragÁn, J., and Mujeriego, R. (2005). Effect of water depth on the removal of organic matter in horizontal subsurface flow constructed wetlands. *Journal of Environmental Science and Health, Part A, 40*(6-7), 1457-1466.

Babatunde, A. O., Zhao, Y. Q., Doyle, R. J., Rackard, S. M., Kumar, J. L. G., and Hu, Y. S. (2011). Performance evaluation and prediction for a pilot two-stage on-site constructed wetland system employing dewatered alum sludge as main substrate. *Bioresource Technology, 102*(10), 5645-5652.

Barsanti, L., and Gualtieri, P. (2014). *Algae: Anatomy, biochemistry, and biotechnology*. CRC press.

Cao, W., Wang, Y., Sun, L., Jiang, J., and Zhang, Y. (2016). Removal of nitrogenous compounds from polluted river water by floating constructed wetlands using rice straw and ceramsite as substrates under low temperature conditions. *Ecological Engineering, 88*, 77-81.

Cole, J. J., Likens, G. E., and Strayer, D. L. (1982). Photosynthetically produced dissolved organic carbon: An important carbon source for planktonic bacteria1. *Limnology and Oceanography, 27*(6), 1080-1090.

Crites, R., and Technobanoglous, G. (1998). *Small and decentralized wastewater management systems*. McGraw-Hill.

Currie, D. J., and Kalff, J. (1984). A comparison of the abilities of freshwater algae and bacteria to acquire and retain phosphorus. *Limnology and Oceanography, 29*(2), 298-310.

Daigger, G. T., and Boltz, J. P. (2011). Trickling filter and trickling filter-suspended growth process design and operation: A state-of-the-art review. *Water Environment Research, 83*(5), 388-404.

García, J., Aguirre, P., Barragán, J., Mujeriego, R., Matamoros, V., and Bayona, J. M. (2005). Effect of key design parameters on the efficiency of horizontal subsurface flow constructed wetlands. *Ecological Engineering, 25*(4), 405-418.

Hosetti, B., and Frost, S. (1998). A review of the control of biological waste treatment in stabilization ponds. *Critical Reviews in Environmental Science and Technology, 28*(2), 193-218.

Kadlec, R. H., and Wallace, S. (2008). *Treatment wetlands* (2nd Edition ed.). CRC press, Florida.

Klug, J. L. (2005). Bacterial response to dissolved organic matter affects resource availability for algae. *Canadian Journal of Fisheries and Aquatic Sciences, 62*(2), 472-481.

Knowles, P., Dotro, G., Nivala, J., and García, J. (2011). Clogging in subsurface-flow treatment wetlands: Occurrence and contributing factors. *Ecological Engineering, 37*(2), 99-112.

Li, J., Wen, Y., Zhou, Q., Xingjie, Z., Li, X., Yang, S., and Lin, T. (2008). Influence of vegetation and substrate on the removal and transformation of dissolved organic matter in horizontal subsurface-flow constructed wetlands. *Bioresource Technology, 99*(11), 4990-4996.

Lotito, A. M., De Sanctis, M., Di Iaconi, C., and Bergna, G. (2014). Textile wastewater treatment: Aerobic granular sludge vs activated sludge systems. *Water Research, 54*(0), 337-346.

Mara, D. (1996). Waste stabilization ponds: Effluent quality requirements and implications for process design. *Water Science and Technology, 33*(7), 23-31.

Maynard, H. E., Ouki, S. K., and Williams, S. C. (1999). Tertiary lagoons: A review of removal mecnisms and performance. *Water Research, 33*(1), 1-13.

Miguel, A., Meffe, R., Leal, M., González-Naranjo, V., Martínez-Hernández, V., Lillo, J., Martín, I., Salas, J. J., and Bustamante, I. (2014). Treating municipal wastewater through a vegetation filter with a short-rotation poplar species. *Ecological Engineering, 73*(0), 560-568.

Nivala, J., Knowles, P., Dotro, G., García, J., and Wallace, S. (2012). Clogging in subsurface-flow treatment wetlands: Measurement, modeling and management. *Water Res, 46*(6), 1625-1640.

Pipes, W. O. (1962). Ph variation and bod removal in stabilization ponds. *Journal (Water Pollution Control Federation), 34*(11), 1140-1150.

Reinoso, R., Torres, L. A., and Bécares, E. (2008). Efficiency of natural systems for removal of bacteria and pathogenic parasites from wastewater. *Science of The Total Environment, 395*(2–3), 80-86.

Roadcap, G. S., Kelly, W. R., and Bethke, C. M. (2005). Geochemistry of extremely alkaline (ph > 12) ground water in slag-fill aquifers. *Ground Water, 43*(6), 806-816.

Rodríguez, E., Onstad, G. D., Kull, T. P. J., Metcalf, J. S., Acero, J. L., and von G., U. (2007). Oxidative elimination of cyanotoxins: Comparison of ozone, chlorine, chlorine dioxide and permanganate. *Water Research, 41*(15), 3381-3393.

Schippers, P., Lürling, M., and Scheffer, M. (2004). Increase of atmospheric co2 promotes phytoplankton productivity. *Ecology Letters, 7*(6), 446-451.

Senzia, M. A., Mashauri, D. A., and Mayo, A. W. (2003). Suitability of constructed wetlands and waste stabilisation ponds in wastewater treatment: Nitrogen transformation and removal. *Physics and Chemistry of the Earth, Parts A/B/C, 28*(20–27), 1117-1124.

Shen, Q., Zhu, J., Cheng, L., Zhang, J., Zhang, Z., and Xu, X. (2011). Enhanced algae removal by drinking water treatment of chlorination coupled with coagulation. *Desalination, 271*(1–3), 236-240.

Stefanakis, A. I., Akratos, C. S., Gikas, G. D., and Tsihrintzis, V. A. (2009). Effluent quality improvement of two pilot-scale, horizontal subsurface flow constructed wetlands using natural zeolite (clinoptilolite). *Microporous and Mesoporous Materials, 124*(1–3), 131-143.

Steinmann, C. R., Weinhart, S., and Melzer, A. (2003). A combined system of lagoon and constructed wetland for an effective wastewater treatment. *Water Research, 37*(9), 2035-2042.

Tao, W., and Wang, J. (2009). Effects of vegetation, limestone and aeration on nitritation, anammox and denitrification in wetland treatment systems. *Ecological Engineering, 35*(5), 836-842.

Vymazal, J. (2005). Constructed wetlands for wastewater treatment. *Ecological Engineering, 25*(5), 475-477.

Chapter 2

Factors affect the Algal Bloom in Wastewater Stabilization Ponds and Potential Mitigation Methods

2.1 Introduction

WSPs are considered to be the sustainable technology for small communities that require low-cost and low-maintenance wastewater treatment facilities. They can effectively attenuate organic and nutrient concentrations as well as provide disinfection for municipal wastewater (Maynard et al., 1999; Reinoso et al., 2008; Senzia et al., 2003). However, due to the configuration of WSPs and limited control over these systems, concerns related to performance may arise during certain parts of the year. Elevated temperatures and high levels of solar radiation may lead to deteriorated effluents being discharged from the facility during certain periods of the treatment season. Shallow WSP basins encourage sunlight penetration, which, along with the increased temperature, may provide a favorable environment for algae to thrive during the summer months. This can potentially stimulate excessive algal growth in these WSPs, which coupled with extensive consumption of dissolved CO_2, can result in sustained high pH levels in the system and effluent.

Eutrophication of freshwater and costal marine ecosystems resulting from increased anthropogenic activities and nutrient loadings to receiving environments has become a global problem (Michalak et al., 2013). Eutrophication refers to water pollution caused by an excess of nutrients, such as nitrogen (N), phosphorous (P), and potassium (K).

These nutrients may be released to receiving water bodies through sewage, groundwater, and/or agricultural runoff, potentially leading to the excessive growth of algae, in the form of a bloom. Algal bloom events can occur in a variety of water bodies including fresh water lakes and rivers such as: Lake Erie, (Michalak et al., 2013), Lake Tai (Qin et al., 2010), Lake Winnipeg (Schindler et al., 2012), Yangtze River (Zhou et al., 2017). Algal blooms strongly affect ecosystems and communities who rely on affected water resources. One of the adverse effects of algal blooms are the accumulation of organic matter, as the rates of organic production exceed those of consumption in these water bodies. Under eutrophic conditions, this can lead to the continuous accumulation of organic matter, which consequently destroys the balance of the aquatic ecosystem and enhances the further growth of algae (Jäger et al., 2017). Algae, as photoautotrophic microorganisms, derive their energy for food synthesis from light and are capable of using carbon dioxide as their principal source of carbon. During an algal bloom, the large population of algae can quickly deplete the inorganic carbon source of the water body. As carbonate balance is very important in most aquatic environments, and pH level is governed by the carbonate system, this depletion often causes elevated pH levels. These elevated pH levels can reach a point that is toxic to aquatic life. Another concern associated with algal blooms is the generation of algal toxins, which can not only can affect other organisms, but can also pose important challenges to human health (Deng et al., 2017; He et al., 2016).

In this chapter, the factors affecting the evolution of algal blooms in WSP systems are reviewed. Potential mitigation method will be identified, and the most practical solution will be discussed in detail.

2.2 Factors affecting algal growth in WSP systems

2.2.1 Climate conditions

In the last few decades, climate change and global warming are becoming worldwide concerns, and could be one of the contributing factors to the occurrence of algal bloom events. The Fifth Assessment Report of the IPCC (Intergovernmental Panel on Climate Change) has reported an increase in average air temperature of 0.25°C/decade (IPCC, 2013). As a result of this global warming, the average lake surface temperature and the level of carbon dioxide (CO_2) in the atmosphere have both increased significantly in the past few decades (Yan et al., 2017).

A great number of studies have investigated the relationship between surface water temperature and climatic condition with the growth rate of algae (Coles & Jones, 2000; Raven & Geider, 1988). Cyanobacteria are the predominant algae commonly reported in the algal bloom events that have been extensively studied. LÜrling et al. (2013) conducted a literature survey and a laboratory-scale experiment to investigate the effect of temperature on the growth of cyanobacteria. Their results showed that the optimum growth temperature for cyanobacteria was 29.2°C with a corresponding mean growth rate of 0.92 day^{-1}. Johnk et al. (2008) conducted a study using a phytoplankton competition model coupled with a one-dimensional hydrodynamic model driven by meteorological data to predict the relationship between cyanobacterial growth rates and temperature. Their model predicted that high temperatures led to increased growth rates in cyanobacteria. Another study conducted by Coles and Jones (2000) also confirmed that cyanobacteria exhibited higher photosynthetic activity at warmer temperatures. These results correspond with observed occurrences at the Amherstview WPCP, where algal blooms have been reported during the summer and early autumn, when average water surface temperatures are generally at their highest.

In addition to temperature, light conditions directly affect the photosynthetic activity and the growth of algae. Both the length and intensity of solar radiation from sunlight can affect the growth of algae in water systems. Other researchers have shown that increases in sunlight duration was directly proportional to increases in the number of algae (Al-Qasmi et al., 2012). Amini Khoeyi et al. (2012) also confirmed that the intensity of light had a significant influence on algal growth, where the algae concentration was reported to nearly triple at 100μmol photons $m^{-2}s^{-1}$ compared to 62.5μmol photons $m^{-2}s^{-1}$. Maassarani et al. (2015) conducted a modeling study of algal growth in arctic WSPs and demonstrated the effect of temperature and cloud cover on algal growth in WSPs.

2.2.2 Inorganic carbon

Carbon, the key element for all life on Earth, has a complex global cycle that involves physical, chemical and biological processes. It flows between four major reservoirs including the atmosphere, the hydrosphere, the lithosphere, and living organisms (Barsanti & Gualtieri, 2014). As algae are photoautotrophic, the availability of inorganic carbon can affect the presence of algae in WSP systems. Typically, algae first consume dissolved CO_2 that is either transported from the atmosphere or produced by heterotrophic aquatic microorganisms. When the rate of inorganic carbon utilization exceeds the CO_2 transport rate from the atmosphere, the inorganic carbon available form in the aqueous carbonate system is employed. The bicarbonate and carbonate ions are consumed to supply dissolved CO_2 for algal growth as shown in Figure 2.1. Some algal species can even directly utilize bicarbonate ion as an inorganic carbon source for growth. The production of hydroxide ions during these reactions is the main reason why pH levels increase, and as a result it is not uncommon to observe elevated pH values (pH = 10-11) in WSPs. Schippers et al. (2004) conducted a study to investigate the relationship between atmospheric CO_2 and algal growth in eutrophic freshwater. Their results indicated that the growth of algae doubled with the doubling of atmospheric CO_2 concentrations under eutrophic conditions. They also concluded that freshwaters with low alkalinity appeared to be very sensitive to atmospheric CO_2 fluctuations.

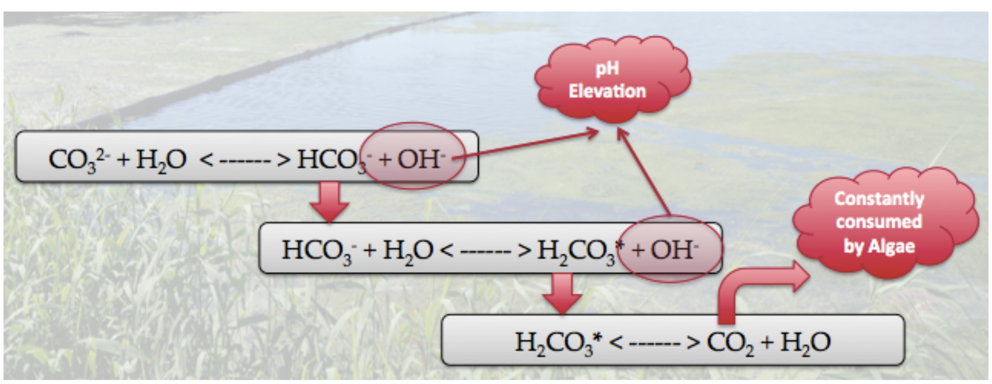


Figure 2.1 The Effects of Algae on Carbonate System in WSP Systems

2.2.3 Nutrients

Aside from climatic conditions and carbon sources, nutrient availability in WSPs is also very important. Of all the essential minerals, nitrogen and phosphorus are the two most important nutrients that affect algal growth (Barsanti & Gualtieri, 2014). Phosphorus is necessary in DNA, RNA, and energy transfer; and nitrogen is needed for protein synthesis. Hence, both are required to support the growth of algae and are the key limiting nutrients in most aquatic ecosystems (Conley et al., 2009). Schindler (1988) produced convincing evidence regarding the importance of phosphorous as a primary limiting nutrient in a whole-lake study. It is required in the cellular synthesis of nucleic acids and membrane phospholipids, as well as for energy transfer through tri- and bi-phosphorylated nucleotides (Degerholm et al., 2006). Orthophosphate is the most readily available dissolved inorganic phosphorous for algal use and is commonly monitored to indicate the availability of phosphorous in WSPs (Shun et al., 1994).

Although, it is clear that phosphorous is of great importance as a limiting nutrient in freshwater ecosystems, scientists have indicated that nitrogen could be both a primary or secondary limiting nutrient as well (Elser et al., 1990). Goldman (1981) demonstrated that the addition of nitrogen alone could enhance algal growth rates in Lake Tahoe. Another study conducted by Elser and Kimmel (1985) further demonstrated that much greater algal growth was achieved when both nitrogen and phosphorus were added to the system.

Since both phosphorous and nitrogen have been shown to be limiting factors in algal growth, studies have focused on determining whether the systems have been phosphorous-limited or nitrogen-limited. The atomic concentration of nitrogen and phosphorous in the water has often been used to indicate differential nutrient limitations. Redfield first reported that an N:P ratio < 16:1 could be used to indicate that nitrogen is less abundant than P with respect to algal metabolic demand. Currie and Kalff (1984) conducted mesocosm experiments with different N:P ratios to investigate the effects of nutrients limitations and concluded that nitrogen more directly controlled the growth of algae.

The degree to which limited nutrient availability potentially reduces algal growth rates has been assessed in a number of ways including physiological studies, experimental studies, and ecosystem studies. Elser et al. (1990) conducted a review and noted that little support could be found that P was the predominant limiting nutrient. Conley et al. (2009) further demonstrated that the regulation of both nitrogen and phosphorus was the best approach to controlling algal blooms in fresh water lakes.

2.2.4 Competition from Heterotrophic Microorganisms

As mentioned above, the synergy between algae and heterotrophic microorganisms is an important feature of WSPs. Therefore, the amount of algal growth in WSPs could have an effect on the growth of heterotrophic bacteria and vice versa, since both require the same nutrients (nitrogen and phosphorus). Aside from nutrients, carbon is another essential element required for microbial growth. However, algae require inorganic carbon sources such as dissolved CO_2, carbonate and/or bicarbonate ions, while heterotrophic microorganisms require organic carbon such as dissolved organic matter (DOM) to sustain their growth. Microorganisms can only grow when both carbon and nutrients are sufficiently available in the system. Therefore, a number of studies have focused on determining algal and heterotrophic microorganism responses to changes in nutrients and DOM in freshwater lakes and ponds system.

The interactions between algae and heterotrophic microorganisms often seem paradoxical. A study conducted by Currie and Kalff (1984) showed that heterotrophic bacteria were stronger competitors for nutrients, particularly for phosphorus and should outcompete algae easily under phosphorus-limited environments. However, the reality is that algae and bacteria coexist in all lakes, and algae even outcompete bacteria in some oligotrophic lake. One of the rationales provided by Klug (2005) was that algae are nutrients-limited and bacteria are energy-limited (carbon-limited) in many cases. Under energy-limited conditions, bacteria depend on the extracellular release of organic carbon by algae, which further stimulate the growth of algae (Cole et al., 1982). When bacteria are under nutrient-limited conditions rather than energy-limited conditions, this reduces or eliminates the dependence on algae-produced organic carbon. Under these conditions, bacteria are in direct competition with algae for mineral nutrients, and their enhanced ability to assimilate nutrients should stimulate their growth to outcompete algae (Drakare, 2002; Jansson et al., 1999). Drakare (2002) conducted a laboratory-scale study to investigate the competitive behavior of heterotrophic bacteria and phytoplankton (cyanobacteria) under different concentrations of phosphorus as an inorganic nutrient, and different relationships between the supply of dissolved organic carbon (DOC) (in the form of glucose) and light. Mixed cultures of heterotrophic bacteria and phytoplankton isolated from dystrophic lakes were employed in their study. The results clearly showed that heterotrophic bacteria had higher maximum specific growth rate than cyanobacteria under all treatment conditions, and cyanobacteria were unable to compete with heterotrophic bacteria for nutrients. Blomqvist et al. (2001) conducted a field-scale study to investigate the effects of DOC on the interaction of heterotrophic bacteria and algae in two oligotrophic lakes. Additional DOC, added in the form of white sugar (sucrose) during two consecutive years, resulted in a significant increase in bacterial biomass and a sharp decrease in the biomass of autotrophic phytoplankton. It was concluded that the increase of available organic carbon had pronounced effects on the biota.

2.3 Potential mitigation methods

As algal blooms can negatively affect the water quality in WSPs, a number of mitigation methods, involving physical, chemical, and biological processes, have been extensively studied to remove algae from WSPs, as well as to attenuate the elevated pH effluents in order to meet the regulatory discharge guidelines.

2.3.1 Physical mitigation processes

With the exception of filtration, most physical treatment processes have not been shown to be effective at removing algae in WSP. The installation of a gravel filter bed is an option to reduce the growth rate of algae, as well as attenuate the wastewater pH, but is susceptible to clogging over time (Sapkota & Bavor, 1994; Steinmann et al., 2003). Other physical treatment processes, such as sonication, are often used in combination with chemical treatment processes to enhance the coagulation and flocculation of algal biomass (Zhang et al., 2006). Ultrasounic irradiation can also be used as an effective method to enhance the removal of algae by coagulation (Heng et al., 2009). Dissolved air floatation (Bare et al., 1975) and active aeration are also employed in WSPs, not only to improve the algal removal efficiency, but also to encourage the introduction of CO_2 into the system in order to balance the carbon cycle (Roadcap et al., 2005; Schramke, 1992).

2.3.2 Chemical mitigation processes

Chemical processes such as coagulation, flocculation, and chlorination have been proposed to removal algal cells in a wide variety of applications (Shen et al., 2011). Among these chemical treatment processes, coagulation and flocculation are the primary mechanisms used to remove algae from the water column through precipitation. Alum is a common coagulant and can effectively control algae and phosphorus concentrations via coagulation and flocculation processes (Al-Layla & Middlebrooks, 1975). Aluminum modified materials, such as aluminum modified clay, are also commonly used as alternative coagulants to control the algal blooms, and has been fully implemented in the field. Liu et al. (2016b) investigated three different aluminum-modified clays, including aluminum chloride modified clay (AC-MC), aluminium sulfate modified clay (AS-MC), and polyaluminum chloride modified clay (PAC-MC), for the removal of algae. Their results showed that AC-MC and AS-MC were more effective than PAC-MC. The primary mechanism of the removal of algae by modified clays was reported to be sweep flocculation by transformation of the hydrolyzed monomers (Al_a) into $Al(OH)_3$ upon addition to the aqueous algal culture; most of AC-MC and AS-MC could be hydrolyzed to Al_a, while only small fraction of PAC-MC could be hydrolyzed to Al_a. Shi et al. (2016) investigated another inexpensive and biodegradable modifier, cationic starch (CS), to transform local soils into an effective flocculant for *Microcystis aeruginosa* removal. CS is a commonly used organic coagulant used to flocculate negatively charged pollutants, such as algae, in wastewater treatment. Their results showed that 86% of *M. aeruginosa* cells were removed within 30 min, when 10 mg/L of CS modifier was employed with a soil concentration of 100 mg/L.

In addition, enhanced coagulation methods are becoming increasingly popular and have included pretreatment processes to further improve the algal coagulation efficiency. A number of studies have shown that pretreatment with preoxidants such as ClO_2, O_3 (Rodríguez et al., 2007), $KMnO_4$ (Ma & Liu, 2002), $CuSO_4•5H_2O$ (García-Villada et al., 2004) can enhance algal removal. These preoxidants can improve conventional coagulation by inactivating or destabilization of algal cells, or liberating extracellular organic matter (Shen et al., 2011).

Surfactants or biosurfactants have also been tested for the mitigation of algal blooms. Sun et al. (2004b) used the chemically synthesized surfactant cocamidopropyl betaine (CAPB) for algal blooms mitigation. Their results showed that more than 90% of *Cochlodinium polykrikoides* were lysed with an intial concentration of 10 mg/L CAPB after 24 hours. Sun et al. (2004a) also tested another surfactant called sophorolipid to mitigate the effects of algal blooms. Their results indicated that the optimum concentration of sophorolipid was 10-20 mg/L, and quick lysis of *Heterosigma akashiwo* and *C. polykrikoides* could be achieved.

2.3.3 Biological mitigation processes

Similar to WSPs, constructed wetlands (CWs) are also a sustainable wastewater technology that has been employed for treating wastewater. It typically serves as a tertiary or polishing treatment process and has been approved as a reliable treatment system for decades. This technology is attractive because of its low-costs and low-maintenance requirements (Gschlößl et al., 1998). Previous studies have shown that CWs can be used to mitigate the cyanobacterial or algal bloom. Steinmann et al. (2003) tested a combination of a lagoon and a horizontal subsurface flow planted filter dam (constructed wetland) systems to attenuate the excessive growth of algae and the resulting elevated pH effluent. The results showed that the system can effectively buffer the pH level to below 8.5 at the outlet. They concluded that the retention of algae was related to the enhanced treatment of organic components, including five-day biological oxygen demand (BOD_5), total nitrogen (TN), and total phosphorous (TP). Wu et al. (2010) investigated a biopond-wetland system to control cyanobacterial bloom and stabilize and increase biodiversity in a pond. Their results demonstrated that the biopond-wetland system could control cyanobacterial blooms, as the system overall removal efficiencies of Chl-a, TN, TP, and ammonia were 83%, 57%, 70%, and 66%, respectively, in summer, and 66%, 40%, 53%, and 49%, respectively, in winter. Free water surface CWs also have been shown to be capable of attenuating extreme pH waters to neutral levels. Acidic wastewater from food processing at Connell, Washington, and alkaline wastewater at

Estevan, Saskatchewan have both been successfully neutralized by FWS CWs (Kadlec & Wallace, 2008).

2.4 Summary

WSPs are a sustainable wastewater treatment technology that is widely employed in North America. However, extended hydraulic retention times coupled with higher ambient temperatures and suitable nutrient loadings can encourage the growth of algae, which can deteriorate the effluent water quality and increases effluent pH levels. Several factors play a role in affecting algal growth, including both environmental conditions and human activities.

Potential mitigation methods have been extensively investigated, and physical, chemical, and biological mitigation approaches are available to address the algal bloom events and the resulting elevated effluent pH events in WSPs. Among those methods, CWs, are a sustainable mitigation technology, and a potential candidate that can provide a cost-effective yet efficient treatment performance to deal with these events.

2.5 Reference

Abou-Elela, S. I., Golinielli, G., Abou-Taleb, E. M., and Hellal, M. S. (2013). Municipal wastewater treatment in horizontal and vertical flows constructed wetlands. *Ecological Engineering, 61*, 460-468.

Aguirre, P., Ojeda, E., GarcÍa, J., BarragÁn, J., and Mujeriego, R. (2005). Effect of water depth on the removal of organic matter in horizontal subsurface flow constructed wetlands. *Journal of Environmental Science and Health, Part A, 40*(6-7), 1457-1466.

Al-Layla, M. A., and Middlebrooks, E. J. (1975). Effect of temperature on algal removal from wastewater stabilization ponds by alum coagulation. *Water Research, 9*(10), 873-879.

Al-Qasmi, M., Raut, N., Talebi, S., Al-Rajhi, S., and Al-Barwani, T. (2012). *A review of effect of light on microalgae growth.* Paper Proceedings from the Proceedings of the world congress on engineering.

Amini Khoeyi, Z., Seyfabadi, J., and Ramezanpour, Z. (2012). Effect of light intensity and photoperiod on biomass and fatty acid composition of the microalgae, chlorella vulgaris. *Aquaculture International, 20*(1), 41-49.

Babatunde, A. O., Zhao, Y. Q., Doyle, R. J., Rackard, S. M., Kumar, J. L. G., and Hu, Y. S. (2011). Performance evaluation and prediction for a pilot two-stage on-site constructed wetland system employing dewatered alum sludge as main substrate. *Bioresource Technology, 102*(10), 5645-5652.

Bare, W. F. R., Jones, N. B., and Middlebrooks, E. J. (1975). Algae removal using dissolved air flotation. *Journal (Water Pollution Control Federation), 47*(1), 153-169.

Barsanti, L., and Gualtieri, P. (2014). *Algae: Anatomy, biochemistry, and biotechnology*. CRC press.

Blomqvist, P., Jansson, M., Drakare, S., Bergström, A. K., and Brydsten, L. (2001). Effects of additions of doc on pelagic biota in a clearwater system: Results from a whole lake experiment in northern sweden. *Microbial Ecology, 42*(3), 383-394.

Cao, W., Wang, Y., Sun, L., Jiang, J., and Zhang, Y. (2016). Removal of nitrogenous compounds from polluted river water by floating constructed wetlands using rice straw and ceramsite as substrates under low temperature conditions. *Ecological Engineering, 88*, 77-81.

Cole, J. J., Likens, G. E., and Strayer, D. L. (1982). Photosynthetically produced dissolved organic carbon: An important carbon source for planktonic bacteria1. *Limnology and Oceanography, 27*(6), 1080-1090.

Coles, J. F., and Jones, R. C. (2000). Effect of temperature on photosynthesis-light response and growth of four phytoplankton species isolated from a tidal freshwater river. *Journal of Phycology, 36*(1), 7-16.

Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., Lancelot, C., and Likens, G. E. (2009). Controlling eutrophication: Nitrogen and phosphorus. *Science, 323*(5917), 1014-1015.

Crites, R., and Technobanoglous, G. (1998). *Small and decentralized wastewater management systems*. McGraw-Hill.

Currie, D. J., and Kalff, J. (1984). A comparison of the abilities of freshwater algae and bacteria to acquire and retain phosphorus. *Limnology and Oceanography, 29*(2), 298-310.

Daigger, G. T., and Boltz, J. P. (2011). Trickling filter and trickling filter-suspended growth process design and operation: A state-of-the-art review. *Water Environment Research, 83*(5), 388-404.

Degerholm, J., Gundersen, K., Bergman, B., and Söderbäck, E. (2006). *Phosphorus-limited growth dynamics in two baltic sea cyanobacteria, nodularia sp. And aphanizomenon sp* (Vol. 58).

Deng, Y., Wu, M., Zhang, H., Zheng, L., Acosta, Y., and Hsu, T.-T. D. (2017). Addressing harmful algal blooms (habs) impacts with ferrate(vi): Simultaneous removal of algal cells and toxins for drinking water treatment. *Chemosphere, 186*(Supplement C), 757-761.

Drakare, S. (2002). Competition between picoplanktonic cyanobacteria and heterotrophic bacteria along crossed gradients of glucose and phosphate. *Microbial Ecology, 44*(4), 327-335.

Elser, J. J., and Kimmel, B. L. (1985). Nutrient availability for phytoplankton production in a multiple-impoundment series. *Canadian Journal of Fisheries and Aquatic Sciences, 42*(8), 1359-1370.

Elser, J. J., Marzolf, E. R., and Goldman, C. R. (1990). Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of north america: A review and critique of experimental enrichments. *Canadian Journal of Fisheries and Aquatic Sciences, 47*(7), 1468-1477.

García, J., Aguirre, P., Barragán, J., Mujeriego, R., Matamoros, V., and Bayona, J. M. (2005). Effect of key design parameters on the efficiency of horizontal subsurface flow constructed wetlands. *Ecological Engineering, 25*(4), 405-418.

García-Villada, L., Rico, M., Altamirano, M., Sánchez-Martín, L., López-Rodas, V., and Costas, E. (2004). Occurrence of copper resistant mutants in the toxic cyanobacteria microcystis aeruginosa: Characterisation and future implications in the use of copper sulphate as algaecide. *Water Research, 38*(8), 2207-2213.

Goldman, C. R. (1981). Lake tahoe: Two decades of change in a nitrogen deficient oligotrophic lake. *Verh. Int. Ver. Limnol, 21*, 45-70.

Goldman, J. C., and Shapiro, J. (1973). Carbon dioxide and ph: Effect on species succession of algae. *Science, 182*(4109), 306-307.

Gschlößl, T., Steinmann, C., Schleypen, P., and Melzer, A. (1998). Constructed wetlands for effluent polishing of lagoons. *Water Research, 32*(9), 2639-2645.

He, X., Liu, Y.-L., Conklin, A., Westrick, J., Weavers, L. K., Dionysiou, D. D., Lenhart, J. J., Mouser, P. J., Szlag, D., and Walker, H. W. (2016). Toxic cyanobacteria and drinking water: Impacts, detection, and treatment. *Harmful Algae, 54*(Supplement C), 174-193.

Heng, L., Jun, N., Wen-jie, H., and Guibai, L. (2009). Algae removal by ultrasonic irradiation–coagulation. *Desalination, 239*(1), 191-197.

Hosetti, B., and Frost, S. (1998). A review of the control of biological waste treatment in stabilization ponds. *Critical Reviews in Environmental Science and Technology, 28*(2), 193-218.

IPCC. (2013). Fifth assessment report: Climate change 2013: The physical science basis.

Jäger, C. G., Hagemann, J., and Borchardt, D. (2017). Can nutrient pathways and biotic interactions control eutrophication in riverine ecosystems? Evidence from a model driven mesocosm experiment. *Water Research, 115*(Supplement C), 162-171.

Jansson, M., Bergström, A.-K., Blomqvist, P., Isaksson, A., and Jonsson, A. (1999). Impact of allochthonous organic carbon on microbial food web carbon dynamics and structure in lake örträsket. *Archiv für Hydrobiologie, 144*(4), 409-428.

Johnk, K. D., Huisman, J. E. F., Sharples, J., Sommeijer, B. E. N., Visser, P. M., and Stroom, J. M. (2008). Summer heatwaves promote blooms of harmful cyanobacteria. *Global Change Biology, 14*(3), 495-512.

Kadlec, R. H., and Wallace, S. (2008). *Treatment wetlands* (2nd Edition ed.). CRC press, Florida.

Klug, J. L. (2005). Bacterial response to dissolved organic matter affects resource availability for algae. *Canadian Journal of Fisheries and Aquatic Sciences, 62*(2), 472-481.

Knowles, P., Dotro, G., Nivala, J., and García, J. (2011). Clogging in subsurface-flow treatment wetlands: Occurrence and contributing factors. *Ecological Engineering, 37*(2), 99-112.

Li, J., Wen, Y., Zhou, Q., Xingjie, Z., Li, X., Yang, S., and Lin, T. (2008). Influence of vegetation and substrate on the removal and transformation of dissolved organic matter in horizontal subsurface-flow constructed wetlands. *Bioresource Technology, 99*(11), 4990-4996.

Liu, Y., Cao, X., Yu, Z., Song, X., and Qiu, L. (2016). Controlling harmful algae blooms using aluminum-modified clay. *Marine Pollution Bulletin, 103*(1), 211-219.

Lotito, A. M., De Sanctis, M., Di Iaconi, C., and Bergna, G. (2014). Textile wastewater treatment: Aerobic granular sludge vs activated sludge systems. *Water Research, 54*(0), 337-346.

LÜrling, M., Eshetu, F., Faassen, E. J., Kosten, S., and Huszar, V. L. M. (2013). Comparison of cyanobacterial and green algal growth rates at different temperatures. *Freshwater Biology, 58*(3), 552-559.

Ma, J., and Liu, W. (2002). Effectiveness and mechanism of potassium ferrate(vi) preoxidation for algae removal by coagulation. *Water Research, 36*(4), 871-878.

Maassarani, R., Champagne, P., and Hall, G. (2015). *Modelling the effects of varying climate on a waste stailization pond in canadian high arctic.* (Master), Queen's University.

Mara, D. (1996). Waste stabilization ponds: Effluent quality requirements and implications for process design. *Water Science and Technology, 33*(7), 23-31.

Maynard, H. E., Ouki, S. K., and Williams, S. C. (1999). Tertiary lagoons: A review of removal mecnisms and performance. *Water Research, 33*(1), 1-13.

Michalak, A. M., Anderson, E. J., Beletsky, D., Boland, S., Bosch, N. S., Bridgeman, T. B., Chaffin, J. D., Cho, K., Confesor, R., Daloğlu, I., DePinto, J. V., Evans, M. A., Fahnenstiel, G. L., He, L., Ho, J. C., Jenkins, L., Johengen, T. H., Kuo, K. C., LaPorte, E., Liu, X., McWilliams, M. R., Moore, M. R., Posselt, D. J., Richards, R. P., Scavia, D., Steiner, A. L., Verhamme, E., Wright, D. M., and Zagorski, M. A. (2013). Record-setting algal bloom in lake erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proceedings of the National Academy of Sciences of the United States of America, 110*(16), 6448-6452.

Miguel, A., Meffe, R., Leal, M., González-Naranjo, V., Martínez-Hernández, V., Lillo, J., Martín, I., Salas, J. J., and Bustamante, I. (2014). Treating municipal wastewater through a vegetation filter with a short-rotation poplar species. *Ecological Engineering, 73*(0), 560-568.

Nivala, J., Knowles, P., Dotro, G., García, J., and Wallace, S. (2012). Clogging in subsurface-flow treatment wetlands: Measurement, modeling and management. *Water Res, 46*(6), 1625-1640.

Pipes, W. O. (1962). Ph variation and bod removal in stabilization ponds. *Journal (Water Pollution Control Federation), 34*(11), 1140-1150.

Qin, B., Zhu, G., Gao, G., Zhang, Y., Li, W., Paerl, H. W., and Carmichael, W. W. (2010). A drinking water crisis in lake taihu, china: Linkage to climatic variability and lake management. *Environmental Management, 45*(1), 105-112.

Raven, J. A., and Geider, R. J. (1988). Temperature and algal growth. *New Phytologist, 110*(4), 441-461.

Reinoso, R., Torres, L. A., and Bécares, E. (2008). Efficiency of natural systems for removal of bacteria and pathogenic parasites from wastewater. *Science of The Total Environment, 395*(2–3), 80-86.

Roadcap, G. S., Kelly, W. R., and Bethke, C. M. (2005). Geochemistry of extremely alkaline (ph > 12) ground water in slag-fill aquifers. *Ground Water, 43*(6), 806-816.

Rodríguez, E., Onstad, G. D., Kull, T. P. J., Metcalf, J. S., Acero, J. L., and von G., U. (2007). Oxidative elimination of cyanotoxins: Comparison of ozone, chlorine, chlorine dioxide and permanganate. *Water Research, 41*(15), 3381-3393.

Sapkota, D. P., and Bavor, H. J. (1994). Gravel media filtration as a constructed wetland component for the reduction of suspended solids from maturation pond effluent. *Water Science and Technology, 29*(4), 55-66.

Schindler, D. W. (1988). Experimental studies of chemical stressors on whole lake ecosystems. *Internationale Vereinigung fuer Theoretische und Angewandte Limnologie Verhandlungen IVTLAP, 23*(1).

Schindler, D. W., Hecky, R. E., and McCullough, G. K. (2012). The rapid eutrophication of lake winnipeg: Greening under global change. *Journal of Great Lakes Research, 38*(Supplement 3), 6-13.

Schippers, P., Lürling, M., and Scheffer, M. (2004). Increase of atmospheric co2 promotes phytoplankton productivity. *Ecology Letters, 7*(6), 446-451.

Schramke, J. A. (1992). Neutralization of alkaline coal fly ash leachates by co2(g). *Applied Geochemistry, 7*(5), 481-492.

Senzia, M. A., Mashauri, D. A., and Mayo, A. W. (2003). Suitability of constructed wetlands and waste stabilisation ponds in wastewater treatment: Nitrogen transformation and removal. *Physics and Chemistry of the Earth, Parts A/B/C, 28*(20–27), 1117-1124.

Shen, Q., Zhu, J., Cheng, L., Zhang, J., Zhang, Z., and Xu, X. (2011). Enhanced algae removal by drinking water treatment of chlorination coupled with coagulation. *Desalination, 271*(1–3), 236-240.

Shi, W., Bi, L., and Pan, G. (2016). Effect of algal flocculation on dissolved organic matters using cationic starch modified soils. *Journal of Environmental Sciences, 45*(Supplement C), 177-184.

Shun, Y., McKelvie, I. D., and Hart, B. T. (1994). Determination of alkaline phosphatase-hydrolyzable phosphorus in natural water systems by enzymatic flow injection. *Limnology and Oceanography, 39*(8), 1993-2000.

Stefanakis, A. I., Akratos, C. S., Gikas, G. D., and Tsihrintzis, V. A. (2009). Effluent quality improvement of two pilot-scale, horizontal subsurface flow constructed wetlands using natural zeolite (clinoptilolite). *Microporous and Mesoporous Materials, 124*(1–3), 131-143.

Steinmann, C. R., Weinhart, S., and Melzer, A. (2003). A combined system of lagoon and constructed wetland for an effective wastewater treatment. *Water Research, 37*(9), 2035-2042.

Sun, X.-X., Choi, J.-K., and Kim, E.-K. (2004a). A preliminary study on the mechanism of harmful algal bloom mitigation by use of sophorolipid treatment. *Journal of Experimental Marine Biology and Ecology, 304*(1), 35-49.

Sun, X.-X., Han, K.-N., Choi, J.-K., and Kim, E.-K. (2004b). Screening of surfactants for harmful algal blooms mitigation. *Marine Pollution Bulletin, 48*(9), 937-945.

Tao, W., and Wang, J. (2009). Effects of vegetation, limestone and aeration on nitritation, anammox and denitrification in wetland treatment systems. *Ecological Engineering, 35*(5), 836-842.

Vymazal, J. (2005). Constructed wetlands for wastewater treatment. *Ecological Engineering, 25*(5), 475-477.

Vymazal, J. (2008). Constructed wetlands, subsurface flow. In Sven Erik JørgensenBrian D. Fath (Ed.), *Encyclopedia of ecology* (pp. 748-764). Oxford: Academic Press.

Wu, Y., Kerr, P. G., Hu, Z., and Yang, L. (2010). Removal of cyanobacterial bloom from a biopond–wetland system and the associated response of zoobenthic diversity. *Bioresource Technology, 101*(11), 3903-3908.

Yan, X., Xu, X., Wang, M., Wang, G., Wu, S., Li, Z., Sun, H., Shi, A., and Yang, Y. (2017). Climate warming and cyanobacteria blooms: Looks at their relationships from a new perspective. *Water Research*.

Zhang, G., Wang, B. O., Zhang, P., Wang, L. I., and Wang, H. U. I. (2006). Removal of algae by sonication-coagulation. *Journal of Environmental Science and Health, Part A, 41*(7), 1379-1390.

Zhou, Z.-X., Yu, R.-C., and Zhou, M.-J. (2017). Resolving the complex relationship between harmful algal blooms and environmental factors in the coastal waters adjacent to the changjiang river estuary. *Harmful Algae, 62*(Supplement C), 60-72.

Chapter 3

Substrates Applied in Constructed Wetland Systems for Wastewater Treatment: A Review (2008-2017)

Abstract: Constructed wetlands (CWs) are a sustainable wastewater treatment technology that has been widely employed for treating a variety of wastewaters in North America. The benefits of employing CWs in wastewater treatment include low capital and operational costs, and minimal maintenance requirement. As a sustainable technology, the treatment in CWs is provided by the interaction of vegetation, substrate and microorganisms within these systems, and do not require external chemical and energy sources. Among those elements, substrates play an important role in CWs, as they not only provide the rooting medium for vegetation, but also encourage the growth of a diversity of microorganisms. In recent years, a variety of substrate materials have been studied that are employed in CW systems, and cost-effective, environmental friendly, and readily available substrates are more desirable. Those substrate materials can be separated into two main categories: mineral-based and organic-based substrates. Mineral-based substrates are mainly derived from mineral deposits, while organic-based substrates mostly come from the decomposition plants and animals, as well as their waste products. This paper provides a comprehensive review of CW systems, as well as the substrate materials that have been most commonly investigated and applied in the past decade.

Keywords: Constructed wetland, substrate, organic, mineral, sustainable

3.1 Introduction

Constructed wetlands (CWs) are engineered systems that take advantage of many of the same processes that occur in natural wetlands, but do so in an engineered environment (Kadlec & Wallace, 2008). Modern CWs have been designed to promote specific characteristics of wetland ecosystems, with the aim of improving wastewater treatment performance and have been widely applied to treat a variety of wastewaters including municipal wastewater (Abou-Elela et al., 2013; Kõiv et al., 2009; Wang et al., 2005), industrial wastewater (Calheiros et al., 2009; Chen et al., 2006), agricultural runoff (Beutel et al., 2013; Schierano et al., 2017), and landfill leachate (Sim et al., 2013; Wallace et al., 2015).

CWs used for wastewater treatment can be classified into different categories depending on the predominant macrophytes (free-floating, rooted emergent, and submerged macrophytes), the water level in relation to the surface (free water surface, subsurface) and, in the case of subsurface wetlands, the direction of flow (horizontal and vertical). Currently, there are a few types of CWs that have been extensively used and studied for the treatment of wastewater, including: free water surface (FWS) (Jin et al., 2017b; Maine et al., 2017), horizontal subsurface flow (HSSF) (Schierano et al., 2017; Stefanakis et al., 2016), and vertical subsurface flow (VSSF) (Paing et al., 2015; Yun et al., 2015), floating wetlands (Cao et al., 2016; Saeed et al., 2016), and hybrid wetlands (Sehar et al., 2015b; Zhao et al., 2016).

3.2 Constructed wetland types

3.2.1 Free water surface constructed wetlands

Although the very first experiment conducted in a CW was by German scientist Kathe Seidel using horizontal and vertical subsurface flow in late 1960s, the first fully implemented CW was a FWS system built in the Netherlands in 1967 (Jong, 1976). This type of wetland consists of an open water area, floating or emergent vegetation and rooting media. Figure 3.1 is a technical schematic of a typical FWS CW. It is similar to a natural wetland system, but incorporates a number of engineering design considerations. Deep inlet and outlet deep zones are designed to prevent the clogging of water distribution pipes and encourage the removal of suspended solids. Substrate or rooting media in a FWS CW are provided to facilitate the growth of a wide variety of potential vegetation. The presence of vegetation or macrophytes is one of the most distinguishing features of CWs and differentiates them from unplanted soil filters or lagoons. Vymazal (2013a) conducted a literature survey of 643 FWS CWs from 43 countries and reported that 150 plant species have been used in FWS CWs including *Typha, Scirpus* (Schoenoplectus), *Phragmites, and Juncus*, which are the most common plants used in North American FWS CWs. A typical FWS CW has a free water depth of 20-40cm, with 20-30cm of rooting soil or substrate. The shallow pond depth favours the removal of organics by facilitating more oxygen to transfer throughout the water column of the CWs (Vymazal, 2013a). Generally speaking, a longer hydraulic retention time allows for a longer contact time between the wastewater and microorganisms in CWs, which generally translates to a higher quality effluent (Wu et al., 2015). However, retention times longer than 5 days in one treatment cell are not recommended, since this can allow undesirable microorganisms, such as algae to grow. Multiple cells or cells in series are recommended to allow the flow to be distributed more evenly and improve the hydraulic performance by minimizing the occurrence of dead zones (Kadlec & Wallace, 2008; USEPA, 2000). This type of wetland can be used in a wide range of climates, including the arctic, however, treatment performance may be compromised by the colder water temperatures, which slow treatment processes that rely on biological activity (Werker et al., 2002; Wittgren & Mæhlum, 1997).

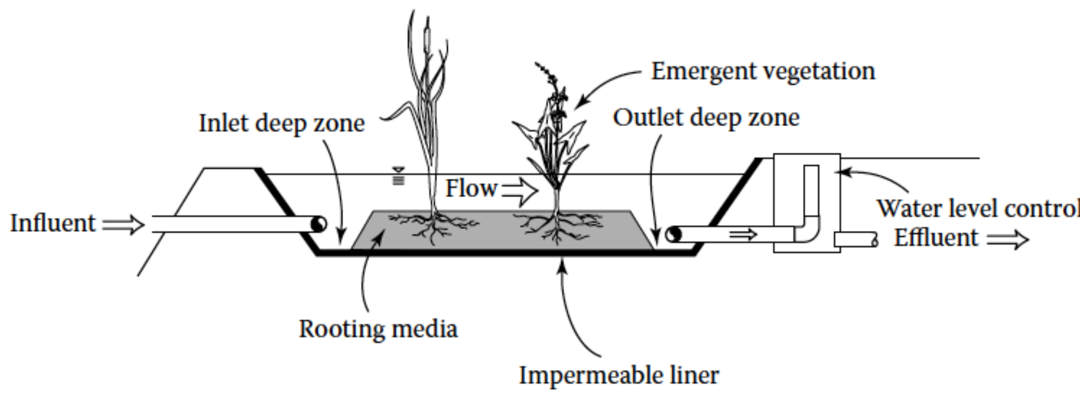


Figure 3.1 Technical Schematic of a Typical FWS CW (Kadlec & Wallace, 2008)

The main removal mechanisms for suspended solids in FWS CW include: sedimentation, filtration, aggregation and surface adhesion. Settable organics are removed through sedimentation and filtration, while soluble organic compounds are removed through both aerobic and anaerobic biological degradation. Nitrogen can be effectively removed in FWS CWs through the traditional nitrification/denitrification pathway. NH_4-N is oxidized to NO_2-N or NO_3-N by nitrifying bacteria under aerobic conditions, and NO_2-N or NO_3-N is reduced to nitrogen gas or nitrous oxide by denitrifying bacteria under anaerobic conditions. NH_4-N can also be removed through volatilization when pH levels are high during the day as a result of the algal photosynthesis. Phosphorous is removed through adsorption or absorption processes. (Vymazal, 2014). Depending upon the local regulations and soil conditions, berms and liners can be used to control flow and infiltration (Kadlec & Wallace, 2008).

3.2.2 Horizontal subsurface flow constructed wetlands

HSSF CWs typically consist of a porous media such as gravel or soil bed planted with wetland vegetation as shown in Figure 3.2. During the treatment process, wastewater is fed through the inlet of the system and flows through the porous media beneath the surface in a horizontal flow path until it reaches the outlet, where it is collected and discharged (Kadlec & Wallace, 2008; Vymazal, 2008). Compared with FWS CWs, HSSF CWs contain roughly the same components, with the exception of the substrate which fills the entire treatment area. Wastewater passes through the system below the substrate surface without the presence of a free water present. As such, wastewater is not exposed to surface influences (such as wildlife) during the treatment process, which greatly reduces the potential for contamination by organisms such as pathogenic fecal bacteria. When properly engineered and operated, HSSF CWs do not provide a habitat for mosquitoes and other unwanted wildlife (Kadlec & Wallace, 2008). Plants play an important role in HSSF CWs as well, providing a source of substrate for microbial growth, oxygen by diffusion from the roots to the rhizosphere, which enhances biological and nutrient uptake processes. At lower temperatures, plants also provide insulation.

The configuration of HSSF discourages the transfer of oxygen into the system, resulting in substantial inhibition of aerobic processes. The shallow top layer of the water column and rhizosphere are two areas where aerobic conditions may exist due to the atmospheric oxygen transfer and oxygen exuded from the roots to the rhizosphere, respectively. The remaining area of substrate is predominated by anoxic/anaerobic processes (Vymazal, 2008). HSSF CWs exhibit higher removal efficiencies for suspended solids than FWS CWs as a result of filtration and sedimentation processes within the substrate. Particulate organic matter can also be removed through these processes as well, while soluble organic matter is decomposed by both aerobic and anaerobic microbial processes. Nitrogen is primarily removed by nitrification/denitrification as in the FWS CWs. However, the nitrification process is hindered by the limited amount of oxygen/aerobic conditions in the HSSF wetlands results in a weak NH_4-N removal (Abou-Elela et al., 2013). Conversely, the denitrification process benefits from the anaerobic conditions, which favour denitrifying bacteria. Phosphorous is removed by adsorption and precipitation in HSSF wetlands. The selection of substrate is critical, with high phosphorus-binding capacity materials (such as calcium, iron and aluminum rich mineral substrates) preferred in order to promote phosphorous removal (Yin et al., 2017).

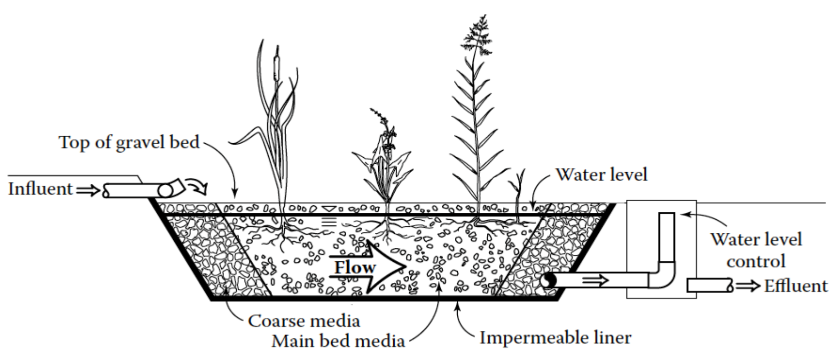


Figure 3.2 Technical Schematic of a Typical HSSF CW (Kadlec & Wallace, 2008)

Although maintenance costs remain low, HSSF CWs are generally more expensive than FWS CWs due to the cost associated with the large amounts substrate required. As such, they are commonly installed in small-scale applications. Clogging is one of the major issues common to all subsurface CWs. The cumulative biological, chemical, and physical treatment processes may cause gradual clogging of the substrate/porous media, which may be accompanied by hydraulic malfunctions and/or decrease in treatment performance (Knowles et al., 2011). As such, regular monitoring and maintenance with periodic substrate replacement is needed to maintain treatment performance.

3.2.3 Vertical subsurface flow constructed wetlands

Vertical subsurface flow (VSSF) CWs were originally introduced by Seidel (Seidel, 1953), but did not spread quickly due to the high cost of construction and operation, as well as their high maintenance requirements. Recently, however, these systems have gained more attention because of the more stringent discharge limits that have been introduced in many jurisdictions in the last decade and the quality of discharged effluent these systems can produce (Abou-Elela et al., 2013; Huang et al., 2015). VSSF CWs consist essentially of the same components as HSSF CWs. Figure 3.3 represents a typical technical schematic of a VSSF CW. The differences between VSSF CWs and HSSF CWs are the direction of flow of the wastewater and the mode of operation. In VSSF CWs, wastewater flows through the system vertically either from bottom to the top or vice versa. They can be operated under two different modes to achieve different treatment objectives. When operated to promote aerobic conditions, wastewater is fed through in large batches and then percolates down through the substrates, subsequently, a new batch is fed through when the top bed is free of water. This enables the passive diffusion of oxygen from the atmosphere into the bed. As a result, VSSF CWs are far more aerobic than HSSF CWs and provide ideal conditions to promote nitrification. However, the aerobic conditions unavoidably inhibit the subsequent denitrification process.

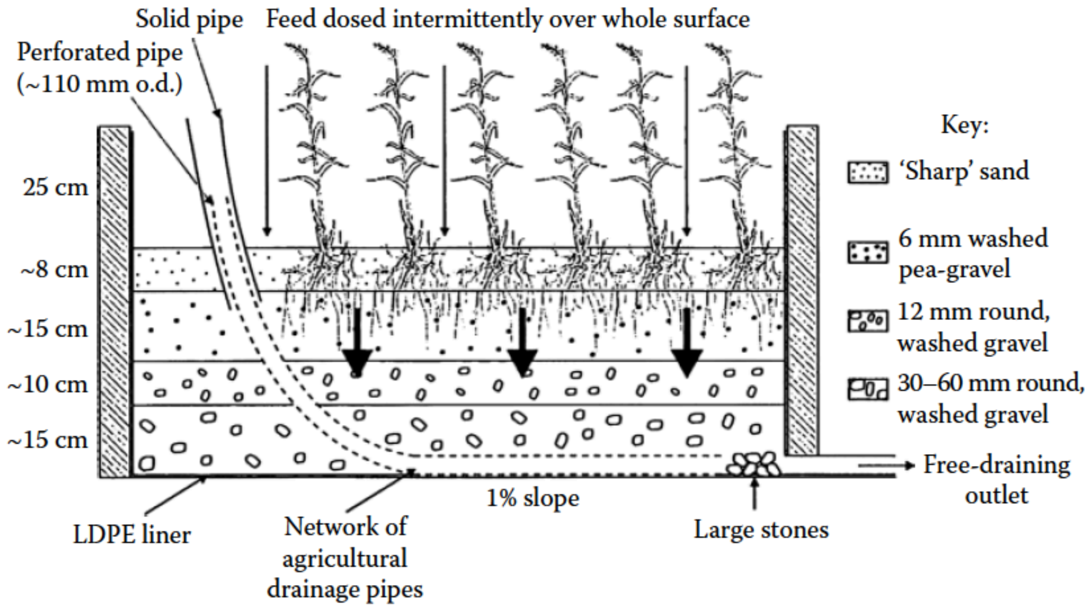


Figure 3.3 Technical Schematic of a Typical VSSF CW (Kadlec & Wallace, 2008)

3.2.4 Floating constructed wetlands

Floating vegetation islands form naturally in a variety of water bodies and the function and operation of floating CWs are based on the nature of these dense and often varied vegetation islands. The structure of floating CWs mainly consists of emergent vegetation established upon a buoyant mat, where the upper part of the emergent vegetation is primarily above water level, while the roots are hang down to the water column, developing an extensive beneath water-level root zone (Pavlineri et al., 2017). As water passes beneath the buoyant mat, constituents can be removed by the emergent vegetation, biofilm development, extracellular enzyme release, and contaminant settling through various nutrient and metal phytoremediation removal mechanisms (Yeh et al., 2015).

Floating CWs are mainly employed to remove excess nitrogen and phosphorous from water bodies, as these are the key nutrients responsible for algal blooms. Biomass from emergent vegetation can be harvested and used as fertilizer or animal feed to add economic value to the system.

3.2.5 Hybrid constructed wetlands

Hybrid CWs refer to wetland systems made up of various types of CWs used in combination to achieve specific treatment objectives or higher treatment efficiencies, particularly for nitrogenous compounds. The hybrid systems most frequently consist of HSSF and VSSF systems in series, relying on the advantages of each system in sequence (Cooper, 1999). The combined VSSF-HSSF wetland systems have frequently been used to achieve fully-nitrified effluents, as VSSF systems can provide suitable conditions for nitrification, while HSSF systems can provide suitable conditions for denitrification.

3.3 Substrates in constructed wetlands

Substrates in CWs play a vital role in facilitating the removal of different kinds of contaminants from the water column. They not only provide the medium to allow the rooted macrophytes to grow, but also provides an environment for biofilm to develop. A variety of substrates have been applied and tested in CW applications, with different types creating different environments that can support a variety of microorganisms, which in turn promote different biochemical processes.

The literatures covered in this review will focus research studies from 2008 to 2017. CWs, as natural wastewater treatment systems, are mainly designed to stimulate the decomposition of organic matter, as well as the reduction of nutrients. As such, this review will mainly highlight the removal of organic matter, nitrogenous compounds and phosphorous.

Considering that a number of studies have examined multiple substrates on the removal of specific contaminants or tested individual substrates and their ability to remove multiple contaminants, a comprehensive side by side comparison of substrates has not been completed to date. To offer a comprehensive overview, the literatures included in this review is listed in Table 1 in reverse chronological order with general information on the study including: wastewater type, wetland flow, macophytes, substrate, and experimental scale and size. Table 2 shows the removal efficiencies of pollutants of interest across a number of studies. Substrates were separated into two categories: mineral-based substrates and organic-based substrates. Mineral-based substrates are typically naturally occurring inorganic solids with a specific chemical composition, and an ordered atomic arrangement. Some of them are recognized as conventional substrates, such as gravel, as they have been widely utilized in CW applications (Abou-Elela et al., 2013; Dotro et al., 2012; Mateus et al., 2012). Recently, alternative mineral-based substrates, such as zeolites, have become more and more attractive due to their advantageous physical and chemical properties for nutrient retention. Organic-based substrates are mostly derived from residual biomass from plants and animals, as well as their waste products, such as peat and wheat straw. However, they can also be made by chemical reactions in the laboratory as well. Some of the most widely used organic substrates in CWs include rice straw, mulch and alum sludge (Cao et al., 2016; Herrera-Melián et al., 2014; Zhao et al., 2011).

3.3.1 Mineral-based substrates

3.3.1.1 Gravel

Gravel is the most widely used substrate material in CWs due to its availability and relatively low cost. It is also considered to be a conventional substrate for wetland applications. A great number of CW studies have been conducted by applying gravel as the substrate or as part of a combination of substrates. Gravel is a suitable choice for removing organic matter as reported noted in the following studies.

Li et al. (2008) employed gravel in two pilot-scale HSSF CWs with a hydraulic retention time (HRT) of 4 days to study the fate and transformation of dissolved organic matter over a period of approximately half of a year. Microbial analyses of the wastewater revealed that the main mechanism responsible for dissolved organic matter removal was microbial activity by both aerobic and anaerobic bacteria. Although they indicated that the substrate played an important role as a carrier for bacteria, the substrates themselves did not show significant influence in terms of directly removing organics.

Zurita et al. (2009) used a special gravel called volcanic red-orange extrusive rock to compare the treatment performance of HSSF and VSSF CWs. They found that the HSSF CW removed TSS, NO_3-N, and TN effectively, while the VSSF CW exhibited high removal efficiencies for BOD, COD, and TP. They also discovered that the number of plant species could affect the removal of organics, as a wetland with three different species of vegetation showed a higher organics removal efficiency than the wetland only containing one species.

Abou-Elela et al. (2013) monitored two large-scale subsurface CWs for the treatment of municipal wastewater for three years, both of which applied gravel as the sole substrate. Both wetlands performed well with respect to BOD, COD, and TSS removal. However, the VSSF system outperformed the HSSF system in terms of nitrification, primarily due to the better oxygen transfer within the wetland. The higher oxygen concentration in the VSSF system was also reported to provide a more effective pathogen removal compared to HSSF.

Avila et al. (2013) tested a hybrid CW system consisting of two alternating VSSF wetlands, one HSSF wetland, and one FWS wetland in series for the treatment of urban wastewater. Gravel was used as a substrate in both the VSSF and HSSF wetlands. Their system demonstrated a reliable and robust technology for the removal of COD, TSS, and NH_4-N under low hydraulic loading rate (0.18 m/d). This study is among the few studies that tested gravel in CWs for the elimination of emerging organic contaminants (EOCs). Overall, it was found that most of the selected EOCs could be effectively removed except for antibiotics. Further studies are necessary to improve wastewater effluent quality at high hydraulic loading rates.

As noted above, gravel can provide the conditions for the removal organic matter and solids. However, the low specific surface area and cation exchange capacity of gravel limit its ability to remove nitrogenous compounds and phosphorous through adsorption or cation exchange reactions. Therefore, alternative substrates have been investigated primarily to improve the efficiency of nitrogen and phosphorous removal.

3.3.1.2 Decomposed granite

Decomposed granite is similar to gravel and is formed from the natural weathering and erosion of solid granite. Granite is typically finer and more stable than gravel. While decomposed granite is most commonly used for build paths, driveways, and garden trails, it can also be applied in CW as a substrate.

Lai and Lam (2009) used completely decomposed granite and sand to remove phosphorous in a surface flow reed bed located in Hong Kong. Their study indicated that granite contributed to the high concentrations of amorphous iron and aluminum that provide abundant specific surface area for phosphorous retention. As such, a high phosphorous sorption capacity was recorded. However, they found that low phosphorous influents could lead to a potential release of previously adsorbed phosphorous from the sediments back into the water column upon resuspension of bottom sediments caused by wind and water currents.

Dotro et al. (2012) applied granite (diameter 0.1 - 20 mm) in a pilot-scale HSSF CW to promote the treatment of chromium-bearing tannery wastewater. A chromium retention efficiency of 67% to 77% was achieved throughout the experimental period. However, contrary to the study by Lai and Lam (2009), they noted that the limited surface area and cation exchange capacities (0.69 m^2/g, 2.06 meq/100g) significantly limited the retention ability of granite compared to other sorbents.

3.3.1.3 Limestone

Limestone is a sedimentary rock and it mainly consists of the minerals calcite and aragonite, which are different crystal forms of calcium carbonate. Limestone is relatively abundant in nature and make up 10% of sedimentary rocks in the world. Limestone typically has a high calcium content and can directly immobilize phosphates by precipitation reactions with dissolved calcium compounds in the pore water (Kõiv et al., 2010). Raising the pH level is another benefit of applying limestone in CWs, which makes them very useful for treating acid mine drainage.

Guan et al. (2009) tested a combination of three inexpensive substrates, including limestone, in a HSSF CW without vegetation to remove phosphorous from a eutrophic freshwater lake in China. A 41% TP removal efficiency was achieved at an influent concentration of 0.63 mg/L TP in their 44-days experiment. Limestone showed the best phosphorous adsorption performance compared to cinder and loess, which were also used in this study, providing a maximum removal capacity of 2.002 mg P/g limestone. This difference in adsorption performance was attributed to the high calcium content of the limestone (CaO percentage 35.5%).

Lizama Allende et al. (2012) performed a column study demonstrating that applying limestone in a VSSF CW could effectively remove both arsenic (99%) and iron (98%) from a synthetic acid mine drainage wastewater. However, boron could only be removed during the initial stage of the study and was not further removed after four weeks. The effectiveness of limestone in removing iron was largely attributed to its ability to raise pH under acidic conditions, as iron tends to precipitate in high pH environments. The precipitation of iron also caused a simultaneous co-precipitation of arsenic, as positive correlations were found between iron and arsenic concentration in this study.

Mateus et al. (2012) applied limestone, with a CaO percentage of 55%, from a local quarry in a HSSF CW to evaluate its ability to remove phosphorous. The initial phosphorous removal efficiency averaged 80% in the first month, but the average phosphorous removal efficiency was reduced to 60% by the end of the 18-month experimental period. Saturation of the sorption spaces and low biological activity before the establishment of macrophytes in the limestone wetland may have contributed to the decline in phosphorous removal after the first month. Therefore, it was proposed that limestone be employed in CWs as a tertiary treatment, where the phosphorous loading is typically lower, in order to extend the lifespan of the substrate.

Tao and Wang (2009) focused on nitrogenous compound removals in CWs, and investigated the integration of partial nitrification and anaerobic ammonium oxidation (ANAMMOX) by employing limestone as a substrate. With an HRT of 7 days, limestone showed an effective NH_3 and TN removal efficiency when used as a rooting substrates.

Most importantly, limestone increased the pH by 0.4 - 0.9 units, which created ideal conditions for ANAMMOX by increasing the nitrite production.

3.3.1.4 Quartz

Quartz is a mineral composed of silicon and oxygen atoms giving an overall chemical formula of SiO_2. It is the most important sand-forming mineral and has been previously utilized for wastewater treatment. Dorman et al. (2009) applied quartz in a pilot-scale CW to reduce the concentration and the toxicity of constituents of concern such as zinc, chromium, mercury, arsenic, and selenium in simulated ash basin water from a coal-burning power plant. The wetland system showed effectiveness in removing zinc, arsenic, and mercury. However, the removal efficiency of selenium was low, as the effluent concentration was even higher than influent concentrations on occasion. Most of the constituents of concern removals occurred in reducing reactors, which supported a dissimilatory sulfate reduction process. The authors claimed that the rate of contaminants removal was dependent on influent concentration, while the extent of removal was independent of influent concentration. However, the relationship between contaminant removal and substrates type was weak and very little discussion focused on this point.

Jiang et al. (2014) evaluated quartz sand (with quartz crystals (SiO_2) as the predominant mineral), a stable silicate mineral, for adsorptive removal of phosphorous. Only 58.81% of TP was removed during the batch column test, and the corresponding adsorptive capacity was 55.98 mg/kg. Compared to the other substrates (ceramsite, shale and anthracite) in this study, quartz sand exhibited the worst performance. The authors claimed that low phosphorous removal capacity by quartz sand could be attributed to adsorption mechanisms, where electrostatic attraction was predominant for the quartz sand, whereas the chemisorption of the phosphorous was predominant with the other substrates.

3.3.1.5 Zeolite

To date, more than 2000 separate types of zeolites from similar sedimentary rocks of volcanic origin and converted through geological processes, have been recognized in more than 40 countries. Both natural and artificial zeolites attract attention in environmental applications due to their superior physical-chemical properties (Stefanakis et al., 2009). Zeolites are microporous materials with voids smaller than 2 nm, and a very large cation exchange capacity, which presents an advantage over other wetland substrate materials in terms of the diversity of microorganisms, as well as the removal of nitrogen and phosphorous. Several studies have been conducted in the past to explore the full potential of utilizing both natural and artificial zeolites in wetland applications (Li et al., 2015; Stefanakis et al., 2009; Yalcuk & Ugurlu, 2009).

Yalcuk and Ugurlu (2009) employed a combination of zeolite, sand and gravel in a VSSF CW to remove organic matters, NH_4-N, and phosphorous present in landfill leachate. Their study indicated that zeolite can be an effective substrate to remove NH_4-N and phosphorous. However, the presence of competitive ions such as K^+, Na^+, Ca^{2+} and Mg^{2+} in leachate can reduce the NH_4-N adsorption capacity of zeolite (Kietlińska & Renman, 2005). In addition, due to the low biodegradability of landfill leachate (BOD_5/COD ratio less than 0.1), the removal of organic matter was not effective.

Stefanakis et al. (2009) evaluated the effluent quality of two pilot-scale HSSF CWs, with natural zeolite (clinoptilolite), treating synthetic wastewater. High removal efficiencies were found for TKN (83.2%) and NH_4-N (85.5%) compared to wetlands without zeolite (TKN 30.0% and NH_4-N 6.0%, respectively). Interestingly, an increase in temperature only slightly improved the treatment performance in this study. These results were contrary to some other studies, which indicated that biological activity was strongly affected by temperature, and that temperature increases typically significantly enhance the treatment performance. They also noted that fine-grained zeolite proved to be effective in terms of removing organic matter and nitrogenous compounds, while coarse-grained zeolite was better for retaining phosphorous.

Peng et al. (2012) developed a continuous circular-flow corridor wetland for the treatment of the secondary swine wastewater effluent with zeolite. The unique design of the circular-flow corridor wetland provided consistent treatment efficiency even under low-temperature conditions, whereas most wetland applications struggle to provide the same performance during winter. A minimum of 93.9% of removal efficiency was achieved for COD, NH_4-N and phosphorous. These results supported the results from Stefanakis et al. (2009) which showed that zeolite played a vital role in NH_4-N removal during winter, as most of the NH_4-N was removed via adsorption pathways rather than biological activity, which is reduced during winter.

Huang et al. (2013) used natural zeolite (clinoptilolite) in a VSSF CW treating swine wastewater under different recirculation ratios. Removal efficiencies ranging from 82.4% - 94.0% of NH_4-N were recorded for this study, which was found to be higher than a wetland of the same configuration filled with volcanic rock (51.3%-69.4%). Quantitative analyses indicated that ammonium-oxidizing archaea were the dominant ammonium-oxidizing prokaryotes associated with zeolite, whereas *Nitrosospira*-like ammonium-oxidizing bacteria were the dominant ammonium-oxidizing prokaryotes associated with the volcanic rock. These results suggested that these substrates showed a high selectivity for ammonium-oxidizing prokaryotes, which positively affected the NH_4-N removal in CWs.

Liu et al. (2014) further proved the superior ability of zeolite for removing NH_4-N, and a very high NH_4-N removal efficiency (>97%) was achieved in a zeolite-based tidal subsurface flow CW. They confirmed that a large surface area, large micropores and high cation exchange capacity were key to the effective removal of NH_4-N in CWs.

Fei et al. (2015) suggested that the NH_4-N and TN removal ability of zeolite could be further improved by micro-aeration, with areal removal rates of 1.04 g/m^{2}d and 1.10 g/m^{2}d, respectively, compared to 0.58 g/m^{2}d, and 0.65 g/m^{2}d without micro-aeration. However, the authors did indicate that reported removal rates of nitrogenous compounds using zeolite varied widely in the literature due to the variety of available zeolites.

Li et al. (2015) focused on nutrient removal from slightly nutrient-polluted wastewater, where they applied zeolite as a filter medium in both column and CW reactors. Results from column tests showed that a 77% of NH_4-N removal efficiency was achieved with an initial concentration of only 1.75 mg/L. During subsequent reactor experiments, it was found that nutrient uptake by plants played a major role in the removal of both NH_4-N and PO_4-P. However, the presence of substrates such as zeolite could stabilize the wetland system and provide consistent nutrient mitigation when the plant uptake fluctuated between the growth and harvest seasons due to their physical-chemical sorption capacity. Zeolite was reported to have an alumino-silicate cage structure with a higher affinity for NH_4-N than other cations such as Na^+, Ca^{2+}, and Mg^{2+} ions.

Aside from investigating nutrient removal, Lizama Allende et al. (2012) tested different substrates in VSSF CW columns to investigate their effectiveness in removing heavy metals and metalloids from acid mine drainage. Zeolite showed a promise for arsenic and iron removal.

Zeolites have been widely applied in CWs to enhance nitrogen removal, and several studies have reported >90% removal of NH_4-N even under low temperatures. However, the cost of zeolite may be prohibitive for its applicate in large-scale systems.

3.3.1.6 Slag

There are three main types of slags including blast furnace iron slag, basic oxygen furnace steel slag, and electric arc furnace steel slag. Blast furnace slags are the by-products of iron production, while basic oxygen furnace and electric arc furnace slags are by-products of steel production (Proctor et al., 2000). Slags are primarily comprised of fluxing agents (mainly lime) used during the iron and steel making process. Several studies have applied slags in CWs, with most being focused on their potential to remove phosphorous.

Wu et al. (2011) used steel slag in a laboratory-scale non-vegetated VSSF CW to test its long-term performance for phosphorous removal. 90.2% of TP and 96.2% of soluble reactive phosphorous removal efficiencies were achieved when the average phosphorous loading rate varied between 0.9 and 1.5 g TP/m^2 d.

Li et al. (2013) conducted a study to assess the phosphorous removal ability of water-quenched slag, which was collected from a local steel plant and pretreated with 1% of CaO. Their results indicated that phosphorous loading played a vital role in determining the removal efficiency, as 85% of TP removal was achieved when the phosphorous loading was in the range of 12.2 - 36.8 g/m^2d, while the TP removal efficiency decreased to 65% when the loading increased to 48.9 g/m^2d. One of their findings was that only 0.74% of adsorbed phosphorous could be desorbed, which demonstrated that phosphorous adsorption to the slag was not completely reversible. This result suggested that water-quenched slag could be a promising substrate to remove phosphorous in CWs, as most other adsorbents tended to release phosphorous back to water column when adsorption equilibrium was reached.

Yun et al. (2015) examined the phosphorous removal performance of both steel slag and modified steel slag in pilot-scale VSSF wetlands. The maximum phosphorous adsorption capacity was reached at 12.7 mg/g and 9.5 mg/g for modified steel slag and steel slag, respectively. They suggested that optimal performance could be achieved with an HRT of 2 days and influent phosphorous concentration in the range of 3 mg/L and 4.5 mg/L.

Blanco et al. (2016) assessed the potential of basic oxygen furnace steel slag aggregates as substrates in CWs aimed at phosphorous removal. Batch experiments with basic oxygen furnace steel slag showed a PO_4-P removal efficiency between 84 and 99%, with a maximum PO_4-P removal capacity of 8.78 mg/g. The following continuous flow experiments achieved removal efficiencies greater than 95% with a removal capacity of 3.1 mg/g. The removal efficiency depended on Ca^{2+} and OH^-, as calcium phosphate precipitation was identified as the main phosphorous removal mechanism. However, high pH values and electrical conductivity concentrations are side effects of using slag, and further treatment was advised for effluent pH levels rise beyond regulatory effluent discharge requirements.

Li et al. (2016) designed a combined gravel-slag-wood chip substrate for a subsurface CW to explore the potential of utilizing slag to remove organic matter and nitrogenous compounds. The system, along with intermittent aeration, worked well in terms of removing nitrogenous compounds. The gravel and slag produced specific oxygen rich and deprived zones, which proved to be efficient in the removal of nitrogenous compounds and organic matter.

3.3.1.7 Ceramsite

Ceramsite is a lightweight aggregate produced by foaming in a rotary kiln. It has a spherical shape, and the surface is smooth and hard. It has an internal honeycomb structure, with a low density, low thermal conductivity, and high strength characteristics.

Liu et al. (2014) applied biological ceramsite in a tidal flow CW to investigate the removal of NH_4-N. However, only a 34% of the NH_4-N removal efficiency was observed with a maximum NH_4-N adsorption capacity of 2 mg NH_4-N /g ceramsite. The characteristic analyses of biological ceramsite revealed that the micropore volume was drastically decreased over the 200-days operation of their study, and most of these volumes were occupied by NH_4-N, as NH_4-N content in the substrate was high (11.3 mg/g). They concluded that the decreased micropore volume for NH_4-N adsorption might explain the overall poor NH_4-N removal performance over the operation period.

Fei et al. (2015) demonstrated that applying ceramsite with appropriate micro-aeration in a HSSF CW system could effectively enhance the removal of NH_4-N, TN and COD. Maximum removal rates of 1.53 g/m^{2}d, 1.41 g/m^{2}d, and 7.68 g/m^{2}d were achieved for NH_4-N, TN and COD, respectively. When sintered at 1,000℃, many unevenly distributed pores (0.5 μm - 10.0 μm) were identified in the ceramsite microstructure, which is very suitable for microbial growth (Xu et al., 2008). High nitrogen removal rates indicated that the microstructure of ceramsite favored the growth of both nitrifying and denitrifying bacteria.

Cao et al. (2016) applied ceramsite in a floating CW to remove nitrogenous compounds under low temperatures. The ceramsite was collected from a polluted river, and was purified and screened using a 35-mesh sieve with a diameter of 0.47mm. The average NH_4-N, NO_3-N and TN removal efficiencies were 71.6%, 42.2% and 65.6%, respectively. In addition to removing nitrogenous compounds, ceramsite was also noted to facilitate the removal Chl-*a* from the wastewater with an average removal efficiency of 44.94% at an influent concentration of 59.79 mg/L.

Wu et al. (2016) used a cominbed sludge-ceramsite substrate, a highly porous material derived from drinking-water and wastewater treatment sludges. They used a small VSSF CW to enhance the treatment performance of organic matter and nitrogenous compounds. Greater than 85% removal efficiencies of COD and nitrogenous compounds was achieved with the addition of intermittent aeration. However, the performance decreased drastically when intermittent aeration was not provided.

3.3.1.8 Shale

Shale is a sedimentary rock that is formed from the pressure of layers of sediment compressing silt and clay that have settled on the bottom of bodies of water. Drizo et al. (2000) investigated the performance of shale as a sole substrate in CW applications in the late 1990s, where they concluded that shale was an effective alternative substrate in terms of PO_4-P and NH_4-N removal.

Tang et al. (2009) conducted laboratory column experiments to evaluate phosphorous using shale. A maximum phosphorous adsorption capacity of 619.7 mg P/kg shale was reported, and they concluded that the phosphorous adsorption capacity increased as the particle size of shale decreased.

Kasak et al. (2015) applied hydrated oil shale ash in a pilot-scale hybrid CW system to remove organic material, nitrogen and phosphorous. High phosphorous removal efficiencies (98% - 99%) were achieved throughout the entire experiment, and the median effluent phosphorous concentration was 0.2 mg/L for an influent concentration of 17.8 mg/L. They suggested that effective phosphorous removal could be attributed to Ca-phosphate precipitation and the formation of insoluble complexes such as calcium phosphate ($Ca_3(PO_4)_2$) (Kõiv et al., 2010). The capacity of hydrated oil shale ash to remove phosphorous was measured at 17 mg P/g shale ash. Another significant observation was the relatively low CO_2 emission due to its high CO_2 binding capacity that provided by a high amount of reactive calcium oxide (CaO).

3.3.1.9 Oyster Shell

Wang et al. (2013) explored the potential of using oyster shells in a VSSF wetland to remove phosphorous from swine wastewater. The oyster shell was a high calcium by-product of the marine aquaculture, and were collected along the southern coast of the Fujian Province in China. Phosphorous adsorption capacity was investigated in a column study, and was found to be 3.17 mg/g. The following pilot-scale study showed maximum soluble reactive phosphorous and TP removal efficiencies of 96.80% and 95.88%, when the hydraulic loading rate was 0.02 m^3/m^2d. The removal efficiencies decreased to 87.76% and 87.96%, respectively, when the hydraulic loading was increased to 0.06 m^3/m^2d. They concluded that Ca-P precipitation and adsorption were the main mechanisms used to remove phosphorous from VSSF CWs using oyster shells, while plant uptake played a very limited role in phosphorous removal.

Yen and Chou (2016) used oyster shells in a bio-medium tank with vegetation, which was part of a recirculating aquaponic system for the treatment of synthetic wastewater. The results confirmed that oyster shells could effectively remove phosphorous through the production of calcium phosphate precipitate. A scanning electron microscope image showed that the high roughness of the oyster shell surface could readily facilitate microbial adhesion and growth. Their results also showed that oyster shells could remove NH_4-N and BOD_5.

3.3.1.10 Bauxite

Bauxite is a naturally occurring mixture of minerals, rich in hydrated aluminum and ferric oxides, and low in alkali metals, alkaline earths metals and silicates. Due to its high content in iron and aluminum content, bauxite is believed to be an economical material for phosphorous removal. However, a study conducted by Stefanakis and Tsihrintzis (2012a) tested bauxite in a pilot-scale VSSF CW, and surprisingly, the results showed that bauxite did not significantly enhance phosphorous removal. In a subsequent study, Stefanakis and Tsihrintzis (2012b) used bauxite in a gravity filter with vegetation to further purify the effluent from their previous study. In this study, bauxite exhibited a higher phosphorous retentiuon efficiency (up to 67%). They concluded that the contaminant loading rate played an important role in phosphorous removal efficiency by bauxite in a CW.

Despland et al. (2014) investigated nutrient removal and microbial communities in a non-vegetated HSSF CW by applying Bauxsol™ pellets. A Bauxsol™ pellet is a complex mixture of minerals predominantly composed of iron and aluminum oxy-hydroxides from bauxite refinery residue. The high phosphorous retention and high trace-metal binding ability of Bauxsol™ pellets made them more appealing compared to naturally occurring bauxite. Their results illustrated its high phosphorous binding ability with a phosphorous removal efficiency of 95%. Further microbiological studies showed a well-adapted bacterial community attached to Bauxsol™, and an increased richness in bacterial strains were observed overtime. However, TN removal was relatively low (26% -28%), which was mostly be attributed to the inability to remove NO_3-N from the system. A lack of oxygen supply or aeration, as well as organic material likely also hindered the denitrification process.

3.3.1.11 Calcium silicate hydrate

Calcium silicate hydrate is a type of wollastonite made from quicklime and quartz by using hydrothermal synthesis. It has been used as a low-cost, non-toxic, inorganic seeding material for phosphorous recovery (Li et al., 2017). Calcium silicate hydrate has been reported to be excellent for phosphorous control due to its unique characteristics. A study by (Chen et al., 2009) showed that a phosphorous adsorption capacity of 137 mg

P/g could be achieved. Despite its phosphorous retention ability, calcium silicate hydrate has rarely used in CWs applications to date.

Li et al. (2015) employed calcium silicate hydrate in a hydroponic CW to compare its nutrient removal ability to zeolite. In this study, calcium silicate hydrate proved to be effective in the removal of phosphorous, and a much higher removal efficiency of PO_4-P at 90.8% was recorded as it mainly removed PO_4-P through precipitation and crystallization rather than adsorption. However, calcium silicate hydrate required a longer HRT to remove NH_4-N compared to zeolite, as the removal efficiency sharply increased after 24 hours of operation.

3.3.1.12 Calcium attapulgite

Yin et al. (2017) assessed the feasibility of employing thermally-treated calcium-rich attapulgite (TCAP) for removing phosphorous in subsurface flow wetlands. Results from both batch and long-term column experiments indicated that TCAP could be a suitable substrate for CW. The phosphorous sorption capacity of TCAP was in the range of 4.46 to 5.99 mg P/g based on a batch study, and an average phosphorous removal efficiency of 93.1% to 95.4% was achieved in a 150-day column experiment with an eight-hour HRT. The main phosphorous removal mechanism was identified as calcium-phosphorous precipitation, but the species of calcium-phosphorous precipitate formed could vary depending on the influent phosphorous concentrations. As noted in other studies (Barca et al., 2012), the availability of calcium concentration in TCAP might be the limiting factor in phosphorous removal capacity.

3.3.1.13 Clay

Arroyo et al. (2013) applied light expanded clay from the company ARCIRESA in a mesocosm-scale CW in order to specifically remove arsenic and zinc from wastewater. However, the substrates in their study did not play a significant role in heavy metal removal, as the type of flow and plants selection were the main contributors to removal. Moreover, it was also demonstrated that there was no significant difference between utilizing light expanded clay and gravel in their system.

3.3.2 Organic-based substrates

3.3.2.1 Peat

Peat is partially fossilized, decomposed plant matter that is formed in wet areas in the absence of oxygen. Peat has a very high organic content (60% carbon), and is a highly porous substance (80-90%) which typically has a surface area of >200 m^2/g. Due to its unique biological, physical, and chemical properties, it has been used in environmental protection applications in the treatment of wastewaters of various sources and qualities (Kõiv et al., 2006).

Speer et al. (2011) conducted a bench-scale treatability study to investigate the landfill leachate treatment efficiency using peat filters in a semi-passive treatment system. The system effectively removed NH_4-N, and moderately effective removed COD and TP. Wood shaving (pine hamster bedding) was also added to the substrate to reduce the chance of clogging, and a peat to wood shaving ratio of 25:75 (v:v) would experience less peat consolidation. This system was also tested in a pilot-scale at the Merrick Landfill, North Bay, Ontario to evaluated the treatment performance in cold climate in a one-year study (Speer et al., 2012).

Gunes (2007) developed a small-scale CW system using peat as a substrate in treating restaurant wastewater. The system was divided into three layers, and a 10 cm thick peat layer was placed between the bottom and top surface, which was planted with the *Poa trivalis L*. The system was effective in removal of suspended solids and organics (expressed as COD). However, the overall phosphorous removal efficiency was only 40.3%, for a low average effluent concentration of 3.5 mg/L.

Kõiv et al. (2009) studied the treatment capacity of well-mineralized *Sphagnum* peat in both VSSF and HSSF biofilters designed to remove nutrients and organic matter from municipal wastewater and landfill leachate. Peat could maintain good phosphorous removal efficiencies for 6 months in the vertical flow filters, and the maximum phosphorous-binding capacity was 81 mg/kg dry peat. Sufficient O_2 supply and favorable temperatures for the establishment of microbiological communities was important as the vertical flow filters performed far better than the horizontal filters. Moreover, phosphorous removal did not occur when the concentration was lower than 1.5 mg/L in horizontal filters. Therefore, using *Sphagnum* peat in horizontal filters under saturated conditions was not encouraged.

Wang et al. (2010) tested a combination of organic substrates, peat and crushed pine bark for the treatment of liquid sewage sludge with high organic concentrations in a VSSF

CW. The study confirmed that organic substrates could be used to treat organic sludge without any clogging issues throughout the experimental period. The organic substrate did release soluble organic matter, but the amount of leaching decreased over time. The release of nitrogen from the organic substrate was relatively low, though not negligible. Their results also showed that the plant type (*Phragmites australis* in this study compared to *Typha latifolia* and *Iris pseudacorus*), is important and could improve organic matter degradation. The plant variety can also effectively reduce the negative impacts from leaching organic substrates.

Saeed et al. (2012) applied coco-peat in a hybrid wetland system consisting of one horizontal flow and two vertical flow subsurface CWs in the treatment of tannery wastewater in Bangladesh. Coco-peat was extracted from coconut husks with a porosity of 50%. The high porosity combined with the supply of carbon from the organic coco-peat, facilitated oxygen to transfer into the vertical flow wetland and could not sustain a high nitrification and removal of organics. However, it was noted that future longer-term studies were still required to investigate the potential decrease in efficiency.

Kasak et al. (2015) carried out a long-term experiment that employed *Sphagnum* peat in some of their HSSF CWs for treating municipal wastewater. The removal of organic matter was very effective compared to other studies, reaching an effluent BOD_7 concentration of 3.5 mg/L for a mean influent concentration of 20.6 mg/L. The initial phosphorous removal rate was high, but the system gradually lost its phosphorous-binding ability after four months of operation. This was likely due to the decreased availability of adsorption sites on the peat surface. The removal efficiency of nitrogen was quite low in this study compared to others, likely due to the lack of an aerobic zone in the HSSF CWs, which is required for the nitrification.

3.3.2.2 Dewatered alum sludge

Dewatered alum sludge or alum-based water treatment residual is a by-product of drinking water treatment processes where alum (aluminum sulfate) is used as the primary coagulant during the coagulation process. Typically, dewatered alum sludge is considered to be a waste, but this readily available by-product has recently been demonstrated as a potential low-cost alternative substrate for nutrient removal in CWs. Alum sludge is mainly composed of amorphous aluminum species, which have an ideal surface for biofilm growth. Moreover, the electrical conductivity and pH of the alum sludge showed it should also support plant growth (Babatunde et al., 2009).

Babatunde et al. (2009) also assessed the potential phosphate-removing ability of alum sludge as a substrate in a 25-week laboratory scale VSSF CW study. The phosphorous adsorption capacity ranged from 10.2 mg/g to 31.9 mg/g with a phosphorous loading ranging from 18.1 mg/L to 346.1 mg/L. They claimed that the main driving force for the effective phosphorous removal by the alum sludge was the reaction between the abundant aluminum ions and phosphorous through a ligand exchange mechanism.

Zhao et al. (2009) explored the use of dewatered alum sludge in a reed bed designed to treat phosphorous-rich agricultrual wastewater under tidal flow operation. Consistent organics removals were achieved, with an average removal efficiency of 73.3% for COD, and 82.9% for BOD_5. They surmised that dewatered alum sludge could act as a support for biofilm growth, and the significant removals of both BOD_5 and COD provided evidence for this effect. However, with respect to the large-scale application of such a system, further studies on bed clogging and possible release of substances from the dewatered alum sludge should be addressed.

Zhao et al. (2011) also investigated the same substrate in a pilot-scale CW designed to enhance the removal of phosphorous and organic matter from agricultrual wastewater. One-year monitoring of the system showed that the system was promising for the treatment of high strength wastewater as the removal efficiencies reached up to 84%, 78% and 97% for BOD_5, TN, and TP, respectively. The authors indicated that the tidal flow strategy and the implementation of alum sludge contributed to the effective removal of organic matter and TP.

Hu et al. (2012) designed a laboratory-scale alum sludge-based intermittent aeration CW for the purpose of removing nitrogenous compounds. A mean TN removal efficiency of 90% under a nitrogen loading rate of 46.7 g N/m^2d was achieved. The most important outcome of their study was to identify that partial nitrification and simultaneous nitrification-denitrification via nitrite were the main nitrogen conversion pathways in their system under high dissolved oxygen concentrations (3-6 mg/L). This could potentially reduced the amount of carbon required for the full nitrification and denitrification processes to occur, and would allow the system to maintain a high nitrogen removal rate even under carbon limiting conditions.

Bai et al. (2014) tested alum-sludge as a substrate in both continuous and tidal flow CW operations for the removal of organic matter, nutrients, and solids. Both the continuous flow operation and tidal flow operation CWs demonstrated a satisfactory performance for TN and TP removal over their entire experimental period. The effluent TP concentration was nearly zero and the removal efficiency remained above 98% for a phosphorous loading rate of 0.18 g/m^3d after the 260 days of their study. The sources of alum sludge were found to important, as this might affect the characteristics of the residuals, including as nitrogen and organic matter content.

Limitations of applying dewatered alum sludge in large-scale systems include bed clogging, as clogging was experienced after about one year of operation (Bai et al., 2014). Periodical bed resting could be beneficial to prolong the operation time of the bed. Since the alum sludge is mainly composed of aluminum, it can significantly improve phosphorous retention ability in wetland applications. However, excessive aluminum leaching to the effluent can occur. Therefore, extra care must be taken when considering the application of alum sludge as a substrate in CW systems.

3.3.2.3 Wood mulch

Saeed and Sun (2011) employed wood mulch in both HSSF and VSSF CW reactors to investigate nutrient and organic matter removal efficiencies. In this study, the organic wood mulch contained a mixture of 95% solid wood chips and 5% humic substances (lignin, rotted wood). In the VSSF CW, employing wood mulch substantially enhanced nitrification (>99.0% removal efficiency) and overall nitrogen removal (>80.0% TN removal efficiency), as higher void spaces and leaching of organic carbon intensified the conventional nitrification-denitrification nitrogen removal pathway. The humic substances in the wood mulch also enhanced TP removal. However, in the subsequent horizontal flow system, organic wood mulch caused an increase BOD_5, COD, TP and TSS effluent concentrations. This might due to the significant removal that was achieved in the VSSF CW, and parallel comparative studies may be required to demonstrate the full potential of organic wood mulch substrate in horizontal flow wetland systems.

3.3.2.4 Palm tree mulch

Herrera-Melián et al. (2014) applied mulch obtained from branches of the Canarian palm tree as a substrate in a mixed flow, intermittently fed CW treating high strength urban wastewater. The treatment performance of palm tree mulch was similar to that of gravel in CWs in terms of TSS, turbidity and COD removals. However, they were not able to reduce the concentrations of NH_4-N and PO_4-P. These findings were consistent with (Saeed & Sun, 2011) as most of their systems were horizontal flow. Another limitation of applying mulch is that palm tree mulch released color into the water column during the initial stage of the experiment, which was likely caused by the partial leaching of lignin from the organic substrate. Therefore, it was suggested that a mineral-based substrate be employed after the palm tree mulch wetland in order to remove the color as well as to further allow for further removal of solids and organic matter.

3.3.2.5 Palm kernel shells

Jong and Tang (2015) used palm kernel shells, which are one of the palm oil industry by-products, as an alternative substrate for the treatment of wastewater in Malaysia. BOD and COD removals were satisfactory regardless of the presence of palm kernel shells, as the removal efficiencies of palm kernel shells (93.71%, and 96.87%) and the control (sand) were similar (95.16%, and 98.41%). Although palm kernel shells, as a source of carbon, could potentially release soluble organic matter to the effluent, no increase in BOD or COD was found in this study. However, the additional carbon source from the palm kernel shells could stimulate the denitrification process, which effectively reduced the total nitrogen concentration, while nitrate accumulation was noted in the sand cell. Further information on the physico-chemical properties and composition of palm kernel shells would be useful to better understand to what extent the organics in the palm kernel shells affect the treatment.

3.3.2.6 Rice straw

Cao et al. (2016) applied rice straw as part of the substrates in floating CWs to evaluate the removal of nitrogenous compounds from polluted river water under low-temperature conditions. Rice straw is mainly composed of cellulose and lignin, with a porosity of 85% and a specific surface area of about 158 m^2/m^3. The rice straw floating CWs proved to effectively remove NH_4-N, NO_3-N, NO_2-N and TN. The use of rice straw enhanced the biofilm weight and composition of nitrifying and denitrifying bacteria, which enhanced the overall nitrogen removal efficiency. Moreover, the presence of a carbon source from rice straw could further enhance the denitrification process. The Chl-*a* concentrations were also reduced, due to the low concentration of the nitrogenous compounds and high levels of algae-lysing bacteria such as *Pseudomonas* sp. and *Bacillus* sp. Despite the impressive short-term performance, longer-term studies may still be required to demonstrate the feasibility of rice straw for wetland applications, due to its biodegradability, as a frequent supply of additional rice straw maybe required.

3.3.2.7 Rice husk

Tee et al. (2012b) evaluated the potential use of rice husk as a substrate for the enhancement of nitrogen removal in both conventional and baffled HSSF CWs. A 99% NH_4-N removal efficiency was reported in the baffled wetland with vegetation, and most of the NH_4-N was removed in the initial section of their treatment units with the downstream sections only becoming important as the HRT was shortened. However, the NH_4-N removal efficiency significantly decreased (42%) when vegetation was omitted, which indicated that NH_4-N was mainly removed through biological pathways. The mean COD concentration profiles showed evidence of COD release from the rice husk, but the addition of gravel at the end of the system drastically reduced the COD concentration. A maximum COD removal of 79% of was achieved at an HRT of 5 days. Therefore, the ratio between rice husk and gravel could be further studied to ensure improved COD removal.

Tee et al. (2009) also performed a comparison study earlier using the same substrate for the removal of phenol. The rice husk performed well in the treatment of 300 mg/L phenol concentration, and outperformed the gravel when the phenol concentration was increased to 500 mg/L. The removal profile showed that most of the phenol was removed in the initial part of the wetland units followed by a slow removal throughout the remaining part of the units. Therefore, the main removal mechanism of phenol might be via the settling of biosolids, as well as biosorption and biodegradation promoted by biofilm growth.

3.3.2.8 Sugarcane bagasse

Saeed and Sun (2013) employed sugarcane bagasse in two laboratory-scale hybrid systems for the treatment of textile wastewater in Bangladesh. The sugarcane bagasse, a by-product of sugarcane processing contained 40% cellulose, 24% hemicellulose, and 25% lignin. Their system performed well with both high hydraulic (566 - 5660 mm/d) and high pollutant loading rates (9840-19680 g COD/m^2d and 2154-4307 g BOD_5/m^2d) very well. Maximum removal efficiencies of 95.0%, 80.5%, and 72.1% were reported for BOD, NH_4-N, and NO_3-N, respectively. However, due to the high influent concentrations from the textile industry, the effluent concentrations were still above the effluent regulations and further treatments would still be required if sugarcane bagasse was to be applied as the sole substrate.

3.3.2.9 Waste rubber tire chips

Waste rubber tire chips were introduced as a novel substrate and biofilm support in CWs by Chyan et al. (2013) in hopes of reusing waste rubber as well as reducing environmental hazards. They tested waste rubber tire chips in a hybrid CW system, consisting of a FWS and a HSSF wetland in series, to evaluate its performance for treating wastewater. Higher organic (88.1%) and TP removal efficiencies (66-93%) were achieved, and the performance was improved compared to the same wetland system, that employed gravel as a sole substrate. The removal efficiencies of NH_3-N were similar in both systems, but withered plants could adversely affect the effluent NH_3-N concentrations during the winter season. However, mature plants offer a stable treatment environment again after winter. One of the biggest concerns of their study was that they compared the removal efficiencies of waste rubber tire chips in both FWS and HSSF CWs, while the two systems were operated in series rather than in parallel. Therefore, a further parallel study would be beneficial.

3.3.2.10 Wood chips

Li et al. (2016) evaluated the removal of nitrogen and organics in a gravel-wood chip-slag HSSF CW. The results showed that wood chips provide a sufficient internal carbon source to promote the denitrification process and enhanced the overall TN removal efficiency. The authors noted that the order of the substrates was important, as the creation of the alternate aerobic-anaerobic zone could significantly enhance the treatment performance. They also suggested that intermittent aeration could enhance the removal of NH_4-N, NO_2-N and organics removal, but inhibit the NO_3-N removal, which occurs via anaerobic microbial denitrification.

Table 3.1 Substrate employed in constructed wetland system that reviewed, and the generic experiment condition about the study

Substrates	Flow Type	WW Type	Macrophytes	Scale	Reactor Dimension	Reference
Calcium-rich attapulgite	VSSF	Synthetic wastewater	Unvegetated	Bench	5 cm(D) x 50 cm(H)	(Yin et al., 2017)
Basic oxygen furnace slag aggregates	VSSF	Synthetic wastewater	Unvegetated	Bench	12 cm(D) x 30 cm(H)	(Blanco et al., 2016)
Oyster shell, Ceramic ring	HSSF	Synthetic wastewater	*Ipomoea aquatic* *Ocimum basilicum L.*	Bench	38.5 cm(L) x 27.3 cm(W) x 13.5 cm(H)	(Yen & Chou, 2016)
Sludge-ceramsite	VSSF	Synthetic wastewater	*Phragmites australis*	Bench	20 cm(D) x 65 cm(H)	(Wu et al., 2016)
Rice straw, Ceramsite	FCW	River water	*Canna*	Bench	50 cm(L) x 40 cm(W)	(Cao et al., 2016)
Gravel, Wood chips, Slag	BSSF	Synthetic wastewater	*Canna*	Bench	100 cm(L) x 50 cm(W) x 50 cm(H)	(Li et al., 2016)
Peat, Hydrated oil shale ash	VSSF	Municipal wastewater	*Typha latifolia,* *Elymus repens,* *Dactylis glomerata*	Pilot	3 m^2 (A)	(Kasak et al., 2015)
Zeolite, Calcium silicate hydrate	SSF	Synthetic wastewater	Water spinach	Bench	1.1 m(L) x 0.4 m(W) x 0.45 m(H)	(Li et al., 2015)

Substrates	**Flow Type**	**WW Type**	**Macrophytes**	**Scale**	**Reactor Dimension**	**Reference**
Steel slag, Modified steel slag	VSSF	Sewage wastewater	Unvegetated	Bench, Pilot	NM	(Yun et al., 2015)
Zeolite, Ceramsite, Quartz granules	HSSF	Sewage wastewater	*Iris sibirica, Thalia dealbata*	Bench	1.2 m(L) x 0.4 m(W) x 0.7 m(H)	(Fei et al., 2015)
Palm kernel shell	VSSF	Sewage wastewater	*Phragmites karka*	Pilot	NM	(Jong & Tang, 2015)
Zeolite, Quartz sand, Ceramsite, Volcanic rock	TSSF	Synthetic wastewater	*Juncus effusus*	Bench	20 cm(D) x 70 cm(H)	(Liu et al., 2014)
Palm tree mulch	VSSF	Municipal wastewater	*Phragmites australis, Cyperus*	Bench	1.17 m(L) x 0.49 m(W) x 0.48 m(H)	(Herrera-Melián et al., 2014)
Bauxsol™	HSSF	Municipal wastewater	Unvegetated	Pilot	3.0 m(L) x 0.5 m(W) x 0.25 m(H)	(Despland et al., 2014)
Drinking water treatment residuals	VSSF	Secondary effluent	*Phragmites australis*	Bench	9.3 cm(D) x 90 cm(H)	(Bai et al., 2014)
Quartz sand, Ceramsite, Shale Anthracite	VSSF	Synthetic wastewater	Unvegetated	Bench	28 cm(D) x 59.5 cm(H)	(Jiang et al., 2014)

Substrates	Flow Type	WW Type	Macrophytes	Scale	Reactor Dimension	Reference
Waste rubber tire chips	Hybrid HSSF + FWS	Synthetic wastewater	*Phragmites communis L., Typha orientalis Presl.*	Bench	2.0 m(L) x 0.6 m(W) x 0.5 m(H)	(Chyan et al., 2013)
Oyster shell	VSSF	Agricultural wastewater (Swine)	*Phragmites australis*	Bench	1.12 m(D) x 1.3 m(H)	(Wang et al., 2013)
Sugarcane bagasse, Sylhet sand	HSSF, VSSF, Hybrid VSSF + HSSF	Industrial wastewater (Textile)	*Phragmites australis, Dracaena sanderiana, Asplenium platyneuron*	Bench	0.15 m(D) x 1.5 m(H) (VSSF), 1.0 m(L) x 0.45 m(W) x 0.70 m(H) (HSSF)	(Saeed & Sun, 2013)
Gravel, Water quenched slag	VSSF	Primary effluent	*Canna indica*	Pilot	0.8 m(L) x 0.4 m(W) x 0.8 m(H)	(Li et al., 2013)
Natural zeolite, Volcanic rock	VSSF	Agricultural wastewater (Swine)	*Pennisetum hybrid*	Bench	1.0 m(L) x 1.0 m(W) x 0.7 m(H)	(Huang et al., 2013)
Limestone, Cinder residue slag, Blast furnace slag	HSSF, VSSF BSSF	Septic tank effluent	*Canna*	Bench	2.0 m(L) x 1.0 m(W) x 0.75 m(H)	(Cui et al., 2013)
Lava rocks	SSF	Municipal wastewater	Unvegetated	Bench, Pilot	2.6 m(L) x 0.28 m(W) x 0.28 m(H)	(Collison & Grismer, 2013)
Gravel	Hybrid VSSF + HSSF + FWS	Municipal wastewater	*Phragmites australis*	Laboratory	5.5 m^2 (A)	(Avila et al., 2013)
Light expanded clay, Siliceous gravel	VSSF	Synthetic wastewater	*Typha latifolia, Phragmites australis*	Mesocosm	16 cm(D) x 60 cm(H)	(Arroyo et al., 2013)

Substrates	Flow Type	WW Type	Macrophytes	Scale	Reactor Dimension	Reference
Gravel	HSSF, VSSF	Municipal wastewater	*Phragmites australis,* *Canna,* *Cyperus papyrus*	Full	37.87 m (L) x 17.3 m(W) x 0.85 m(H) (HFCW) 21.95 m(L) x 20.85 m(W) (VFCW)	(Abou-Elela et al., 2013)
Rice husk	HSSF	Primary effluent	*Typha latifolia*	Bench	2.0 m(L) x 0.5 m(W) x 0.8 m(H)	(Tee et al., 2012b)
Rock, Zeolite, Bauxite	VSSF	Synthetic wastewater	*Typha latifolia,* *Phragmites australis*	Pilot	0.82 m(D) x 1.5 m(H)	(Stefanakis & Tsihrintzis, 2012a)
Bauxite, Zeolite	VSSF	Synthetic wastewater	*Phragmites australis*	Pilot	0.82 m(D) x 1.5 m(H)	(Stefanakis & Tsihrintzis, 2012b)
Coco-peat, Cupola slag, Pea gravel	Hybrid HSSF + VSSF	Industrial wastewater (Tannery)	*Phragmites australis*	Bench	0.91 m(D) x 0.73 m(H) (VSSF) 1.32 m(L) x 1.01 m(W) x 0.78 m (HSSF)	(Saeed et al., 2012)
Ceramsite, Zeolite	CFC	Secondary effluent	*Acorus calamus* Linn*,* *Phragmites australis*	Bench	1.5 m(L) x 1.0 m(W) x 1.0 m(H)	(Peng et al., 2012)
Limestone	HSSF	Synthetic wastewater	*Phragmites australis*	Bench	1.1 m(L) x 0.9 m(W) x 0.56 m(H)	(Mateus et al., 2012)
Gravel, Shale	VSSF	River water	*Phragmites australis*	Pilot	0.5m(D) x 1.3m(H)	(Liu et al., 2012)

Substrates	Flow Type	WW Type	Macrophytes	Scale	Reactor Dimension	Reference
Cobblestones, Peat and crushed pine bark	VSSF	Waste activated sludge	*Phragmites australis, Typha latifolia, Iris pseudacorus*	Mesocosm	0.95m(L) x 1.15m(W) x 1.0m(H)	(Korboulewsky et al., 2012)
Dewatered alum sludge	VSSF	Agricultural wastewater (Swine)	*Phragmites australis*	Bench	9.3cm(D) x 0.7m(H)	(Hu et al., 2012)
Granitic rock, Gravel	HSSF	Industrial wastewater (Tannery)	*Typha latifolia*	Pilot	3.0m(L) x 1.5m(W) x 1.0m(H)	(Dotro et al., 2012)
Gravel, Organic wood mulch	Hybrid HSSF + VSSF	Synthetic wastewater	*Phragmites australis*	Bench	0.6m(L) x 0.2m(W) x 0.8m(H)	(Saeed & Sun, 2011)
Anthracite, Steel slag	VSSF	Municipal wastewater	Unvegetated	Bench	NM	(Wu et al., 2011)
Alum sludge	TSSF	Agricultural wastewater	*Phragmites australis*	Pilot	1100 L (V)	(Zhao et al., 2011)
Zeolite-contained lava sands	VSSF	Municipal wastewater	*Phragmites australis*	Pilot	150 m^2 (A)	(Bruch et al., 2011)
Dewatered alum sludge	TSSF	Agricultural wastewater	*Phragmites australis*	Pilot	1.17 m^2 (A)	(Babatunde et al., 2011)
Peat, Pine bark	VSSF	Sewage sludge	*Phragmites australis, Typha latifolia,*	Mesocosm	0.95 m(L) x 1.15 m(W) x 1.00 m(H)	(Wang et al., 2010)

Substrates	Flow Type	WW Type	Macrophytes	Scale	Reactor Dimension	Reference
			Iris pseudacorus			
Peat, Hydrated oil-shale ash	VSSF - HSSF	Municipal wastewater, Landfill Leachate	Unvegetated	Pilot	NM	(Kõiv et al., 2009)
Gravel	Hybrid HSSF + VSSF	Municipal wastewater	*Zantedeschia aethiopica, Strelitzia reginae, Anturium andreanum and Agapanthus africanus*	Pilot	3.24 m^2 (A)	(Zurita et al., 2009)
Dewatered alum sludge	TSSF	Agricultural wastewater	*Phragmites australis*	Pilot	NM	(Zhao et al., 2009)
Gravel, Zeolite	HSSF, VSSF	Landfill Leachate	*Typha latifolia*	Bench	1.0m(L) x 0.5m(W) x 0.4m(H)	(Yalcuk & Ugurlu, 2009)
Rice husk-based media	HSSF	Primary effluent with Phenol spike	*Typha latifolia,* Unvegetated	Bench	2.0m(L) x 0.5m(W) x 0.8m(H)	(Tee et al., 2009)
Hornblende, Gravel, Shale, Ironstone	VSSF	Synthetic wastewater	Unvegetated	Bench	NM	(Tang et al., 2009)
Mixture of fishpond bund material, granite, and river sand	FWSF	Stormwater	*Phragmites australis*	Full	16000 m^2 (A)	(Lai & Lam, 2009)

Substrates	Flow Type	WW Type	Macrophytes	Scale	Reactor Dimension	Reference
Aluminium-based water treatment residual	VSSF	Secondary effluent	Unvegetated	Bench	NM	(Babatunde et al., 2009)
Loess, Cinder, Limestone	HSSF	Lake water	Unvegetated	Full	140 m(L) x 10 m(W)	(Guan et al., 2009)
Natural zeolite (Clinoptilolite)	HSSF	Synthetic wastewater	*Phragmites australis,* Unvegetated	Pilot	3 m(L) x 0.75 m(W) x 1 m(H)	(Stefanakis et al., 2009)
Gravel, Zeolite, Slag	HSSF	River water	*Phragmites australis, Typha latifolia, Scirpus validus*	Bench	1.2 m(L) x 0.4 m(W) x 0.6m(H)	(Li et al., 2008)
Limestone, Pebble	Hybrid FWS + HSSF	Synthetic wastewater	*Typha latifolia*	Bench	46 cm(L) x 36 cm(W) x 36 cm(H)	(Tao & Wang, 2009)
Hydrated oil-shale ash	NM	NM	NM	Batch	NM	(Kaasik et al., 2008)
Quartz	NM	Ash basin WW from coal-burning power plants	*Schoenoplectus californicus*	Pilot	1666 L (V)	(Dorman et al., 2009)
Peat	HSSF	Restaurant	*Poa trivalis L*	Pilot		(Gunes, 2007)

* A - Surface Aera, BSSF - Baffled Subsurface Flow, CFC - Circular Flow Corridor, COCs - Constituents of Concerns, FCW - Floating Constructed Wetland, FWS- Free Water Surface Flow, H - Height, HSSF - Horizontal Subsurface Flow, L - Length, NM - Not Mentioned, TSSF, Tidal Subsurface Flow, V - Volume, VSSF - Vertical Subsurface Flow, W - Width, WW - Wastewater

Table 3.2 Mineral-based substrates contaminants removal

Substrate	Cont.	Influent Conc.	HRT/HLR	Effluent Conc.	RE	RR	Reference
Gravel	sCOD	76-110 mg/L	4 days	27.51 mg/L	70.50%		(Li et al., 2008)
Gravel	BOD	115.5 mg/L	4 days	18.5 mg/L	83.3% (VSSF)		(Zurita et al., 2009)
	COD	247.5 mg/L		41.3 mg/L	83.3% (VSSF)		
	TSS	57.5 mg/L		8.5 mg/L	84.7% (HSSF)		
	TN	28.7 mg/L		13.1 mg/L	53.7% (HSSF)		
	TP	8.3 mg/L		3.8 mg/L	50.6% (VSSF)		
	NO3-N	9.3 mg/L		4.3 mg/L	49.3% (HSSF)		
Gravel (HSSF)	BOD	121.7 mg/L	11 days	11.94 mg/L	92.8%		(Abou-Elela et al., 2013)
	COD	246.2 mg/L		29.25 mg/L	91.5%		
	TSS	98.6 mg/L		7.59 mg/L	92.3%		
	NH_4-N	17.2 mg/L		8.8 mg/L	57.1%		
	NO_3-N	0.16 mg/L		0.2 mg/L			
Gravel (VSSF)	BOD	121.7 mg/L	7.7 days	11.24 mg/L	93.6%		(Abou-Elela et al., 2013)
	COD	246.2 mg/L		29 mg/L	92.9%		
	TSS	98.6 mg/L		5.91 mg/L	94%		
	NH_4-N	17.2 mg/L		6.5 mg/L	62.7%		
	NO_3-N	0.16 mg/L		0.44 mg/L			
Gravel	COD	868 mg/L	24 hours/ 0.18m/d		91%		(Avila et al., 2013)
	TSS	60 mg/L			95%		
	NH_4-N	43 mg/L			86%		

Substrate	Cont.	Influent Conc.	HRT/HLR	Effluent Conc.	RE	RR	Reference
Decomposed Granite	TP	50 mg/L	28 days			478-858 mg/kg	(Lai & Lam, 2009)
Granite	COD	2104 mg/L	0.048m/d	979 mg/L			(Dotro et al., 2012)
	TSS	208 mg/L		64 mg/L			
	Cr	1.1 mg/L		0.5 mg/L			
Limestone	TP	0.63 mg/L	$11m^3/s$	0.37 mg/L	41.3%	2.002 mg/g	(Guan et al., 2009)
Limestone	TP	9 mg/L	$40\ L/m^2d$		60%		(Mateus et al., 2012)
Limestone	NH_3-N	56.3 mg/L	7 days	30.7 mg/L	59%	$4.7\ g/m^3d$	(Tao & Wang, 2009)
	NO_3-N			0.3 mg/L		$0.06\ g/m^3d$	
	TN				57%	$4.6\ g/m^3d$	
Limestone	As	3.1 mg/L	$0.073m^3/m^2d$	0.021 mg/L			(Lizama Allende et al., 2012)
	B	32 mg/L		31 mg/L			
	Fe	107 mg/L		1.85 mg/L			
Quartz sand	TP	2.2 mg/L	1- 8 hours		58.81%	55.98 mg/kg	(Jiang et al., 2014)
Quartz	Chromium	36.0-69.9 mg/L	5 days	5.3-26.4 mg/L	52.3-92.4%		(Dorman et al., 2009)
	Zinc	98.2-145.4 mg/L		8.5-89.4 mg/L	9.6-93.7%		
	Arsenic	88.4-325.4 mg/L		7.1-59.0 mg/L	81.9-94.9%		
	Selenium	102.1-307.2 mg/L		37.3-292.0mg/L	0-89.4%		
	Mercury	14.1-33.2 mg/L		0.1-1.8mg/L	91.0-99.1%		
Zeolite	NH_4-N	122 mg/L	11 days	46 mg/L	65.8%		(Yalcuk & Ugurlu, 2009)
	PO_4-P	75 mg/L			29-83.1%		
	COD	211.8 mg/L		110-155 mg/L	15-40%		
Natural zeolite	BOD_5	52.7 mg/L	6-14 days		63.2%		(Stefanakis et al., 2009)
	TKN	37.7 mg/L			83.2%		
	NH_4-N	26.3 mg/L			85.8%		
	TP	5.5 mg/L			40.5%		
Zeolite	COD	320-1010 mg/L	7-13 days		93.9%		(Peng et al., 2012)

Substrate	Cont.	Influent Conc.	HRT/HLR	Effluent Conc.	RE	RR	Reference
	NH_4-N	560-1150 mg/L			95.5%		
	TP	10-233 mg/L			97.4%-99.5%		
Zeolite	NH_4-N	613.04 mg/L	5 days		82.8%-94.0%	11.6 mg/g	(Huang et al., 2013)
Zeolite	NH_4-N	100 mg/L	207 L/m^2d		97%		(Liu et al., 2014)
Zeolite	COD	90.4 mg/L	100 mm/d	22.0 mg/L		6.84 g/m^2d	(Fei et al., 2015)
	TSS	30.2 mg/L		3.9 mg/L		2.63 g/m^2d	
	NH_4-N	29.69 mg/L		19.30 mg/L		1.04 g/m^2d	
	NO_3-N	0.16 mg/L		0.36 mg/L			
	TN	33.34 mg/L		22.34 mg/L		1.10 g/m^2d	
	PO_4-P	2.90 mg/L		2.48 mg/L		0.04 g/m^2d	
	TP	3.38 mg/L		2.78 mg/L		0.06 g/m^2d	
Zeolite	NH_4-N	1.75 mg/L	0.4 m^3/m^2d		77.7%		(Li et al., 2015)
	TN	10.5 mg/L			23.7%		
	PO_4-P	0.15 mg/L			66.6%		
Slag	No text						(Wu et al., 2011)
Water quenched slag	TP	12.2-48.9 g/m^2d			85%	0.17 g/kg	(Li et al., 2013)
Steel slag	TP	3 - 4.5 mg/L	2 days		84%	9.5 mg/g	(Yun et al., 2015)
Modified steel slag	TP	3 - 4.5 mg/L	2 days		89%	12.7 mg/g	
Basic Oxygen Furnace steel slag	TP	15 mg/L	8 hours		84-99%	0.12-8.78 mg/g	(Blanco et al., 2016)
Light ceramsite	NH_4-N	0.50-1.32 mg/L	7 days	0-0.55 mg/L			(Cao et al., 2016)
	NO_3-N	0.41-1.10 mg/L		0-0.22 mg/L			
	NO_2-N	0.18-1.24 mg/L		0.03-0.92 mg/L			
	TN	1.32-2.97 mg/L		0.05-1.32 mg/L			

Substrate	Cont.	Influent Conc.	HRT/HLR	Effluent Conc.	RE	RR	Reference
Sludge-ceramsite	COD	426.2 mg/L	3 days	11.9 mg/L	97.2%		(Wu et al., 2016)
	TKN	37.7 mg/L			83.2%		
	NH_4-N	26.3 mg/L			85.8%		
	TP	5.5 mg/L			40.5%		
Shale	TP	0.516 mg/L	2.2 days			619.7 mg P/kg	(Tang et al., 2009)
Hydrated oil shale ash	NH_4-N	45.5 mg/L	3 days	25.3 mg/L			(Kasak et al., 2015)
	NO_3-N	9.1 mg/L		5.3 mg/L			
	TN	63.3 mg/L		44.0 mg/L			
	PO_4-P	16.2 mg/L		0.2 mg/L			
	TP	17.8 mg/L		0.2 mg/L			
Oyster shell	TP	83.64mg/L	0.02 m^3/m^2d		95.88%		(Wang et al., 2013)
	TP	83.64mg/L	0.06 m^3/m^2d		87.96%		
Oyster shell	BOD_5	18.3 mg/L		6.5 mg/L			(Yen & Chou, 2016)
	NH_3-N	1.92 mg/L		0.35 mg/L			
	NO_3-N	13.5 mg/L		1.6 mg/L			
	PO_4-P	6.5 mg/L		2.7 mg/L			
Calcium Silicate Hydrate	NH_4-N	1.75 mg/L			71.9%		(Li et al., 2015)
	TN	10.5 mg/L			23.7%		
	PO_4-P	0.15 mg/L			86.1%		
Calcium-rich Attapulgite	TP	400 mg/L	4 hours		30%	5.99 mg P/g	(Yin et al., 2017)

Table 3.3 Organic-based substrates contaminants removal

Substrate	Cont.	HRT/HLR	Influent Conc.	Effluent Conc.	RE	RR	Reference
Sugarcane bagasse	BOD	566-2830mm/d	2705.0 mg/L	134.0 mg/L	95.0%		(Saeed & Sun, 2013)
	NH_4-N		158.0 mg/L	30.7 mg/L	80.5%		
	NO_3-N		73.7 mg/L	20.5 mg/L	72.1%		
	SS		133.3 mg/L	50.0 mg/L	62.5%		
Waste Rubber Tire Chips	BOD		109.2 mg/L	9.05 mg/L			(Chyan et al., 2013)
	NH_3-N		34.6 mg/L	23.1 mg/L	33.2%		
	NO_3-N		1.81 mg/L	0.34 mg/L	49.11%		
	TP		4.05 mg/L	1.88 mg/L	39.9%		
Sphagnum peat		53-76 mm/d					(Kõiv et al., 2009)
Dewatered alum sludge	TP	0.125 day/ 1.86 m^3/m^2d	18.1-346.1 mg/L			10.2-31.9mg P/g	(Babatunde et al., 2009)
Dewatered alum sludge	BOD_5	4 hours/			18-88%	4.6-249.2 g/m^2d	(Babatunde et al., 2011)
	COD	0.56 m^3/m^2d			14-84%	35.6-502.0 g/m^2d	
	NH_4-N					6.1-61.3 g/m^2d	
	TN					2.1-52.7 g/m^2d	
	PO_4-P					2.7-14.6 g/m^2d	
Dewatered alum sludge	BOD_5	0.5 m^3/m^2d	110 mg/L		70%		(Zhao et al., 2009)
	COD		213 mg/L		56%		
	SS		72 mg/L		77.6%		
	RP				86.4%		
	SRP				88.6%		
Dewatered alum sludge	BOD_5	0.29 m^3/m^2d	41.2-694.4 mg/L		57-84%		(Zhao et al., 2011)
	COD		407.0-1297.5 mg/L		36-84%		
	NH_4-N		37.9-176.2 mg/L		49-93%		
	TN		43.0-221.9 mg/L		11-78%		

Substrate	Cont.	HRT/HLR	Influent Conc.	Effluent Conc.	RE	RR	Reference
	TP		10.7-33.3 mg/L		75-94%		
Alum sludge	COD	0.09 m^3/m^2d	3000-6000 mg/L		89%		(Hu et al., 2012)
	NH_4-N		312-435 mg/L		56%		
	TN		250-700 mg/L		90%		
Drinking water treatment residue	COD	0.15-0.45 m^3/m^2d	3491 mg/L	45.03-71.10 mg/L			(Bai et al., 2014)
	TP		39 mg/L	1.15-1.88 mg/L			
	TN		442 mg/L	12.96-17.88 mg/L			
	SS		1739 mg/L	2.10-2.73 mg/L			
Organic wood mulch	NH_4-N	0.31 m^3/m^2d	18.4 mg/L	0.1 mg/L (VF)	99.4%		(Saeed & Sun, 2011)
	TN		22.3 mg/L	0.4 mg/L (VF)	97.7%		
	TP		18.4 mg/L	7.3 mg/L (VF)	60.3%		
	BOD		32.5 mg/L	9.3 mg/L (VF)	71.3%		
	TSS		19.4 mg/L	8.4 mg/L (VF)	56.7%		
Palm tree mulch	COD	0.090-0.160 m^3/m^2d	834-1296 mg/L		53-73%		(Herrera-Melián et al., 2014)
	SS		269-662 mg/L		70-78%		
Palm kernel shell	BOD	0.00875 m^3/m^2d	247.31 mg/L		96.87%		(Jong & Tang, 2015)
	COD		4860.0 mg/L		93.71%		
	NH_4-N		127.96 mg/L		96.59%		
	NO_3-N		33.78 mg/L		36.36%		
	TN		309.17 mg/L		83.10%		
Rice Straw	NH_4-N	NM	0.50-1.32 mg/L	0-0.60 mg/L			(Cao et al., 2016)
	NO_3-N		0.41-1.10 mg/L	0-0.22 mg/L			
	NO_2-N		0.18-1.24 mg/L	0.01-0.03 mg/L			
	TN		1.32-2.97 mg/L	0.05-0.66 mg/L			
Rice husk	COD	5 day	160 mg/L		79%		(Tee et al., 2012b)
	NH_4-N		36.5 mg/L		99%		

Substrate	Cont.	HRT/HLR	Influent Conc.	Effluent Conc.	RE	RR	Reference
	TON		31.6 mg/L		100%		

3.4 Conclusion

CWs are an efficient and sustainable technology for enhancing the treatment of wastewater. They are also cost-effective compared to other active wastewater treatment solutions due to their low capital and operational cost, as well as their minimal maintenance requirements. Substrates in CW systems provide not only the medium for vegetation growth, but they can also provide treatment on their own. To date, a large number of mineral-based and organic-based wetland substrates have been studied and used, both in the laboratory and in the field, to evaluate their ability to treat wastewater from a variety of sources of wastewater sources.

Among these potential substrate sources, mineral-based substrates have been extensively explored and studied at the bench-scale to assist in the improvement of wastewater treatment, mainly because of their readily availability and relatively low procurement costs. Gravel was the most widely-used substrate material before alternative substrates became more attractive due to their superior physico-chemical properties. Zeolite is a great option in terms of removing NH_4-N because of its high cation-exchange capacity and affinity for NH_4-N. Zeolite has also exhibited high selectivity for ammonium-oxidizing prokaryotes, which enhance NH_4-N removal as well. Slag can significantly enhance the phosphorous retention ability in CWs, with a maximum phosphorous removal rate of 12.7 mg/g reported for a modified steel slag.

In addition to mineral-based substrates, several organic-based substrates were discovered and tested in the laboratory. Peat and dewatered alum sludge were extensively studied by multiple researchers, while most of the other substrates have not been thoroughly studied to date. Both peat and dewatered alum sludge excelled in terms of phosphorous retention. A maximum phosphorous removal rate of 31.9 mg/g was reported by applying dewatered alum sludge, which was comparatively higher than slag and most of mineral-based substrates.

In the future, further and more extensive pilot-scale and full-scale substrate studies would be recommended as most of the existing studies have been performed in short-term bench-scale studies (especially phosphorous removal studies). Long-term pilot-scale studies are required to further evaluate the performance and sustainability of substrate in the field. Rather than applying a single substrate, combined or co-substrate CW systems are suggested to take advantage of the merits of both mineral-based and organic-based substrates to enhance existing treatment performances. Besides simply focusing on the removal of organics and nutrients, heavy metals and contaminants of emerging concern should be included in future studies, as countries and regulatory agencies are applying more stringent wastewater treatment effluent discharge guidelines on these pollutants with the aim of protecting downstream and receiving environments.

3.5 References

Abou-Elela, S. I., Golinielli, G., Abou-Taleb, E. M., and Hellal, M. S. (2013). Municipal wastewater treatment in horizontal and vertical flows constructed wetlands. *Ecological Engineering, 61*, 460-468.

Arroyo, P., Ansola, G., and Miera, L. E. S. d. (2013). Effects of substrate, vegetation and flow on arsenic and zinc removal efficiency and microbial diversity in constructed wetlands. *Ecological Engineering, 51*, 95-103.

Avila, C., Matamoros, V., Reyes-Contreras, C., Pina, B., Casado, M., Mita, L., Rivetti, C., Barata, C., Garcia, J., and Bayona, J. M. (2013). Attenuation of emerging organic contaminants in a hybrid constructed wetland system under different hydraulic loading rates and their associated toxicological effects in wastewater. *Sci Total Environ, 470-471C*, 1272-1280.

Babatunde, A. O., Zhao, Y. Q., Burke, A. M., Morris, M. A., and Hanrahan, J. P. (2009). Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. *Environmental Pollution, 157*(10), 2830-2836.

Babatunde, A. O., Zhao, Y. Q., Doyle, R. J., Rackard, S. M., Kumar, J. L. G., and Hu, Y. S. (2011). Performance evaluation and prediction for a pilot two-stage on-site constructed wetland system employing dewatered alum sludge as main substrate. *Bioresource Technology, 102*(10), 5645-5652.

Bai, L., Wang, C., Huang, C., He, L., and Pei, Y. (2014). Reuse of drinking water treatment residuals as a substrate in constructed wetlands for sewage tertiary treatment. *Ecological Engineering, 70*(0), 295-303.

Barca, C., Gérente, C., Meyer, D., Chazarenc, F., and Andrès, Y. (2012). Phosphate removal from synthetic and real wastewater using steel slags produced in europe. *Water Research, 46*(7), 2376-2384.

Blanco, I., Molle, P., Sáenz de Miera, L. E., and Ansola, G. (2016). Basic oxygen furnace steel slag aggregates for phosphorus treatment. Evaluation of its potential use as a substrate in constructed wetlands. *Water Research, 89*, 355-365.

Bruch, I., Fritsche, J., Bänninger, D., Alewell, U., Sendelov, M., Hürlimann, H., Hasselbach, R., and Alewell, C. (2011). Improving the treatment efficiency of constructed wetlands with zeolite-containing filter sands. *Bioresource Technology, 102*(2), 937-941.

Calheiros, C. S. C., Rangel, A. O. S. S., and Castro, P. M. L. (2009). Treatment of industrial wastewater with two-stage constructed wetlands planted with typha latifolia and phragmites australis. *Bioresource Technology, 100*(13), 3205-3213.

Cao, W., Wang, Y., Sun, L., Jiang, J., and Zhang, Y. (2016). Removal of nitrogenous compounds from polluted river water by floating constructed wetlands using rice straw and ceramsite as substrates under low temperature conditions. *Ecological Engineering, 88*, 77-81.

Chen, T. Y., Kao, C. M., Yeh, T. Y., Chien, H. Y., and Chao, A. C. (2006). Application of a constructed wetland for industrial wastewater treatment: A pilot-scale study. *Chemosphere, 64*(3), 497-502.

Chen, X., Kong, H., Wu, D., Wang, X., and Lin, Y. (2009). Phosphate removal and recovery through crystallization of hydroxyapatite using xonotlite as seed crystal. *Journal of Environmental Sciences, 21*(5), 575-580.

Chyan, J.-M., Senoro, D.-B., Lin, C.-J., Chen, P.-J., and Chen, I. M. (2013). A novel biofilm carrier for pollutant removal in a constructed wetland based on waste rubber tire chips. *International Biodeterioration & Biodegradation, 85*, 638-645.

Collison, R. S., and Grismer, M. E. (2013). Nitrogen and cod removal from domestic and synthetic wastewater in subsurface-flow constructed wetlands. *Water Environment Research, 85*(9), 855-862.

Cooper, P. (1999). A review of the design and performance of vertical-flow and hybrid reed bed treatment systems. *Water Science and Technology, 40*(3), 1.

Cui, L., Ouyang, Y., Gu, W., Yang, W., and Xu, Q. (2013). Evaluation of nutrient removal efficiency and microbial enzyme activity in a baffled subsurface-flow constructed wetland system. *Bioresource Technology, 146*, 656-662.

Despland, L. M., Clark, M. W., Vancov, T., and Aragno, M. (2014). Nutrient removal and microbial communities' development in a young unplanted constructed wetland using bauxsol™ pellets to treat wastewater. *Science of The Total Environment, 484*, 167-175.

Dorman, L., Castle, J. W., and Rodgers Jr, J. H. (2009). Performance of a pilot-scale constructed wetland system for treating simulated ash basin water. *Chemosphere, 75*(7), 939-947.

Dotro, G., Castro, S., Tujchneider, O., Piovano, N., Paris, M., Faggi, A., Palazolo, P., Larsen, D., and Fitch, M. (2012). Performance of pilot-scale constructed wetlands for secondary treatment of chromium-bearing tannery wastewaters. *J Hazard Mater, 239-240*, 142-151.

Drizo, A., Frost, C. A., Grace, J., and Smith, K. A. (2000). Phosphate and ammonium distribution in a pilot-scale constructed wetland with horizontal subsurface flow using shale as a substrate. *Water Research, 34*(9), 2483-2490.

Fei, Z., Juan, W., Yanran, D., Dongfang, X., Shuiping, C., and Hongjiu, J. (2015). Performance evaluation of wastewater treatment using horizontal subsurface flow constructed wetlands optimized by micro-aeration and substrate selection. *Water Science & Technology, 71*(9), 1317-1324.

Guan, B., Yao, X., Jiang, J., Tian, Z., An, S., Gu, B., and Cai, Y. (2009). Phosphorus removal ability of three inexpensive substrates: Physicochemical properties and application. *Ecological Engineering, 35*(4), 576-581.

Gunes, K. (2007). Restaurant wastewater treatment by constructed wetlands. *CLEAN – Soil, Air, Water, 35*(6), 571-575.

Herrera-Melián, J. A., González-Bordón, A., Martín-González, M. A., García-Jiménez, P., Carrasco, M., and Araña, J. (2014). Palm tree mulch as substrate for primary treatment wetlands processing high strength urban wastewater. *Journal of Environmental Management, 139*(0), 22-31.

Hu, Y., Zhao, Y., Zhao, X., and Kumar, J. L. G. (2012). High rate nitrogen removal in an alum sludge-based intermittent aeration constructed wetland. *Environmental Science and Technology, 46*(8), 4583-4590.

Huang, J., Gao, X., Balch, G., Wootton, B., Jørgensen, S. E., and Anderson, B. (2015). Modelling of vertical subsurface flow constructed wetlands for treatment of domestic sewage and stormwater runoff by subwet 2.0. *Ecological Engineering, 74*, 8-12.

Huang, X., Liu, C., Wang, Z., Gao, C., Zhu, G., and Liu, L. (2013). The effects of different substrates on ammonium removal in constructed wetlands: A comparison of their physicochemical characteristics and ammonium-oxidizing prokaryotic communities. *CLEAN – Soil, Air, Water, 41*(3), 283-290.

Jiang, C., Jia, L., Zhang, B., He, Y., and Kirumba, G. (2014). Comparison of quartz sand, anthracite, shale and biological ceramsite for adsorptive removal of phosphorus from aqueous solution. *Journal of Environmental Sciences, 26*(2), 466-477.

Jong, J. (1976). Purification of wastewater with the aid of rush or reed ponds. *Biological Control of Water Pollution. J. Tourbier & Rw Pierson, Jr., eds*.

Jong, V. S. W., and Tang, F. E. (2015). The use of palm kernel shell (pks) as substrate material in vertical-flow engineered wetlands for septage treatment in malaysia. *Water Science & Technology, 72*(1), 84-91.

Kaasik, A., Vohla, C., Mõtlep, R., Mander, Ü., and Kirsimäe, K. (2008). Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands. *Water Research, 42*(4–5), 1315-1323.

Kadlec, R. H., and Wallace, S. (2008). *Treatment wetlands* (2nd Edition ed.). CRC press, Florida.

Kasak, K., Mander, Ü., Truu, J., Truu, M., Järveoja, J., Maddison, M., and Teemusk, A. (2015). Alternative filter material removes phosphorus and mitigates greenhouse gas emission in horizontal subsurface flow filters for wastewater treatment. *Ecological Engineering, 77*(0), 242-249.

Kietlińska, A., and Renman, G. (2005). An evaluation of reactive filter media for treating landfill leachate. *Chemosphere, 61*(7), 933-940.

Knowles, P., Dotro, G., Nivala, J., and García, J. (2011). Clogging in subsurface-flow treatment wetlands: Occurrence and contributing factors. *Ecological Engineering, 37*(2), 99-112.

Kõiv, M., Kriipsalu, M., and Mander, Ü. (2006). After treatment of landfill leachate in peat filters. *WIT Transactions on Ecology and the Environment, 89*.

Kõiv, M., Liira, M., Mander, Ü., Mõtlep, R., Vohla, C., and Kirsimäe, K. (2010). Phosphorus removal using ca-rich hydrated oil shale ash as filter material – the effect of different phosphorus loadings and wastewater compositions. *Water Research, 44*(18), 5232-5239.

Kõiv, M., Vohla, C., Mõtlep, R., Liira, M., Kirsimäe, K., and Mander, Ü. (2009). The performance of peat-filled subsurface flow filters treating landfill leachate and municipal wastewater. *Ecological Engineering, 35*(2), 204-212.

Korboulewsky, N., Wang, R., and Baldy, V. (2012). Purification processes involved in sludge treatment by a vertical flow wetland system: Focus on the role of the substrate and plants on n and p removal. *Bioresource Technology, 105*, 9-14.

Lai, D. Y. F., and Lam, K. C. (2009). Phosphorus sorption by sediments in a subtropical constructed wetland receiving stormwater runoff. *Ecological Engineering, 35*(5), 735-743.

Li, C., Dong, Y., Lei, Y., Wu, D., and Xu, P. (2015). Removal of low concentration nutrients in hydroponic wetlands integrated with zeolite and calcium silicate hydrate functional substrates. *Ecological Engineering, 82*, 442-450.

Li, C., Yu, H., Tabassum, S., Li, L., Wu, D., Zhang, Z., Kong, H., and Xu, P. (2017). Effect of calcium silicate hydrates (csh) on phosphorus immobilization and speciation in shallow lake sediment. *Chemical Engineering Journal, 317*, 844-853.

Li, H., Chi, Z., Yan, B., Cheng, L., and Li, J. (2016). Nitrogen removal in wood chip combined substrate baffled subsurface-flow constructed wetlands: Impact of matrix arrangement and intermittent aeration. *Environmental Science and Pollution Research*, 1-7.

Li, H., Li, Y., Gong, Z., and Li, X. (2013). Performance study of vertical flow constructed wetlands for phosphorus removal with water quenched slag as a substrate. *Ecological Engineering, 53*, 39-45.

Li, J., Wen, Y., Zhou, Q., Xingjie, Z., Li, X., Yang, S., and Lin, T. (2008). Influence of vegetation and substrate on the removal and transformation of dissolved organic matter in horizontal subsurface-flow constructed wetlands. *Bioresource Technology, 99*(11), 4990-4996.

Liu, M., Wu, S., Chen, L., and Dong, R. (2014). How substrate influences nitrogen transformations in tidal flow constructed wetlands treating high ammonium wastewater? *Ecological Engineering, 73*(0), 478-486.

Liu, X., Huang, S., Tang, T., Liu, X., and Scholz, M. (2012). Growth characteristics and nutrient removal capability of plants in subsurface vertical flow constructed wetlands. *Ecological Engineering, 44*, 189-198.

Lizama Allende, K., Fletcher, T. D., and Sun, G. (2012). The effect of substrate media on the removal of arsenic, boron and iron from an acidic wastewater in planted column reactors. *Chemical Engineering Journal, 179*, 119-130.

Mateus, D. M. R., Vaz, M. M. N., and Pinho, H. J. O. (2012). Fragmented limestone wastes as a constructed wetland substrate for phosphorus removal. *Ecological Engineering, 41*(0), 65-69.

Moore, M. T., Rodgers Jr, J. H., Cooper, C. M., and Smith Jr, S. (2000). Constructed wetlands for mitigation of atrazine-associated agricultural runoff. *Environmental Pollution, 110*(3), 393-399.

Pavlineri, N., Skoulikidis, N. T., and Tsihrintzis, V. A. (2017). Constructed floating wetlands: A review of research, design, operation and management aspects, and data meta-analysis. *Chemical Engineering Journal, 308*, 1120-1132.

Peng, J., Song, Y., Liu, Z., Gao, H., and Yu, H. (2012). Performance of a novel circular-flow corridor wetland toward the treatment of simulated high-strength swine wastewater. *Ecological Engineering, 49*, 1-9.

Proctor, D. M., Fehling, K. A., Shay, E. C., Wittenborn, J. L., Green, J. J., Avent, C., Bigham, R. D., Connolly, M., Lee, B., Shepker, T. O., and Zak, M. A. (2000). Physical and chemical characteristics of blast furnace, basic oxygen furnace, and electric arc furnace steel industry slags. *Environmental Science and Technology, 34*(8), 1576-1582.

Saeed, T., Afrin, R., Muyeed, A. A., and Sun, G. (2012). Treatment of tannery wastewater in a pilot-scale hybrid constructed wetland system in bangladesh. *Chemosphere, 88*(9), 1065-1073.

Saeed, T., and Sun, G. (2011). A comparative study on the removal of nutrients and organic matter in wetland reactors employing organic media. *Chemical Engineering Journal, 171*(2), 439-447.

Saeed, T., and Sun, G. (2013). A lab-scale study of constructed wetlands with sugarcane bagasse and sand media for the treatment of textile wastewater. *Bioresource Technology, 128*, 438-447.

Sawaittayothin, V., and Polprasert, C. (2007). Nitrogen mass balance and microbial analysis of constructed wetlands treating municipal landfill leachate. *Bioresource Technology, 98*(3), 565-570.

Seidel, K. (1953). Pflanzungen zwischen gewassern und land. *Mitteilungen Max-Planck Gesselschaft*, 17-20.

Stefanakis, A. I., Akratos, C. S., Gikas, G. D., and Tsihrintzis, V. A. (2009). Effluent quality improvement of two pilot-scale, horizontal subsurface flow constructed wetlands using natural zeolite (clinoptilolite). *Microporous and Mesoporous Materials, 124*(1–3), 131-143.

Stefanakis, A. I., and Tsihrintzis, V. A. (2012a). Effects of loading, resting period, temperature, porous media, vegetation and aeration on performance of pilot-scale vertical flow constructed wetlands. *Chemical Engineering Journal, 181–182*, 416-430.

Stefanakis, A. I., and Tsihrintzis, V. A. (2012b). Use of zeolite and bauxite as filter media treating the effluent of vertical flow constructed wetlands. *Microporous and Mesoporous Materials, 155*, 106-116.

Tang, X. Q., Huang, S. L., and Scholz, M. (2009). Comparison of phosphorus removal between vertical subsurface flow constructed wetlands with different substrates. *Water and Environment Journal, 23*(3), 180-188.

Tao, W., and Wang, J. (2009). Effects of vegetation, limestone and aeration on nitritation, anammox and denitrification in wetland treatment systems. *Ecological Engineering, 35*(5), 836-842.

Tee, H. C., Lim, P. E., Seng, C. E., and Nawi, M. A. (2012). Newly developed baffled subsurface-flow constructed wetland for the enhancement of nitrogen removal. *Bioresource Technology, 104*, 235-242.

Tee, H. C., Seng, C. E., Noor, A. M., and Lim, P. E. (2009). Performance comparison of constructed wetlands with gravel- and rice husk-based media for phenol and nitrogen removal. *Science of The Total Environment, 407*(11), 3563-3571.

Constructed wetlands treatment of municipal wastewaters (2000). (EPA/625/R-99/010). edn, National Risk Management Research Laboratory, Cincinnati, Ohio, 45268.

Vymazal, J. (2008). Constructed wetlands, subsurface flow. In Sven Erik JørgensenBrian D. Fath (Ed.), *Encyclopedia of ecology* (pp. 748-764). Oxford: Academic Press.

Vymazal, J. (2013). Emergent plants used in free water surface constructed wetlands: A review. *Ecological Engineering, 61, Part B*(0), 582-592.

Vymazal, J. (2014). Constructed wetlands for treatment of industrial wastewaters: A review. *Ecological Engineering, 73*, 724-751.

Wang, R., Korboulewsky, N., Prudent, P., Domeizel, M., Rolando, C., and Bonin, G. (2010). Feasibility of using an organic substrate in a wetland system treating sewage sludge: Impact of plant species. *Bioresource Technology, 101*(1), 51-57.

Wang, X., Bai, X., Qiu, J., and Wang, B. (2005). Municipal wastewater treatment with pond constructed wetland system: A case study. *Water Science & Technology, 51*(12), 325-329.

Wang, Z., Dong, J., Liu, L., Zhu, G., and Liu, C. (2013). Study of oyster shell as a potential substrate for constructed wetlands. *Water Sci Technol, 67*(10), 2265-2272.

Werker, A. G., Dougherty, J. M., McHenry, J. L., and Van Loon, W. A. (2002). Treatment variability for wetland wastewater treatment design in cold climates. *Ecological Engineering, 19*(1), 1-11.

Wittgren, H. B., and Mæhlum, T. (1997). Wastewater treatment wetlands in cold climates. *Water Science and Technology, 35*(5), 45-53.

Wu, H., Fan, J., Zhang, J., Ngo, H. H., Guo, W., Liang, S., Lv, J., Lu, S., Wu, W., and Wu, S. (2016). Intensified organics and nitrogen removal in the intermittent-aerated constructed wetland using a novel sludge-ceramsite as substrate. *Bioresource Technology, 210*, 101-107.

Wu, H., Zhang, J., Ngo, H. H., Guo, W., Hu, Z., Liang, S., Fan, J., and Liu, H. (2015). A review on the sustainability of constructed wetlands for wastewater treatment: Design and operation. *Bioresource Technology, 175*(0), 594-601.

Wu, J., He, F., Xu, D., Wang, R., Zhang, X., Xiao, E., and Wu, Z. (2011). Phosphorus removal by laboratory-scale unvegetated vertical-flow constructed wetland systems using anthracite, steel slag and related blends as substrate. *Water Science and Technology, 63*(11), 2719.

Xu, G., Zou, J., and Li, G. (2008). Ceramsite made with water and wastewater sludge and its characteristics affected by sio2 and al2o3. *Environmental Science and Technology, 42*(19), 7417-7423.

Yalcuk, A., and Ugurlu, A. (2009). Comparison of horizontal and vertical constructed wetland systems for landfill leachate treatment. *Bioresource Technology, 100*(9), 2521-2526.

Yeh, N., Yeh, P., and Chang, Y.-H. (2015). Artificial floating islands for environmental improvement. *Renewable and Sustainable Energy Reviews, 47*, 616-622.

Yen, H. Y., and Chou, J. H. (2016). Water purification by oyster shell bio-medium in a recirculating aquaponic system. *Ecological Engineering, 95*, 229-236.

Yin, H., Yan, X., and Gu, X. (2017). Evaluation of thermally-modified calcium-rich attapulgite as a low-cost substrate for rapid phosphorus removal in constructed wetlands. *Water Research, 115*, 329-338.

Yun, Y., Zhou, X., Li, Z., Uddin, S. M. N., and Bai, X. (2015). Comparative research on phosphorus removal by pilot-scale vertical flow constructed wetlands using steel slag and modified steel slag as substrates. *Water Science and Technology, 71*(7), 996-1003.

Zhao, Y. Q., Babatunde, A. O., Hu, Y. S., Kumar, J. L. G., and Zhao, X. H. (2011). Pilot field-scale demonstration of a novel alum sludge-based constructed wetland system for enhanced wastewater treatment. *Process Biochemistry, 46*(1), 278-283.

Zhao, Y. Q., Zhao, X. H., and Babatunde, A. O. (2009). Use of dewatered alum sludge as main substrate in treatment reed bed receiving agricultural wastewater: Long-term trial. *Bioresource Technology, 100*(2), 644-648.

Zurita, F., De Anda, J., and Belmont, M. A. (2009). Treatment of domestic wastewater and production of commercial flowers in vertical and horizontal subsurface-flow constructed wetlands. *Ecological Engineering, 35*(5), 861-869.

Chapter 4

Effects of Different Substrates in the Mitigation of Algae-induced High pH Wastewaters in Free Water Surface Wetland Systems

Abstract: Wastewater stabilization ponds (WSPs), as part of municipal wastewater treatment strategies, can exhibit variability in performance due to climatic conditions. Under elevated temperatures and strong solar radiation conditions, algal blooms and subsequent high pH effluents have often been observed. To mitigating this effect, four substrates (gravel, peat, organic mulch, and topsoil) were evaluated for their ability to attenuate high pH level synthetic wastewater in a two phases study. A short-term assessment of four substrates followed by a long-term monitoring of the two most promising substrates were undertaken under different hydraulic retention times (HRTs) (2.5, 4, and 6 days) and organic loading rates (OLRs) (20, 70, 135 mg/L COD). The Phase 1 assessment showed that all substrates had the ability to attenuate pH levels below 9.5. Peat could substantially reduce the system pH from 10.3 to 7.7, and 53.7% of the influent total phosphorous (TP) was removed. The other three substrates could effectively reduce pH from 10.3 to 9.2. However, the low alkalinity from gravel (47.5 mg/L), and organic leaching from organic mulch (28.0 mg/L) made them unsuitable for field application. Further study from Phase 2 showed that the pH attenuation ability of the substrates could be influenced by the operational conditions. OLR had more significant impact on system pH compared to the HRT. The pH attenuation performance could be significantly improved when the OLR were increased to 70, and 135 mg/L COD,

respectively, for peat (pH=8.29, 7.97) and topsoil (pH=8.54, 8.16), while it could only do so when HRTs were longer than 4 days (8.70 for peat, 8.35 for topsoil).

Keywords: Algae, constructed wetlands, nutrients, organics, pH, substrate, waste stabilization ponds

4.1 Introduction

In Canada, there are more than 3,500 wastewater treatment facilities, many of which apply biological treatment technologies such as the activated sludge process (Lotito et al., 2014), biofilm-based technologies such as trickling filters (Daigger & Boltz, 2011), vegetated filters (Miguel et al., 2014), as well as pond systems such as oxidation ditches and WSPs (Hosetti & Frost, 1998). Among these technologies, WSPs are considered to be the most sustainable technology for small communities that require low-cost and low-maintenance wastewater treatment facilities. They can effectively attenuate organic and nutrient concentrations, as well as bacteria and pathogen levels in municipal wastewater (Liu et al., 2016a; Maynard et al., 1999; Reinoso et al., 2008; Senzia et al., 2003).

However, due to the configuration of WSPs and limited control over these systems, performance concerns during certain parts of the year may arise (Kayombo et al., 2002). There is a synergistic balance between heterotrophic microorganisms and algae in a WSP system, where they work together to provide treatment for wastewater (Borde et al., 2003; Muñoz & Guieysse, 2006). Shallow WSP basins encourage sunlight penetration throughout the water column depth, which, along with the increased temperature, could provide a favorable environment for algae to thrive during the treatment season. However, these conditions could stimulate excessive algal growth in these WSPs and destroy the synergistic balance between heterotrophic microorganisms and algae. Excessive algal growth in the treatment ponds can deplete dissolved carbon dioxide, a necessary requirement for photosynthesis. Along with the limited replenishment of carbon dioxide from atmospheric diffusion and respiration in heterotrophic microorganisms, the absence of dissolved carbon dioxide can give rise to increases in pH level (>9.5) in the treatment ponds (Nishimura et al., 1984). Moreover, with dissolved carbon dioxides being relatively low, the water chemistry equilibrium will encourage the formation of carbonate and bicarbonate ions from carbon dioxide to maintain the carbonate equilibrium, which further increases the pH level according to the Equation 4.1.

Equation 4.1

$$H_2O + CO_{2(g)} \longleftrightarrow H_2CO_3^* \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$$

High pH level wastewater could (i) shift the ammonium/ammonia equilibrium increasing the rate of ammonia formation and volatilization; (ii) alter the downstream ecological environment if the elevated pH water is discharged to the receiving environment; and, (iii) not meet the regulatory discharge guidelines (pH = 6.5 - 9.5) are set by Environmental Canada (Canada, 2012).

Similar to WSPs, constructed wetlands (CWs) are also considered to be a sustainable treatment technology that mainly attenuates wastewater through naturally occurring biological processes. One of the merits of CWs, compared to WSPs, is that they are more resilient to fluctuations in ambient environmental conditions due to the complexity of their ecosystems (Pietro & Ivanoff, 2015). The components of a typical CW include inlet and outlet structures, substrates, rooting media, and vegetation. Both the individual and the combination of these components are important in terms of treatment performance (Kadlec & Wallace, 2008). As such, temporary high temperatures and/or high solar radiation may not strongly affect the pH and overall treatment performance of a CW, as they would in a WSP. CWs have also been shown to attenuate acidic or alkaline wastewater to neutral levels. For example, acidic wastewater from a food processing plant at Connell, Washington (Kadlec et al., 1997), and alkaline wastewater at Estevan, Saskatchewan (Pries, 1996) and alkaline mine tailing (Kelly et al., 2007) have been attenuated to neutral pH prior to discharge to the environment by FWS CW.

Substrate is an important component of CWs in terms of contaminant and nutrient transport and removal. It provides a surface area to allow sustained biofilm growth, which can enhance microbial processes in CWs. In recent years, alternative substrates (e.g. mulch, zeolite, and volcanic ash) have attracted more attention because of their high surface area and increased nutrient retention capacity compared to the traditional substrates (e.g. gravel). Herrera-Melián et al. (2014) indicated that palm tree mulch could be used as an alternative substrate for mixed flow constructed wetlands to achieve treatment, as well as reduce of the risk of clogging for mineral-based CWs. The reactors with palm tree mulch achieved similar performance levels as the ones with gravel. Treatment efficiency did not depend on the loading rate of COD, suspended solids (SS) or turbidity, and the combination of concentrated influent and lower hydraulic loading rate provided the best treatment performance. Jong and Tang (2015) compared the substrates palm kernel shell (PKS) and sand in a vertical flow subsurface wetland for the treatment of septage. The results demonstrated that PKS achieved better nitrogen removal (83.10%) compared to sand (64.24%) due to the high denitrification activity stimulated by carbon within PKS. Liu et al. (2014) investigated four different substrates including zeolite, quartz sand, biological ceramsite, and volcanic rock in tidal flow CWs. Zeolite exhibited the best performance over the other materials due to a combination of beneficial properties including: high micropore volume, specific surface area, and cation exchange capacity. Bai et al. (2014) proposed the reuse of drinking water treatment residuals (WTR) as a substrate in CWs designed to treat secondary wastewater effluent. Both continuous and tidal operational flow conditions, laboratory-scale columns demonstrated that satisfactory removal of COD, total nitrogen (TN), TP, and SS could be achieved. However, effluent ammonium concentrations were found to be slightly higher than influent concentrations, which may have resulted from the ammonification of organic nitrogen in WTRs. This phenomenon was also reported by Gray et al. (2000), who conducted experiments to evaluate the performance of maerl (calcified seaweed) as a potential substrate for CWs. Significant increases in ammonia were observed at the beginning of the experiment, as the organic nitrogen present in the substrate was converted to ammonium through ammonification. Mateus et al. (2012) investigated the potential for using fragmented moleanos limestone (FML) as a substrate in a subsurface flow CW designed to achieve phosphorus removal. FML is relatively inexpensive and considered a waste material from the extraction of stones. An above average phosphorus removal efficiency of 61% and first order areal constant of 0.062 m/d were reported, suggesting that FML could be a promising substrate especially in the development of a sustainable and cost-effective treatment system, where this material is readily available and cost- effective. Aslam et al. (2007) investigated the feasibility of using compost as potential substrate for a vertical flow CW to treat oil refinery wastewater. They demonstrated satisfactory pollutant removal efficiencies for TSS (51-73%), COD (45-78%), BOD (35-83%), as well as heavy metals such as iron, copper, and zinc during the one-year experimental period.

However, most these studies only focused on the effects of these substrates on the removal of organic matter and nutrients removal from municipal or industrial wastewaters, and primarily in subsurface flow CW systems. There is very little information about the effects of these substrates on FWS CW systems. More importantly, very few studies have focused on the effects of inter relationship between system pH, organics and nutrients on the system, especially for algal-induced high pH wastewaters.

As such, this study aims to provide a comparative evaluation of four locally available substrates (gravel, topsoil, peat, and organic mulch) considered for application in a pilot-scale FWS CW for the polishing of secondary wastewater effluent in an eastern Ontario wastewater treatment plant (WWTP). The main objective of this study was to compare the performance of these substrates, in terms of pH attenuation, as well as organics and nutrients removals under a FWS CW operational configuration using bench-scale reactors without the presence of vegetation. The capability of each substrate for pH attenuation, and organic and nutrient removal were assessed based on their geophysical properties, without the confounding effects of vegetation. The study was undertaken in two phases.

During Phase 1, all substrates were assessed under same operational condition and two promising substrates were identified and applied in Phase 2, during which the two identified substrates were further assessed under different operational conditions. Three different HRTs and OLRs were applied as well as a shock pH-loading test. The outcome of this study was to identify the best available substrates for a future pilot-scale FWS CW study in eastern Ontario.

4.2 Material and methods

4.2.1 Preparation of synthetic wastewater

A synthetic wastewater was prepared every two days and used as the influent for all experimental wetland systems. The synthetic wastewater was prepared using (g in 1 L tap water): 0.00050g $C_6H_{12}O_6$, 0.01008g $NaHCO_3$, 0.00047g $NaNO_3$, 0.00009g NH_4Cl, 0.00004g KH_2PO_4, 0.01339g $MgCl_2 \cdot 6H_2O$, 0.01651g $CaCl_2 \cdot 2H_2O$, 0.00005g $FeSO_4 \cdot 7H_2O$, 0.00003g $MnSO_4 \cdot H_2O$, and 0.70000g NaOH. Synthetic wastewater for the Phase 2 study with different pH and OLRs was achieved by adjusting the $C_6H_{12}O_6$ and NaOH concentrations. All chemicals used were ACS reagent grade or analytical reagent grade used as supplied by Fisher Scientific. The prepared synthetic wastewater was stored in a 300 L Nalgene feed tank, prior to being dosed into the experimental system.

The synthetic wastewater was generally designed to characterize the secondary effluent from an eastern Ontario WWTP, with relatively low organic and nutrient concentrations. Sodium hydroxide and sodium bicarbonate were mainly used to buffer the solution to maintain the pH relatively constant in the synthetic wastewater. An average pH of 10.5

was applied to simulate the high pH events. During the shock pH loading test, the pH of the influent was raided to 11.5 using NaOH and maintained for 24 hours.

4.2.2 Configuration of bench-scale wetland system

All bench-scale reactors were constructed of Plexiglass, and were fabricated and supplied by Kingston Plate and Window Glass in Kingston. The length, width and height of each wetland reactor were 600mm, 200mm, and 800mm, respectively. The experimental system was configured to mimic a FWS CW without vegetation, such that the effects of substrate on the water chemistry could be assessed. To control the flow of the system, a ¼" (6.25mm) hole was drilled into each reactor side panel (0.2m x 0.8m) and equipped with a ¼" male to female PVC ball valve screw. The heights of the influent and effluent ports of the wetland reactor were 250mm and 600mm from the bottom of the reactor, respectively. A 0.2 m layer of substrate was added for each test. The synthetic wastewater was simultaneously pumped into the six reactors from the feed tank using a Masterflex L/S peristaltic pump with a 12-channel, 8-roller cartridge pump head that can hold up to six cartridges at the same time. Masterflex Tygon E-Lab pump tubing was used to connect the reactors to the feed tank.

4.2.3 Substrates

Four locally available substrates: gravel, peat, organic mulch, and topsoil (Figure 4.1), that could potentially attenuate high pH synthetic wastewater, were used in this experiment. All substrates were purchased from The Home Depot (Kingston, Canada). Prior to the experiment, the substrates were washed in deionized water to remove any dirt and undesired materials. Sand was used to serve as controls, and duplicate systems were used for each substrate. The porosity of each substrate was measured by pouring water in a 1 L graduated cylinder packed with substrate. The porosity was determined by the volume of water required to fill the void spaces in the substrates divided by the volume of the substrates (1 L) (Equation 4.2). The physical properties of the substrates are presented in Table 4.1.

Equation 4.2

$$\phi = \frac{V_v}{V_T}$$

Ø: Porosity (dimensionless)

V_v: The volume of void space in substrate (L)

V_T: The total or bulk volume of substrate (L)

Table 4.1 Porosity and density of substrates applied in this experiment

	Gravel	Peat	Topsoil	Organic mulch
Density (kg/m^3)	1545	800	1520	505
Porosity	0.44	0.31	0.50	0.76

Porosity is from 0-1. 0 indicates the lowest porosity and 1 indicates the highest porosity.

4.2.4 Operation of reactors

Initially, deionized water was fed to the experimental systems through a peristaltic pump continuously, allowing the substrates to become hydrated and settled within the reactors. After the substrates had hydrated for two days, the pump was stopped pumping the deionized tap water to the reactor and it was drained completely. Then, the system was begun to feed with the pre-prepared synthetic wastewater. During the start-up phase for each set of experiments, the peristaltic pump was operated at 50 rpm (6.9 L/d) to gradually fill each of the reactors and minimize disturbance of the substrates. When the water levels had reached the operational height (600 mm), the speed of the pump was changed to 140 rpm (19.2 L/d), which was in-line with the design hydraulic retention time (HRT=2.5 days).

The experiments were carried out in two phases. During the Phase 1 study, four substrates were evaluated for a period of two weeks under same HRT and OLRs. Gravel and peat were evaluated in the wetland reactors in duplicate from weeks 1 to 4. To avoid contamination, after four weeks, all substrates that remained in the reactors were removed and the reactors were washed, sterilized and dried before loading the new substrates for the next set of experiment. Organic mulch and topsoil were examined from weeks 5 to 8. In each set of experiments, the bench-scale wetland systems were under continuous flow condition throughout the four-week experimental period. The substrates were allowed to acclimatize to the synthetic wastewater for two HRT cycles, before any sampling and analyses were initiated. Two weeks of intensive sampling and analysis were completed for each substrate to assess their performance and attenuation capacity. The operational condition for the phase one study is listed in Table 4.2.

During the Phase 2 study, the two most promising substrates from the Phase 1 study, which demonstrated the best performance in the phase one study, were further assessed under a range of HRTs, OLRs, as well as shock pH loading conditions. These substrates were also evaluated under continuous flow condition for a period of three months in duplicate systems. Each condition was monitored for a period of two weeks of sampling and analyses, before operational conditions were modified. All operational conditions were applied during the Phase 2 study are listed in Table 4.3.

Table 4.2 Operational condition for the Phase 1 study

Parameters	HRT	Flow Rate	Organic loading rate	Nitrogen loading rate	Phosphorus loading rate
	2.5 d	19.2 L/d	0.33 g/d	0.028 g/d	0.008 g/d

Table 4.3 Operational conditions for the Phase 2 study

Condition	Influent pH	HRT	Organic loading rate
Standard (S)	10.5	2.5 days	25mg/L
Hydraulic retention time 1 (HRT 1)	10.5	4 days	25mg/L
Hydraulic retention time 2 (HRT 2)	10.5	6 days	25mg/L
Organic loading rate 1 (OLR 1)	10.5	2.5 days	50mg/L
Organic loading rate 2 (OLR 2)	10.5	2.5 days	100mg/L
Shock Loading (SL)	11.5	2.5 days	25mg/L

4.2.5 Sampling and analysis

During the Phase 1 study, wastewater samples were collected on a daily basis from the feed tank and outlet of each reactor. Twelve sets of data were collected for pH, redox potential (E_h), alkalinity, ammonium, nitrite, and nitrate. Eight sets of data were collected for TP and TN, and five sets of data were collected for COD. During the Phase 2 study, a two-week monitoring period was applied for each operational condition, and wastewater samples were collected on a bi-daily basis from the outlet of each reactor. For each operational condition, six sets of data were collected for pH, E_h; Four sets of data were collected for TN, TP, nitrate, nitrite, ammonium, COD, and alkalinity.

pH and E_h were analysed using a Fisher Scientific accumet XL60 benchtop meter with Fisher Scientific pH and E_h probes. Ammonium and nitrate were measured using the same bench top meter with Fisher Scientific ammonium and nitrate probes. Nitrite, and alkalinity was determined using Thermo Scientific Orion AQUAfast Colorimetric Tablet Reagents and a HACH DR 2800 spectrophotometer based on USEPA approved methods. The TN and TP analyses were conducted using a Digital Reactor Block 200 and HACH DR 2400 spectrophotometer based on USEPA approved standard procedure for wastewater analysis. The COD analyses were performed based on the standard methods (APHA, 2012).

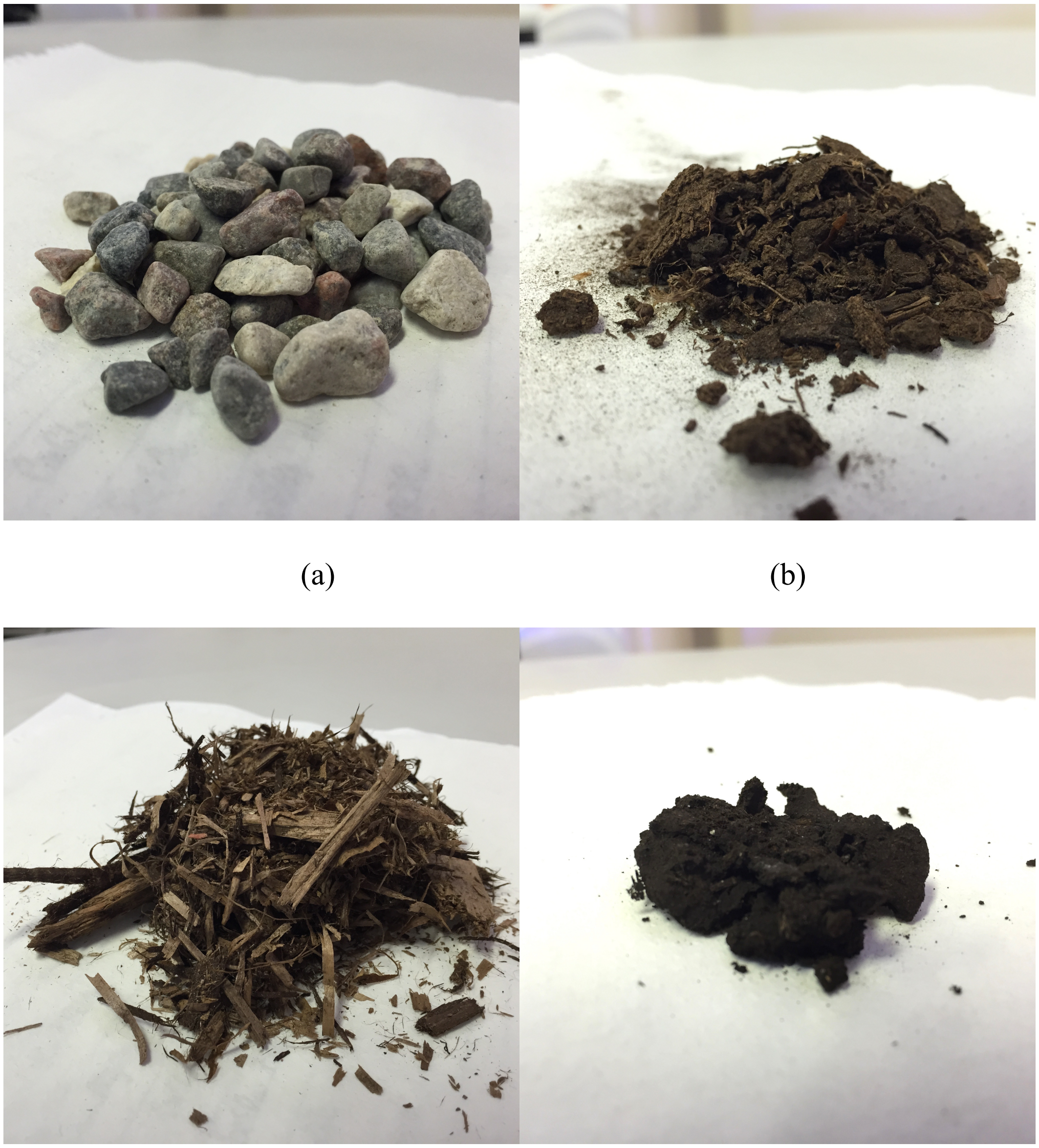
4.2.6 Statistical analysis

In order to compare the pH attenuation capacity of the different substrates in the bench-scale reactors, various parametric and non-parametric statistical analyses were performed using Microsoft EXCEL and XLSTAT.

Statistical normality tests (Shapiro-Wilk, Anderson-Darling, Lilliefors, and Jarque-Bera) were performed to verify whether the distribution of data approximated normality, in order to select the proper parametric and non-parametric statistical method for further analyses, which was accepted when α=0.05. When data approximated normality, the data were analyzed through one-way analysis of variance (ANOVA) when comparing more than two groups or *t*-test when comparing only two groups to illustrate a statistical significant difference ($p<0.05$) of the means, where a significant difference ($p<0.05$) was observed among comparable different substrates. When the data did not approximate normality, the data were analyzed through non-parametric statistical analysis Mann-Whitney test ($p<0.05$) when comparing more than two groups or Kruskal-Wallis test when comparing only two groups. Parametric (Pearson) or non-parametric (Spearman) correlation analysis was also performed according to the normality of the data set. All proposed statistical methods are given in Table 4.4.

Table 4.4 Statistical analysis methods employed in this study

Test	Parametric Analysis	Non-Parametric Analysis
Comparison, 2 groups	*t*-test	Mann-Whitney test
Comparison, >2 groups	ANOVA	Kruskal-Wallis test
Correlation	Pearson	Spearman



(a) (b) (c) (d)

Figure 4.1 Substrate materials that employed in this study: (a) gravel; (b) peat; (c) organic Mulch; (d) topsoil

4.3 Results and Discussions

4.3.1 Overall performance for the phase one study

Table 4.5 summarizes the mean effluent pollutant concentrations and removal efficiencies achieved in each of the experimental reactors with different substrates in the Phase 1 study. In terms of pH attenuation, peat exhibited the highest capacity for pH attenuation after one HRT cycle and maintained this pH level throughout the experimental period. Only gravel and topsoil demonstrated positive COD removal efficiencies, while the organic substrates, peat and organic mulch, showed a tendency to increase the COD concentration in the reactors. In terms of nutrient removal, although the influent synthetic wastewater had relatively low nutrient concentrations (TN= 1.49 mg/L, TP= 0.41 mg/L), the substrates contributed to the further removal of most nutrient constituents. The only exception was the effluent TN concentration of peat. Considering the treatment performance and the pH attenuation objective, peat and topsoil were selected for the Phase 2 study.

4.3.2 pH attenuation

Error! Reference source not found. illustrates the pH variation with time for each of he substrates. As can be clearly seen, peat exhibited a higher capacity to lower system pH, which was initially above 10.5 and was reduced to below 8 after two HRT cycles (Discharge range of pH is in red line). After one HRT cycle (2.5 days), the pH in the reactor decreased from 9.87 to 8.40, and then further to 7.76 and remained at that level until the end of the experiment. The reactors to which gravel, organic mulch, and topsoil were applied exhibited effluent pH levels of 9.21, 9.12, and 9.27, respectively, throughout the experiment. The results demonstrated that pH levels below 9.50 could be consistently achieved within two HRT cycles, which would allow for the polished wastewater effluent to be discharged to the receiving environment. The result from the ANOVA analysis rejected the null hypothesis ($p<0.0001$) that the mean effluent pH of all substrates were equal. However, the ANOVA analysis can only indicate whether there is a significant difference of the mean effluent pH level within the four groups. It cannot identify between which groups there are statistically significant differences. Therefore, post-hoc pairwise comparison analyses (Tukey pairwise comparison test, Fisher test, and Bonferroni test) were performed to identify the statistically significant difference between groups. The three tests uniformly demonstrated that the pH attenuation performance of peat was significantly different from the other substrates, while there was no statistical difference among gravel, organic mulch, and peat, which is shown in Table 4.6.

Table 4.5 Mean pollutant concentrations and removal efficiencies in the wetland reactors during the Phase 1 study. Standard deviation of pollutant concentration is indicated in brackets.

	Unit	**Influent conc.**	**Gravel**		**Peat**		**Topsoil**		**Organic Mulch**	
			EC	EF %	EC	EF %	EC	EF %	EC	EF %
pH	N/A	10.37 (0.20)	9.21 (0.11)	--	7.76 (0.11)	--	9.27 (0.17)	--	9.12 (0.21)	--
E_h	mv	91.4 (5.9)	123.9 (10.1)	--	143.1 (23.9)	--	125.1 (15.3)	--	121.9 (10.5)	--
Alkalinity	mg/L	128.0 (50.0)	47.5 (5.0)	62.9	55.2 (10.0)	56.9	102.3 (33.6)	20.1	105.1 (35.9)	17.9
COD	mg/L	17.38 (7.47)	10.50 (1.98)	39.6	19.00 (1.85)	--	13.63 (4.27)	21.6	28.00 (11.22)	--
Ammonium	mg/L	0.17 (0.08)	0.07 (0.03)	58.8	0.13 (0.04)	23.5	0.05 (0.01)	70.6	0.04 (0.01)	76.5
Nitrate	mg/L	3.02 (0.78)	2.53 (0.69)	16.2	4.13 (1.03)	-36.8	2.02 (0.84)	33.1	4.00 (2.45)	-32.5
Nitrite	mg/L	0.009 (0.003)	0.004 (0.002)	55.6	0.014 (0.010)	--	0.027 (0.022)	--	0.044 (0.015)	--
TN	mg/L	1.49 (0.27)	1.30 (0.48)	12.8	1.64 (0.21)	--	1.00 (0.15)	32.9	1.00 (0.24)	32.9
TP	mg/L	0.41 (0.19)	0.11 (0.02)	73.1	0.19 (0.05)	53.7	0.15 (0.05)	63.4	0.20 (0.03)	51.2

EC - Effluent Concentration, EF - Removal Efficiency

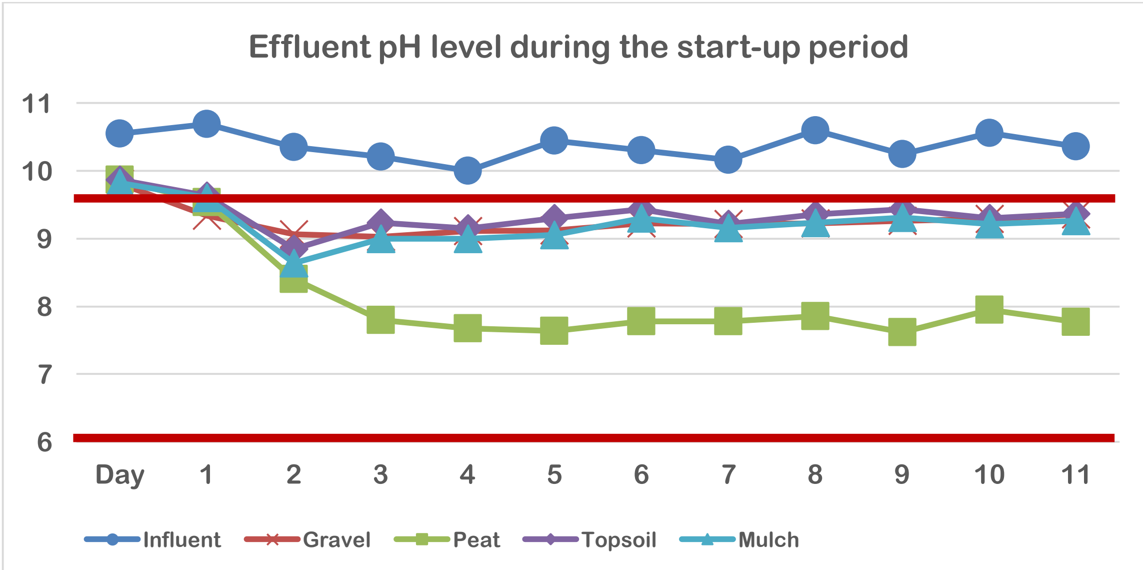


Figure 4.2 pH changes during the start-up experimental period

Table 4.6 Statistical analysis comparing pH attenuation capacity in experimental reactors with different substrates. Note that statistically significant difference (p<0.05) is indicated by bold numbers

	Peat	Gravel	Organic Mulch	Topsoil
Peat	N/A	**<0.0001**	**<0.0001**	**<0.0001**
Gravel	**<0.0001**	N/A	0.999	0.981
Organic Mulch	**<0.0001**	0.999	N/A	0.933
Topsoil	**<0.0001**	0.981	0.933	N/A

4.3.3 Alkalinity

Alkalinity is the measurement of the capacity of water or any solution to neutralize or “buffer” strong acids. This measurement of acid neutralizing capacity is important in terms of understanding how an aqueous environment can resist sudden changes in pH. In natural waters, this capacity is mostly attributed to basic ions such as bicarbonate,

carbonate, hydroxide ions, as well as trace metals that can be neutralized by acid (Snoeyink & Jenkins, 1980). Since the synthetic wastewater that was supplied in this experiment contained very little trace metals, it was assumed that the total alkalinity could be attributed bicarbonate, carbonate, hydroxide ions, as shown in Equation 4.3.

Equation 4.3

$$\text{Total Alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

Table 4.5 summarizes the mean effluent alkalinity from each of the four substrates reactors. The mean effluent alkalinity for organic mulch and topsoil were 105.1 mg/L (2.10 meq/L) and 102.3 mg/L (2.05 meg/L), while the mean effluent alkalinity for peat and gravel were 52.2 mg/L (1.04 meg/L) and 47.5 mg/L (0.95 meg/L), respectively. The ANOVA analysis confirmed that significant differences ($p<0.0001$) could be noted for the mean effluent alkalinities. The Tukey pairwise comparison test indicated significant differences between the reactor with mulch and gravel, mulch and peat, topsoil and gravel, and topsoil and peat, while there was no significant difference between mulch and topsoil.

As can be surmised from Equation 4.3, the total alkalinity of the solution will depend on both system pH and carbonate concentrations. Hence, solutions with lower pH levels will tend to exhibit lower total alkalinities when they contain a relatively similar amount of carbonate concentrations. Peat demonstrated the highest pH attenuation capacity and lowest alkalinity. Gravel had a significantly lower total alkalinity compared to organic mulch and topsoil, which exhibited similar mean effluent pH levels. These results would indicate that there are different pH attenuation mechanisms that occur with different substrates (Snoeyink & Jenkins, 1980).

Peat, due to it physical and chemical properties, contains large amounts of humic and fulvic acids, and humus substances that can directly react with bases in aqueous environments. Organic mulch and topsoil, which share similar physical and chemical properties with peat, contains more organic substances compared to inorganic substrates, such as gravel (Su & Puls, 2007). The organic substances typically contain different kinds of organic compounds, such as organic acids, that can be utilized to neutralize the hydroxide ion without interfering with inorganic carbonate species in the system, which does not apply to gravel. In the case of gravel, calcite precipitation can contribute to the consumption of alkalinity that could encourage a decrease in pH level in the reactor. (Mayes & Younger, 2006) conducted a study to assess the rates of buffering across a natural wetland receiving steel slag drainage in northeast England. The effluent pH was consistently below 9, with calcite precipitation rates (9.88 $g/m^2/d$) up to two folds the peak values (3.66 to 4.35 $g/m^2/d$) observed in natural waters (Dreybrodt et al., 1992). This theory is supported by the low alkalinity concentrations observed in the reactor and the properties of gravel, which contains large amount of calcium.

4.3.4 Nutrients Removal

The influent nitrogen concentration was considered to be relatively low in this experiment, compared to other studies. However, even at these low influent concentrations, the substrates contributed to the removal or partial removal of nitrogen in the experimental reactors. Table 4.5 demonstrated that organic mulch, topsoil, and gravel could achieve high ammonium removal efficiency, 76.6%, 70.6%, and 58.8%, respectively, while peat only showed a removal efficiency of 23.5%. Most of the ammonium in the wastewater is transformed to the ammonia, and removed through mass transfer from the water surface to the atmosphere (Equation 4.4). This process is mainly dependent on the system pH, as a high pH environment (pH>9.3) encourages ammonium volatilization process (Białowiec et al., 2011).

Equation 4.4

$$NH_4^+ + OH^- \leftarrow\!\!\!-\!\!\!-\!\!\!\rightarrow NH_{3(g)} + H_2O$$

The high ammonium removal efficiency provided by organic mulch and topsoil was correlated to their relatively high nitrite concentrations, compared to gravel and peat, as well as their high E_h (nitrification → 100 mv to 350 mv), which would indicate that nitrification might be favored in both reactors. During the nitrification process, hydrogen ions are produced, according to Equation 4.5 and Equation 4.6, which can then lower the pH level of the system. In terms of denitrification, neither substrate exhibited the ability to contribute to or enhance nitrite removal. Saeed and Sun (2012) showed that organic mulch with high organic carbon concentrations, which is served as an additional carbon source, could enhance the denitrification rates in wetland applications. The low denitrification observed in these experiments might be due to the oxidation state measured in each of the reactors. Hence, the system may not have been adequately reducing to support denitrification, which typically occurs under anaerobic condition, where an E_h range of 50 mv to -50 mv allows denitrifiers to thrive. However, the reactors were designed to simulate FWS CW conditions, in which aerobic conditions would be promoted. The reactors exhibited an average E_h of approximately to 120 mv, which would likely have inhibited the growth of denitrifiers, resulting in low denitrification rates.

Equation 4.5

$$NH_4^+ + 1.5O_2 \dashrightarrow H^+ + H_2O + NO_2^-$$

Equation 4.6

$$NO_2^- + 0.5O_2 \dashrightarrow NO_3^-$$

In contrast, gravel showed moderate ammonium removal efficiencies (58.8%), as well as for nitrate (16.2%), nitrite (55.6%), and TN (12.8%). It is the only substrate that demonstrated positive removal efficiencies for all nitrogen species in this experiment. Peat showed similar nitrate accumulation as observed for the organic mulch. However, its low ammonium removal efficiency coupled with very low nitrite concentration indicates that there may have been an external nitrates sources from the substrate. The negative TN removal rates suggested that nitrogen might be leached from the peat.

In terms of phosphorus removal, TP removal efficiencies were higher in the gravel reactor compared to the organic substrates throughout the experimental period. These results were contradictory to a number of studies that have demonstrated that organic substrates generally exhibit higher phosphorus retention capacities due to their chemical properties (Herrera-Melián et al., 2014; Lüderitz & Gerlach, 2002). Peat and organic mulch have been reported to contain substantial humus and humic substances, which have been noted to play an important role in terms of TP removal via adsorption (Saeed

& Sun, 2011). Although the peat and organic mulch demonstrated moderate TP removal efficiencies (53.7% and 51.2%), in this study, gravel (73.1%) showed the highest treatment performance. This may be due to the short experimental period or HRT, which may have minimized the contact time between the wastewater and substrates. This has been reported in other studies. Lantzke et al. (1998) demonstrated that gravel sorption equilibrium could be established fairly quickly (within 48-150 hours). Other phosphorus retention mechanisms tend to occur more slowly than sorption, for example, microbial phosphorus removal and plant uptake in wetland applications (Lantzke et al., 1998). In addition, the organic substrates applied in this experiment may have contained higher phosphorous background concentrations, which limited their ability to achieve higher removal efficiencies.

4.3.5 Organics removal

In this experiment, COD was applied solely to monitor the organic matters in the system due to the nature of the synthetic wastewater. The ANOVA results showed that there was no statistically significant difference in COD removal between the substrates. Since the influent COD was relatively low (17.38 mg/L) due to the wastewater characteristics, and the organic substrates used contain relatively high concentrations of organic carbon, it was anticipated that background concentration of the substrates would play influence effluent COD concentrations and, hence, net COD removal efficiencies. Peat and organic mulch both showed negative COD removal efficiencies as anticipated, and organic mulch even exhibited a mean effluent COD concentration of 28 mg/L, which exceeded the wastewater discharge guidelines (COD < 25 mg/L). The result for the organic mulch corresponded to those presented by Saeed and Sun (2011) where the high COD observed was believed to be the result of organic carbon leaching from organic substrates. Herrera-Melián et al. (2014) applied palm tree mulch in wetland reactors and the lowest COD concentrations they achieved was 40 mg/L, which they attributed to the mulch having a fairly high COD background concentration.

On the other hand, the reactors containing the inorganic substrate, gravel, were observed to further reduce the COD (39.5%). Compared to the organic substrates, inorganic substrate, gravel, has a much lower organic carbon composition. Therefore, there is less opportunity for organic leaching even when the influent COD is relatively low. The positive COD removal efficiency observed further supports this point.

4.3.6 Effects of HRT

HRT is an important parameter in terms of operating a pond system, and it has a direct effect on the treatment performance on the system. The results from the Phase 2 study, in terms of HRT effects are presented in Table 4.7. During the Phase 2 study, three different HRTs, 2.5 days, 4 days, and 6 days, were employed for peat and topsoil to further evaluate their pH attenuation performance. Figure 4.3(a) illustrates mean effluent pH under different HRTs, and the graph clearly shows that longer HRTs provided notably better pH attenuation. The pH was only noted to decrease from 10.5 to around ~9.5 with HRTs of less than 4 days, while it was found to be further attenuated to 8.70 and 8.35 by peat and topsoil, respectively, when the HRT was extended to 6 days. Compared to the Phase 1 study, the pH attenuation capacity of the peat appeared to decrease considerably.

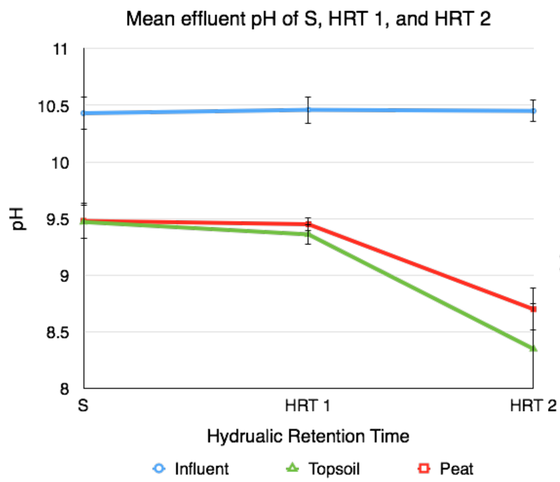
This phenomenon might due to the fact that the humic substances within substrate, more specifically organic acids that can be easily liberated from the peat, may have been largely consumed, and the remaining acidic substances in the peat could not be liberated readily to provide sustained treatment. This indicated that peat might not be the best option to provide long-term pH attenuation alone. However, the pH attenuation capacity showed little difference between the 2.5 days and 4 days HRT for both peat and topsoil.

Figure 4.3(b) illustrates the mean effluent TN for different HRTs. As can be seen nitrogen removal efficiency increased when HRT was increased from 1 to 2, where removal efficiencies increased from 19.2% to 61.6%, and 25.6% to 63.6% for peat and topsoil, respectively. The most common mechanism for nitrogen removal in WSP or CW is the combination of nitrification and denitrification; and the longer contact time between microorganisms and nitrogen contributes to the overall removal of the nitrogen species in experimental reactors.

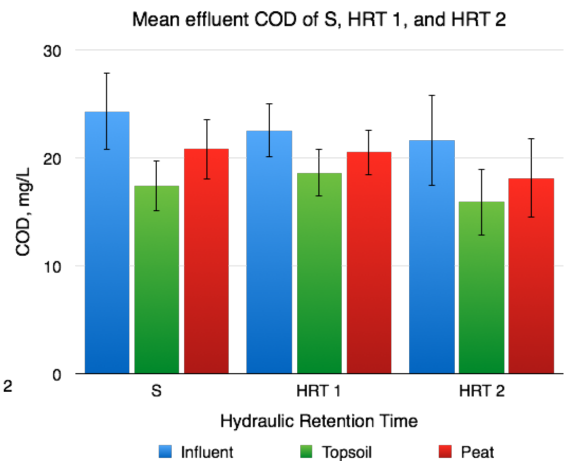
However, not all water quality parameters were affected by the longer HRT. COD and TP removal efficiencies did not increase with increasing HRT (Figure 4.3(c)(d)). Phosphorous retention within the substrates is governed by both adsorption and desorption on the substrate surface. Hence, substrate surface area, which mainly depends on the porosity of the substrate, may have a greater effect on phosphorous removal than HRT. Other considerations include the saturation of sorption site may fully occupied by phosphorous or other ions.

Table 4.7 Mean pollutant concentrations in the wetland reactors as a function of HRT during the Phase 2 study including. Standard deviations of pollutant concentration indicated in brackets.

Parameters	Influent Conc.	Standard (S) HRT = 2.5 Days		HRT 1 HRT = 4 Days		HRT 2 HRT = 6 Days	
		Peat	Topsoil	Peat	Topsoil	Peat	Topsoil
pH	10.37 (0.20)	9.48 (0.15)	9.47 (0.16)	9.45 (0.09)	9.36 (0.06)	8.70 (0.40)	8.35 (0.19)
ORP	91.4 (5.9)	115.63 (11.26)	132.38 (16.15)	130.63 (11.79)	134.38 (12.63)	145.13 (6.92)	155.88 (6.14)
Alkalinity	128.0 (50.0)	85.5 (7.6)	94.9 (5.3)	77.5 (3.0)	87.4 (2.7)	75.4 (5.5)	80.0 (4.4)
COD	17.38 (7.47)	20.8 (4.2)	17.4 (2.5)	20.5 (3.1)	18.6 (2.2)	18.1 (3.7)	15.9 (2.1)
Ammonium	0.17 (0.08)	0.10 (0.03)	0.13 (0.05)	0.10 (0.07)	0.10 (0.04)	0.11 (0.03)	0.15 (0.06)
Nitrate	3.02 (0.78)	2.58 (0.38)	2.09 (0.47)	3.36 (0.50)	2.59 (0.45)	3.94 (0.56)	3.72 (0.89)
Nitrite	0.009 (0.003)	0.027 (0.003)	0.053 (0.006)	0.050 (0.014)	0.044 (0.009)	0.043 (0.014)	0.064 (0.021)
TN	1.49 (0.27)	2.02 (0.19)	1.86 (0.18)	1.92 (0.59)	1.44 (0.88)	0.96 (0.49)	0.91 (0.64)
TP	0.41 (0.19)	0.62 (0.08)	0.81 (0.06)	0.60 (0.10)	0.63 (0.09)	0.73 (0.30)	0.73 (0.19)



(a)



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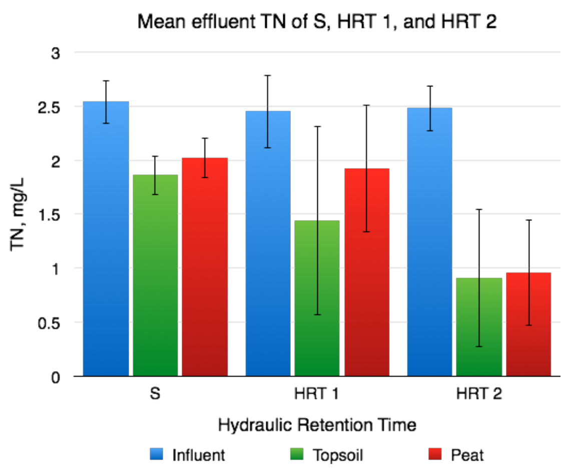
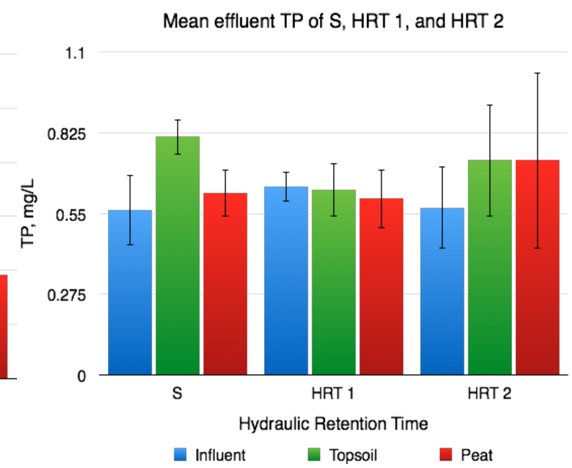


(c)



(d)

Figure 4.3 (a) Mean effluent pH levels under S, HRT 1, and HRT 2; (b) Mean effluent COD concentrations under S, HRT 1 and HRT 2; (c) Mean effluent TN concentrations under S, HRT 1, and HRT 2; (d) Mean effluent TP concentrations under S, HRT 1, and HRT 2.

Positive organics removal efficiencies were noted in the Phase 2 study for S (HRT=2.5 days), HRT 1 (HRT=4 days), and HRT 2 (HRT=6 days), which was unlike the Phase 1 study, however, there was no statistically significant difference between these conditions. This further supported the results obtained during Phase 1 study where low influent COD concentration coupled with the background concentration contributed by the substrate might result in low net removal efficiencies. This was consistent with studies by Akratos and Tsihrintzis (2007) and Sehar et al. (2015a) studies that also showed that longer HRTs did not further increase the COD removal efficiency. The low COD removal efficiency could also due to the lack of the vegetation, which can introduce oxygen through their roots to encourage the breakdown of organics.

4.3.7 Effects of Organic Loading Rate

Although the organic loading from secondary effluent is consistently low, it is still possible that a sudden rise in organic loading during some events such as algae decay could occur in WSPs. Therefore, influent wastewater with organic loading rates different from S (COD=20 mg/L) were fed to the system to evaluate the effect on the overall system performance. The results are presented in the Table 4.8. The result from operational condition S was used to compare with the results from the OLR 1 (COD=70 mg/l) and OLR 2 (COD=135 mg/L) conditions. The system was operated at OLR 1 for two weeks prior to adjusting the conditions to OLR 2. The mean influent organic loading rates for S, OLR 1 and OLR 2 were 20.50 COD mg/L, 70.43 COD mg/L, and 135.67 COD mg/L, respectively.

With the influent pH was maintained around 10.5, the mean effluent pH was found to significantly decreased as the influent COD increased. The effluent pH decreased from 9.47 to 8.16 in reactors with topsoil, and from 9.48 to 7.97 in reactors with peat. The data strongly indicated that increasing organic loading rate enhanced pH attenuation in both reactors. The paired *t* test was used to statistical compared the pH attenuation capacity, and the results are presented in Table 4.9 and Table 4.10. For both the topsoil and peat reactors, there was a statistically significance between effluent pH when the organic loading was increased from S to OLR 1. Same trend was also noted when the operational conditions was changed from OLR 1 to OLR 2 (Figure 4.4). When the two substrates were compared side by side, no pH attenuation differences could be found under operational condition S and OLR 2, while there was a difference under condition OLR 1.

Table 4.8 Mean pollutant concentrations and removal efficiencies in the wetland reactors as a function of OLR during the Phase 2 study. Standard deviation of pollutant concentrations indicated in the brackets.

	Influent	OLR 1 Influent COD = 70 mg/L		OLR 2 Influent COD = 135 mg/L	
		Peat	Topsoil	Peat	Topsoil
pH	10.37 (0.20)	8.29 (0.05)	8.54 (0.19)	7.97 (0.23)	8.16 (0.19)
ORP	91.4 (5.9)	123.67 (8.52)	122.17 (3.25)	134.00 (7.37)	130.67 (4.04)
Alkalinity	128.0 (50.0)	81.7 (4.3)	85.6 (3.4)	72.5 (3.2)	78.2 (2.4)
COD	--	42.2 (6.3)	37.2 (4.0)	83.2 (2.4)	78.8 (6.0)
Ammonium	0.17 (0.08)	0.11 (0.04)	0.09 (0.02)	0.06 (0.02)	0.06 (0.05)
Nitrate	3.02 (0.78)	2.70 (0.28)	1.79 (0.49)	1.92 (0.15)	1.57 (0.18)
Nitrite	0.009 (0.003)	0.023 (0.021)	0.010 (0.003)	0.026 (0.010)	0.013 (0.004)
TN	1.49 (0.27)	1.92 (0.28)	1.54 (0.22)	2.21 (0.80)	1.79 (0.44)
TP	0.41 (0.19)	0.41 (0.07)	0.72 (0.09)	0.61 (0.05)	1.11 (0.17)

In addition, COD removal efficiency also increased and was correlated to the increase of influent COD concentration. The COD removal efficiencies were 22.3%, 45.5%, and 40.5% for S, OLR 1, and OLR 2, respectively, in the topsoil reactors, and were 15.7%, 37.4%, and 38.9% in peat reactors. Sehar et al. (2015a) argued that the optimal HRT for COD removal is 8 days and the highest removal efficiency that could be achieved was 80.67% and was achieved with the present of vegetation. The increased COD removal efficiency also indicated the growth number of heterotrophic bacteria, which can break down the organic matters. This could also be coincided with increased pH attenuation capacity likely due to the presence of heterotrophic bacteria that could increase system pH by replenishing dissolved CO_2 concentration through their respiration process. The combination of pH and COD removal efficiencies illustrated this point. This finding is supported by the results from the correlation matrix (Table 4.11 and Table 4.12) where COD was shown to be strongly negatively correlated to pH in the peat reactor (r = -0.599) with confidence (p = 0.006) and in the topsoil reactor (r = -0.305) with a slightly higher p value (p = 0.190).

Table 4.9 Statistical comparison between operational conditions S vs. OLR 1, and OLR 1 vs. OLR 2 for topsoil and peat. Statistically significant statistical differences (p<0.05) are indicated in bold numbers.

	p values from paired *t* test	
	Topsoil	Peat
S vs. OLR 1	**<0.0001**	**<0.0001**
OLR 1 vs. OLR 2	**0.006**	**0.007**

Table 4.10 Statistical comparison between topsoil and peat under operational conditions S, OLR 1, and OLR 2. Statistically significant statistical differences (p<0.05) are indicated in bold numbers.

Topsoil vs. Peat	Mean pH effluent		*p* values from paired *t* test
	Topsoil	Peat	
S	9.47	9.48	0.913
OLR 1	8.54	8.29	**0.013**
OLR 2	8.16	7.97	0.148

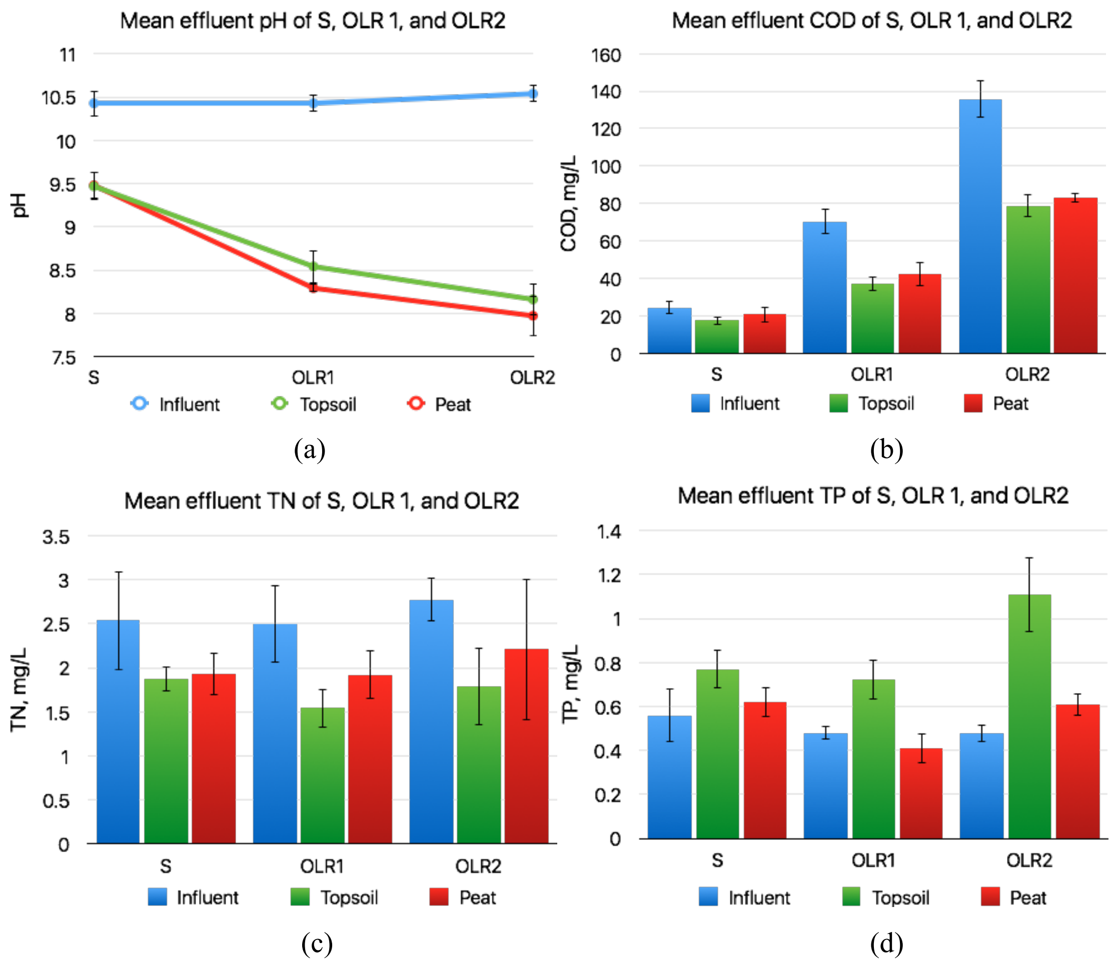


Figure 4.4 Mean effluent pH level (a), COD concentrations (b), TN concentrations (c), and TP concentrations (d) under operational conditions S, OLR 1, and OLR 2

Table 4.11 and Table 4.12 present the correlation coefficient (r) matrix for the data collected for the topsoil and peat reactors during the Phase 2 study. These tables can assist in understanding the correlation among these water quality parameters. The values in bold are different from 0 with a significance level alpha=0.05, which means that the number in bold rejects the premise that the correlation is due to random sampling. Three sets of correlations were found in both reactors including pH vs alkalinity ($CaCO_3$ mg/L), nitrate (mg/L) vs COD (mg/L), nitrate (mg/L) vs TN (mg/L) with both significance level alpha<0.05. The correlation plots are presented in Figure 4.5. The most obvious result was pH vs Alkalinity, since the computation of alkalinity includes pH. High pH meant high concentrations of hydroxide ions, which contribute to the alkalinity concentration. COD was negatively correlated with both nitrate, and nitrite in both reactors, which would imply that high COD concentrations encourage the reduction of nitrate and nitrite species. This finding was consistent with studies by Saeed and Sun (2012) and Tee et al. (2012a) in which organic carbon availability will affect the denitrification. Interestingly, the correlation matrix showed that the reduction of nitrate and nitrite did not result in the removal of TN. TN was also negatively correlated with nitrate and nitrite. This would suggest that organic substrates applied in this study have the tendency to release the organic nitrogen species, which led to higher TN concentrations in the reactors.

Table 4.11 The correlation coefficient (r) matrix for topsoil

Variables	PH	COD	ALK	TN	TP	NO_3-N	NO_2-N	NH_4-N
pH	**1**	-0.305	**0.773**	0.299	-0.263	0.073	0.245	0.190
COD	-0.305	**1**	-0.383	0.266	0.417	**-0.648**	**-0.717**	**-0.554**
ALK	**0.773**	-0.383	**1**	0.127	**-0.501**	0.247	0.261	0.229
TN	0.299	0.266	0.127	**1**	**0.567**	**-0.526**	-0.052	-0.337
TP	-0.263	0.417	**-0.501**	**0.567**	**1**	**-0.472**	-0.193	-0.124
NO_3-N	0.073	**-0.648**	0.247	**-0.526**	**-0.472**	**1**	**0.607**	**0.540**
NO_2-N	0.245	**-0.717**	0.261	-0.052	-0.193	**0.607**	**1**	0.413
NH_4-N	0.190	**-0.554**	0.229	-0.337	-0.124	**0.540**	0.413	**1**

*Values in bold are different from 0 with a significance level alpha = 0.05

Table 4.12 The correlation coefficient (r) matrix for peat

Variables	PH	COD	ALK	TN	TP	NO_3-N	NO_2-N	NH_4-N
pH	**1**	**-0.599**	**0.551**	0.073	0.249	0.394	0.191	0.337
COD	**-0.599**	**1**	-0.233	**0.498**	**-0.466**	**-0.722**	-0.410	-0.371
ALK	**0.551**	-0.233	**1**	0.204	-0.044	0.002	-0.275	**0.464**
TN	0.073	**0.498**	0.204	**1**	-0.390	**-0.511**	-0.275	-0.177
TP	0.249	**-0.466**	-0.044	-0.390	**1**	0.126	0.297	0.082
NO_3-N	0.394	**-0.722**	0.002	**-0.511**	0.126	**1**	0.443	0.298
NO_2-N	0.191	-0.410	-0.275	-0.275	0.297	0.443	**1**	0.020
NH_4-N	0.337	-0.371	**0.464**	-0.177	0.082	0.298	0.020	**1**

*Values in bold are different from 0 with a significance level alpha = 0.05

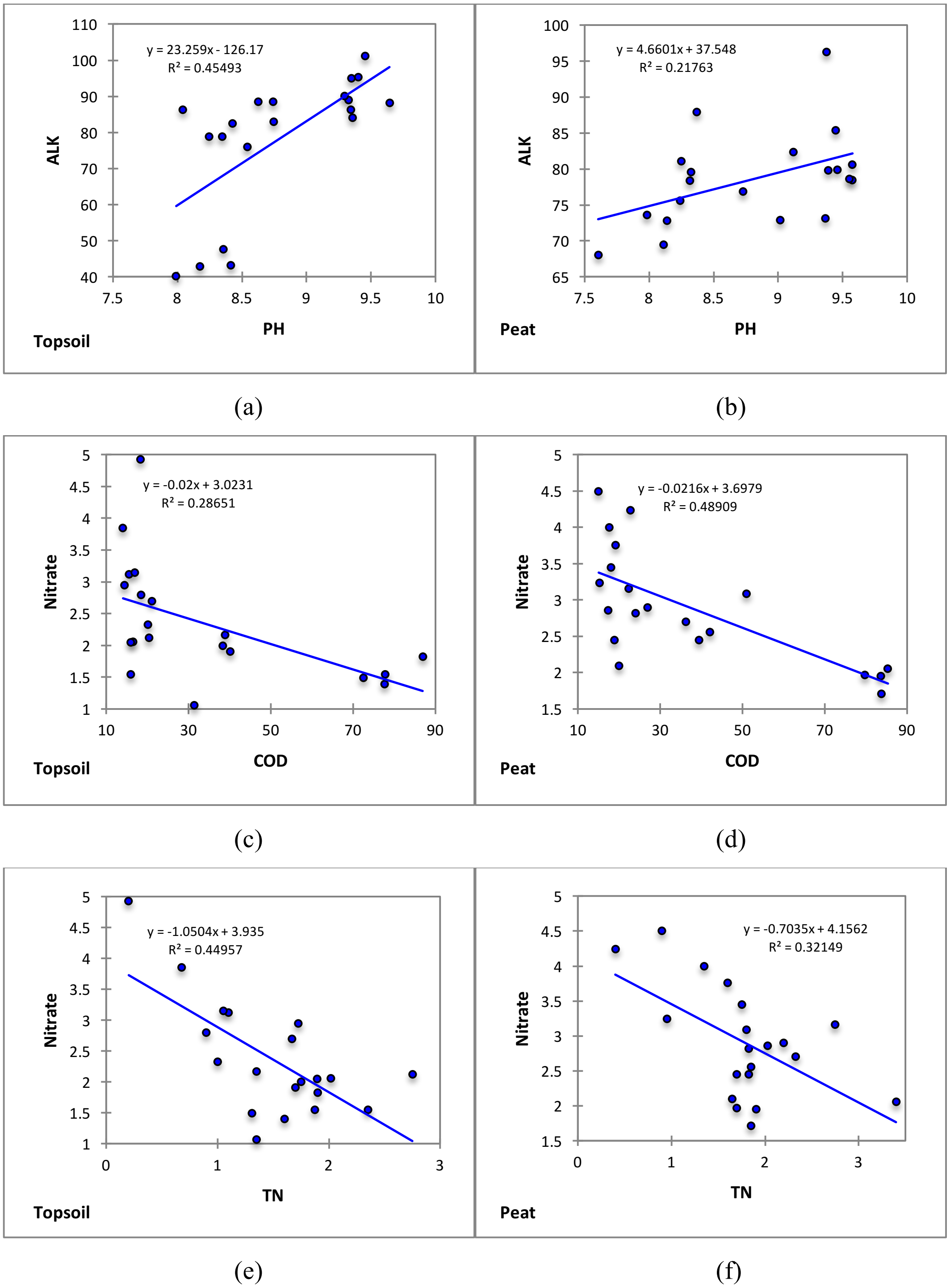


Figure 4.5 Correlation plots of (a) pH vs alkalinity in topsoil; (b) pH vs alkalinity in peat; (c) nitrate vs COD in topsoil; (d) nitrate vs COD in peat; (e) nitrate vs TN in topsoil; (f) nitrate vs TN in peat.

4.4 Conclusion

Four locally available substrate materials were tested in the bench-scale reactors, and all four substrates in the Phase 1 study demonstrated their ability to attenuate pH to below 9.5, which would be in compliance with wastewater discharge guidelines. Among these substrates, peat showed the highest attenuation capacity and reduced the effluent pH to 7.7 without adversely affecting effluent quality. Acid-base neutralization reactions were likely the main pH attenuation mechanism due to the low alkalinity. Topsoil and organic mulch could also attenuate the pH to below discharge guidelines as well. However, the pH reduction for topsoil and organic mulch was likely mainly due to the generation hydrogen ions during nitrification. Peat and topsoil demonstrated effective constituent removals, as well as providing adequate pH attenuation, which would fulfill discharge guidelines. Therefore, these two substrates were selected for the Phase 2 study.

The Phase 2 study demonstrated that HRT and OLR operational conditions could affect the system pH. OLR had a more significant impact on system pH compared to the HRT. The pH attenuation performance was significantly improved when the OLR was increased to 70, and 135 mg/L COD, respectively, for peat (pH=8.29, 7.97) and topsoil (pH=8.54, 8.16). Improvements in pH attenuation could only be observed at HRTs longer than 4 days for peat (pH=8.70) and topsoil (pH=8.35). Therefore, the optimization of the operational conditions could also enhance pH attenuation with substrates and can better mitigate the high pH events at the WWTP.

4.5 References

Akratos, C. S., and Tsihrintzis, V. A. (2007). Effect of temperature, hrt, vegetation and porous media on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands. *Ecological Engineering, 29*(2), 173-191.

Standard methods for the examination of water and wastewater (2012). 22th edn, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Aslam, M. M., Malik, M., Baig, M. A., Qazi, I. A., and Iqbal, J. (2007). Treatment performances of compost-based and gravel-based vertical flow wetlands operated identically for refinery wastewater treatment in pakistan. *Ecological Engineering, 30*(1), 34-42.

Bai, L., Wang, C., Huang, C., He, L., and Pei, Y. (2014). Reuse of drinking water treatment residuals as a substrate in constructed wetlands for sewage tertiary treatment. *Ecological Engineering, 70*(0), 295-303.

Białowiec, A., Janczukowicz, W., and Randerson, P. F. (2011). Nitrogen removal from wastewater in vertical flow constructed wetlands containing lwa/gravel layers and reed vegetation. *Ecological Engineering, 37*(6), 897-902.

Borde, X., Guieysse, B. t., Delgado, O., Muñoz, R., Hatti-Kaul, R., Nugier-Chauvin, C., Patin, H., and Mattiasson, B. (2003). Synergistic relationships in algal–bacterial microcosms for the treatment of aromatic pollutants. *Bioresource Technology, 86*(3), 293-300.

Wastewater systems effluent regulations (2012). (SOR/2012-139). edn, Environmental Canada.

Daigger, G. T., and Boltz, J. P. (2011). Trickling filter and trickling filter-suspended growth process design and operation: A state-of-the-art review. *Water Environment Research, 83*(5), 388-404.

Dreybrodt, W., Buhmann, D., Michaelis, J., and Usdowski, E. (1992). Geochemically controlled calcite precipitation by co2 outgassing: Field measurements of precipitation rates in comparison to theoretical predictions. *Chemical Geology, 97*(3–4), 285-294.

Gray, S., Kinross, J., Read, P., and Marland, A. (2000). The nutrient assimilative capacity of maerl as a substrate in constructed wetland systems for waste treatment. *Water Research, 34*(8), 2183-2190.

Herrera-Melián, J. A., González-Bordón, A., Martín-González, M. A., García-Jiménez, P., Carrasco, M., and Araña, J. (2014). Palm tree mulch as substrate for primary treatment wetlands processing high strength urban wastewater. *Journal of Environmental Management, 139*(0), 22-31.

Hosetti, B., and Frost, S. (1998). A review of the control of biological waste treatment in stabilization ponds. *Critical Reviews in Environmental Science and Technology, 28*(2), 193-218.

Jong, V. S. W., and Tang, F. E. (2015). The use of palm kernel shell (pks) as substrate material in vertical-flow engineered wetlands for septage treatment in malaysia. *Water Science & Technology, 72*(1), 84-91.

Kadlec, R. H., Burgoon, P. S., and Henderson, M. E. (1997). Integrated natural systems for treating potato processing wastewater. *Water Science and Technology, 35*(5), 263-270.

Kadlec, R. H., and Wallace, S. (2008). *Treatment wetlands* (2nd Edition ed.). CRC press, Florida.

Kayombo, S., Mbwette, T. S. A., Mayo, A. W., Katima, J. H. Y., and Jørgensen, S. E. (2002). Diurnal cycles of variation of physical–chemical parameters in waste stabilization ponds. *Ecological Engineering, 18*(3), 287-291.

Kelly, J., Champagne, P., and Michel, F. (2007). Assessment of metal attenuation in a natural wetland system impacted by alkaline mine tailings, cobalt, ontario, canada. *Mine Water and the Environment, 26*(3), 181-190.

Lantzke, I., Heritage, A., Pistillo, G., and Mitchell, D. (1998). Phosphorus removal rates in bucket size planted wetlands with a vertical hydraulic flow. *Water Research, 32*(4), 1280-1286.

Liu, L., Hall, G., and Champagne, P. (2016). Effects of environmental factors on the disinfection performance of a wastewater stabilization pond operated in a temperate climate. *Water, 8*(1).

Liu, M., Wu, S., Chen, L., and Dong, R. (2014). How substrate influences nitrogen transformations in tidal flow constructed wetlands treating high ammonium wastewater? *Ecological Engineering, 73*(0), 478-486.

Lotito, A. M., De Sanctis, M., Di Iaconi, C., and Bergna, G. (2014). Textile wastewater treatment: Aerobic granular sludge vs activated sludge systems. *Water Research, 54*(0), 337-346.

Lüderitz, V., and Gerlach, F. (2002). Phosphorus removal in different constructed wetlands. *Acta Biotechnologica, 22*(1-2), 91-99.

Mateus, D. M. R., Vaz, M. M. N., and Pinho, H. J. O. (2012). Fragmented limestone wastes as a constructed wetland substrate for phosphorus removal. *Ecological Engineering, 41*(0), 65-69.

Mayes, W. M., and Younger, P. L. (2006). Buffering of alkaline steel slag leachate across a natural wetland. *Environmental Science and Technology, 40*(4), 1237-1243.

Maynard, H. E., Ouki, S. K., and Williams, S. C. (1999). Tertiary lagoons: A review of removal mecnisms and performance. *Water Research, 33*(1), 1-13.

Miguel, A., Meffe, R., Leal, M., González-Naranjo, V., Martínez-Hernández, V., Lillo, J., Martín, I., Salas, J. J., and Bustamante, I. (2014). Treating municipal wastewater through a vegetation filter with a short-rotation poplar species. *Ecological Engineering, 73*(0), 560-568.

Muñoz, R., and Guieysse, B. (2006). Algal–bacterial processes for the treatment of hazardous contaminants: A review. *Water Research, 40*(15), 2799-2815.

Nishimura, H., Nakajima, M., and Kumagai, M. (1984). Exchange of oxygen and carbon dioxide across the water surface during algal blooms in a pond. *Water Research, 18*(3), 345-350.

Pietro, K. C., and Ivanoff, D. (2015). Comparison of long-term phosphorus removal performance of two large-scale constructed wetlands in south florida, u.S.A. *Ecological Engineering, 79*(0), 143-157.

Pries, J. (1996). *Constructed wetland treatment systems in canada.* Paper Proceedings from the Constructed wetlands in cold climates. Proceedings of the symposium held at the Niagara-on-the-Lake, Ontario, Canada.

Reinoso, R., Torres, L. A., and Bécares, E. (2008). Efficiency of natural systems for removal of bacteria and pathogenic parasites from wastewater. *Science of The Total Environment, 395*(2–3), 80-86.

Saeed, T., and Sun, G. (2011). A comparative study on the removal of nutrients and organic matter in wetland reactors employing organic media. *Chemical Engineering Journal, 171*(2), 439-447.

Saeed, T., and Sun, G. (2012). A review on nitrogen and organics removal mechanisms in subsurface flow constructed wetlands: Dependency on environmental parameters, operating conditions and supporting media. *Journal of Environmental Management, 112*, 429-448.

Sehar, S., Sumera, Naeem, S., Perveen, I., Ali, N., and Ahmed, S. (2015). A comparative study of macrophytes influence on wastewater treatment through subsurface flow hybrid constructed wetland. *Ecological Engineering, 81*, 62-69.

Senzia, M. A., Mashauri, D. A., and Mayo, A. W. (2003). Suitability of constructed wetlands and waste stabilisation ponds in wastewater treatment: Nitrogen transformation and removal. *Physics and Chemistry of the Earth, Parts A/B/C, 28*(20–27), 1117-1124.

Snoeyink, V. L., and Jenkins, D. (1980). *Water chemistry*. Wiley, New York.

Su, C., and Puls, R. W. (2007). Removal of added nitrate in cotton burr compost, mulch compost, and peat: Mechanisms and potential use for groundwater nitrate remediation. *Chemosphere, 66*(1), 91-98.

Tee, H.-C., Lim, P.-E., Seng, C.-E., and Nawi, M.-A. M. (2012). Newly developed baffled subsurface-flow constructed wetland for the enhancement of nitrogen removal. *Bioresource Technology, 104*, 235-242.

Chapter 5

Peat as substrate for small-scale constructed wetlands polishing secondary effluents from municipal wastewater treatment plant

Abstract: With the recent development of constructed wetland (CW) technology, it has become a mainstream treatment technology for the mitigation of a variety of wastewaters. This study reports on the treatment performance and pH attenuation capacity of three different configurations of small-scale on-site surface flow constructed wetlands (SFCW): T1 (Peat + *Typha latifolia*), T2 (*T. latifolia* alone), and T3 (Peat alone) treating secondary effluent from the Amherstview Water Pollution Control Plant (WPCP) for two treatment periods (start-up period and operational period). The aim of this study was to compare the nutrients removal efficiencies between the different treatments, as well as to evaluate the effects of substrate and vegetation on the wetland system. For a hydraulic retention time of 2.5 days, the results showed that all treatment systems could attenuate the pH level during both the start-up and operational periods, while significant nutrient removal performance could only be observed during the operational period. Peat was noted to be a better SFCW substrate in promoting the removal of nitrate (NO_3-N), total nitrogen (TN), and phosphorus. The addition of *T. latifolia* further enhanced NO_3-N and TN removal efficiencies, but employing *T. latifolia* alone did not yield effluents that could meet the regulatory discharge limit (1.0 mg/L) for phosphorus.

Keywords: Constructed wetland; peat; pH; *Typha latifolia*; wastewater stabilization pond

5.1 Introduction

Constructed wetlands (CWs) are considered to be a sustainable passive wastewater treatment technology, and have been used to treat a variety of wastewaters for decades, including domestic or municipal wastewater (Jácome et al., 2016; Pandey et al., 2013), industrial wastewater (Paing et al., 2015; Saeed & Sun, 2013), agricultural (Giácoman-Vallejos et al., 2015; Gottschall et al., 2007; Speer et al., 2009), acid mine drainage (Clyde et al., 2016) river and lake water (Martín et al., 2013; Mawuli et al., 2015; Saeed et al., 2016), groundwater (Stefanakis et al., 2016), landfill leachate (Sim et al., 2013; Speer et al., 2012; Wallace et al., 2015), highway (Zhao et al., 2016) and airport (Murphy et al., 2015) runoff. They take advantage of many of the same processes that occur in natural wetlands, but do so in a more controlled or engineered system (Kadlec & Wallace, 2008). To date, surface flow and subsurface flow wetlands are the two main categories of CW applications (Pandey et al., 2013). In recent years, subsurface flow constructed wetlands (SSFCWs) have been extensively studied, as their treatment efficiency, in terms of nutrients mass removal per unit area, is typically higher than that of surface flow constructed wetlands (SFCWs). Alternative influent feeding modes, such as tidal flow, step feed, and upflow mode, have also been investigated to further enhance treatment performance. Although SFCWs represent an older and less sophisticated configuration, they remain an effective treatment approach. Despite their lower treatment efficiencies compared to SSFCW, the lower construction cost and maintenance requirements associated with SFCW are desirable for smaller and more rural communities, especially when dealing with micro-polluted wastewaters or secondary effluents from wastewater treatment plants.

Substrate and vegetation are two of the three main wetland components along with hydrology (Vymazal, 2013b) that need to be considered in the design of CWs, and they play an important role in SFCW function. Hence, their selections have to be made carefully in order to achieve the desire treatment objectives of the system. In general, local soils are used as the rooting medium in SFCW and was primarily used to sustain the growth of wetland vegetation. However, recent studies have shown that contribution to treatment of the overall system by these substrates has been limited. Therefore, alternative substrates have become more attractive and a number of studies have been conducted using alternative substrates in wetland applications (Herrera-Melián et al., 2014; Liu et al., 2014; Mateus et al., 2012; Saeed & Sun, 2011). These include natural, manufactured and reclaimed materials. Although manufactured materials could provide better treatment performance, natural and reclaimed products are generally preferable due to their low economic cost and geographical availability (Yin et al., 2017).

Peat is a natural and organic substrate with a structure containing mostly humic substances. Previous studies (Gunes, 2007; Kasak et al., 2015; Lizama Allende et al., 2012; Saeed et al., 2012) have employed peat in CW applications, but most of these only focused on nutrient removal. As an organic substrate with relative acidic properties, peat could also be used to attenuate high pH wastewater such as alkaline mine drainage and algal-induced, elevated pH secondary effluents. One study concluded that peat could be used effectively for the attenuation of pH in synthetic wastewater, when employed in bench-scale wetland system without the presence of vegetation (Jin et al., 2017b).

Typha latifolia (*T. latifolia*) is an emergent plant which has been reported to be present on all continents except Central and South America, and it is the most widely represented vegetation species in CWs across North America (Vymazal, 2013a). It can grow aggressively and tends to out-compete other species planted in wetlands. Its relatively short growing period and advanced extensive branching horizontal rhizome system are ideal for CW applications, as they can substantially reduce nutrient concentrations through nutrient uptake and increase the rate of sedimentation by reducing current velocity.

Several comparative CW studies have been published that compare the treatment performance achieved by applying different substrates or vegetation. Most of these studies have focused on the comparison between either substrates or vegetation alone and have not compared the effects of substrates and vegetation as they act in unison (Calheiros et al., 2009; Saeed & Sun, 2011; Saeed & Sun, 2013; Schierano et al., 2017; Sehar et al., 2015b; Toscano et al., 2015). This study fills this gap and identifies the role that substrate and vegetation play in CW applications.

The objective of this paper was to assess the effects of peat and *T. latifolia* on the attenuation of pH and treatment of a municipal secondary effluents in three small-scale on-site SFCW reactors at the Amherstview Water Pollution Control Plant (WPCP) located on the northern shore of Lake Ontario in Ontario (Canada). The performance of all treatment configurations including substrate alone, vegetation alone, and substrate and vegetation together, were monitored and compared over a period of one year. The individual treatment contributions of *T. latifolia* and peat to the treatment system were also evaluated to characterize their effects on the overall performance of the SFCW.

5.2 Materials and methods

5.2.1 Wastewater

The Amherstview WPCP, which currently services a population over 10,000 and treats an average of 3,500 m^3/day of municipal wastewater, consists of a direct activated sludge treatment process, followed by tertiary treatment and effluent polishing that takes place in three wastewater stabilization ponds operated in series (Figure 5.1). The wastewater applied to the small-scale on-site SFCW in this study was directly diverted from the influent of the second wastewater stabilization pond, which was characterized as a secondary effluent from the treatment plant.

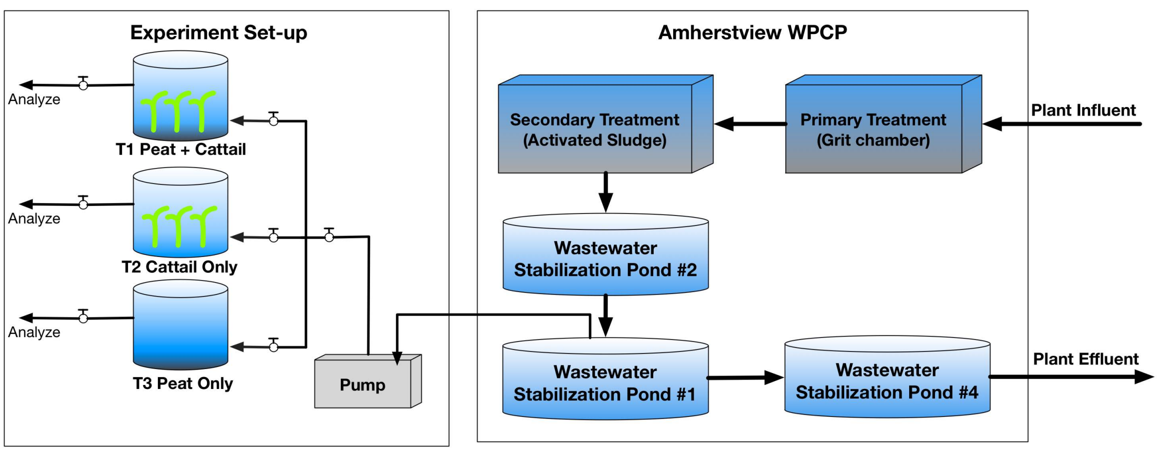


Figure 5.1 Schematic design of the experiment set-up and the treatment processes flow at the Amherstview WPCP

5.2.2 Wetland Reactors

Three outdoor small-scale surface flow wetland reactors were built on-site at the Amherstview WPCP using open top cylindrical high-density polyethylene tanks with 6.5m^3 volumes (diameter: 2.13 m, height: 1.82 m). Three 5 cm holes were drilled along the outer of each tank to act as inlet (200 mm height), outlet (600 mm height), and drain (50 mm height) (Figure 5.2).

Locally available substrate and vegetation were employed in this study. Peat moss was purchased from the Home Depot in Kingston (Canada) and was applied in this experiment as substrate that could potentially attenuate high pH effluents. The properties of the peat moss used in this study are listed in Table 1. The porosity was determined by dividing the volume of water required to fill the void spaces in the substrate by the volume of the substrate. *T. latifolia* was collected from the Bayview Bog Field Site (BBFS) (44°15’20”N, 76°38’56”W), which is a natural wetland complex located in Loyalist Township and governed by the Cataraqui Region Conservation Authority (CRCA). The plants were harvested by Loyalist Township using a backhoe. The plants were then transported to the Amherstview WPCP by pickup trucks covered with tarpaulins to keep the plants moisturized. After receiving the plants, they were immediately transplanted to the individual wetland reactors. It is recognized that because the *T. latifolia* were transplanted from a natural wetland, some of the native soil was inevitably also relocated to the reactors as the goal was to minimize damage to the root zone of the plants during the transplantation process.

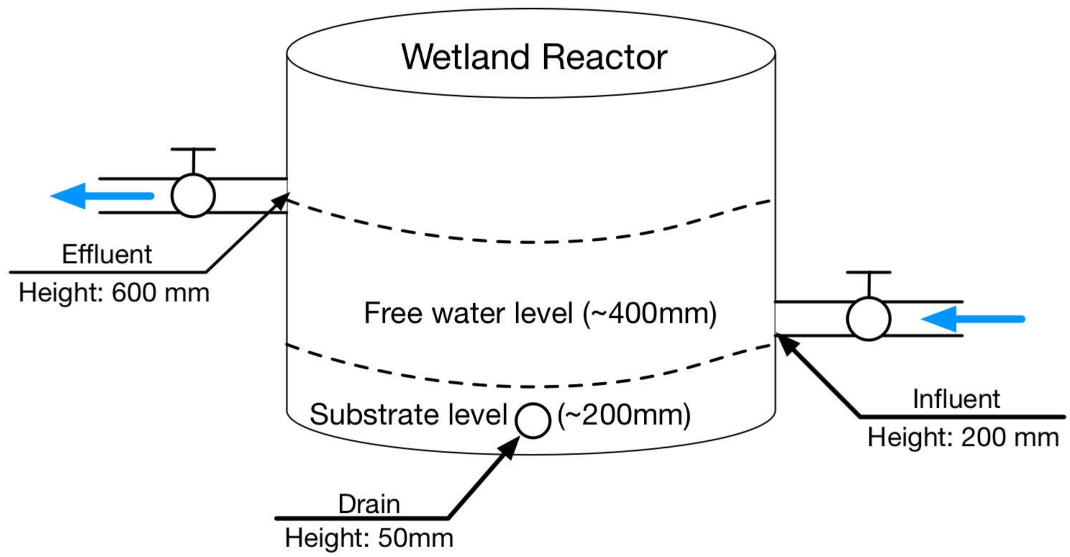


Figure 5.2 Detail design and dimensions of the individual treatment wetland reactors (not to scale)

The wetland reactor configurations tested included: Reactor T1, peat moss and *T. latifolia*; Reactor T2, *T. latifolia* alone; Reactor T3, peat moss alone. Reactor T1 contained both a 20 cm peat moss layer, as well as approximately 20 stalks of *T. latifolia*. Reactor T2 contained *T. latifolia* alone, with approximately 20 stalks of *T. latifolia* transplanted to this reactor. The native wetland soil was used as growing media at a depth of 20 cm. Reactor T3 contained peat moss substrate alone at a depth of 20 cm. All three wetland reactors had a free water surface level of 40 cm on top of the substrate in the tank.

Table 5.1 Physical properties of the peat applied in this study

Substrate	Density (kg/m^3)	Porosity*
peat	800	0.31

5.2.3 System Operations

Wastewater was pumped into the system from the influent of the second wastewater stabilization pond of the Amherstview WPCP using a Pentair centrifugal pump. Wastewater was distributed equally to the three wetland reactors through parallel connections. One inch polybutylene pipe was used as the main influent pipe, which was connected between the wastewater stabilization pond to the front of each treatment reactor, passing through the pump. Three quarters of an inch PVC pipe was then used to connect the one inch polybutylene pipe to the inlet of the wetland reactors using a one inch to three quarters of an inch reduction adaptor. Valves were installed to control flow to each reactor, which can only be applied to PVC tubing. One inch PVC pipes were used to connect each tank outlet to the effluent pipe. A PVC ball valve was placed before the inlet and after the outlet of each wetland reactor to control the flow.

The hydraulic retention time of each wetland reactor was determined based on the design of the pilot-scale SF CW at the Amherstview WPCP, and was set to a constant value of 2.5 days for the duration of the entire experiment. All wetland reactors were commissioned in the summer of 2016. A two-month acclimation period was provided to allow the substrate and vegetation to establish. After the establishment of the substrates and vegetation, the system was operated and fed with secondary effluent wastewater. The study was separated into two treatment periods, as the wetland reactors required a start-up period before normal operation. The start-up period for this experiment was from September 29 to November 17 2016, and the operational period was from May 17 to July

31 2017. Sample data from November 17 2016 to May 16 2017 were not available in that period due to freezing during the winter conditions.

5.2.4 Sampling and analysis

Wastewater samples were collected on a bi-weekly basis (Mondays and Thursdays) during the start-up period, and on a weekly basis (Wednesdays) during the operational period. Weather data was collected by a meteorological station near the Kingston Airport, which is approximately 10 km away from the study site. Samples were collected from the effluent pipe of each wetland reactor as well as the second wastewater stabilization pond (influent), and were kept in a cooler at 4°C until all laboratory testing could be completed. Samples were analyzed in duplicate. For each sample, analysis was carried out for pH, chemical oxygen demand (COD), ammonium (NH_4-N), NO_3-N, phosphate (PO_4-P), TN, and total phosphorus (TP). During the operational period, DO, alkalinity, and total suspended solids (TSS) were also measured. pH was analyzed using a Fisher Scientific Accumet XL60 benchtop meter with a Fisher Scientific pH probe manufactured by Fisher Scientific, USA. DO was measured using a YSI DO meter. Alkalinity, NH_4-N, NO_3-N and PO_4-P concentrations were analyzed using a Hach model DR 2800 spectrophotometer according to APHA Standard Methods. TN was measured using the Hach TNT Persulfate Digestion Method No. 10072. TP was measured using the Hach PhosVer® 3 with Acid Persulfate Digestion Method 8190. COD was analyzed with the same spectrophotometer according to the APHA Standard Methods. TSS was analyzed according to the APHA Standard Methods (APHA, 2012; Jin et al., 2017b).

5.2.5 Statistical analysis

To compare the performance of the different wetland reactor treatments, parametric and non-parametric statistical analyses were performed using Microsoft EXCEL. These were used to evaluate wastewater treatment performance, including removal efficiency (R, %), and removal rates (RR, g/ m^2d) as defined by Equation 5.1 and Equation 5.2, respectively.

Equation 5.1

$$R\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

Equation 5.2

$$RR\ (g/m^2\ d) = \frac{(C_0 - C_t) \times Q}{A}$$

where R is the removal efficiency (%), RR is the removal rates (g/ m^2d), C0 is the influent concentration (mg/L), Ct is the effluent concentration (mg/L), Q is the flow rate (m^3/d), A is the area of reactors (m^2).

Normality tests were performed to verify whether the distribution of data approximated normality. Both graphical (histogram and normality plot) and statistical (skewness and kurtosis) methods were used to determine the data distribution. When data approximated normality, the data were analyzed through one-way analysis of variance (ANOVA) and illustrated the statistically significant difference (p value < 0.05) of the means across all treatments at a significant level of 0.05. When a significant difference was observed, post-hoc comparison analysis (Tukey post-hoc test) was performed to determine the statistically significant difference between treatments at a significant level of 0.05.

5.3 Results and discussions

5.3.1 Overall performance

Table 5.2 and Table 5.3 provide the mean effluent nutrient concentrations and mean pollutant removal efficiencies in three wetland reactors during both the start-up and operational period, respectively. The average influent hydraulic loading rate was 0.16 m^3/m^2 d (2.5 days hydraulic retention time) for each reactor.

Overall, the results showed that pH could be effectively attenuated in all reactors during both treatment periods. Higher NO_3-N and TN removal efficiencies were recorded during the operational period compared to the start-up period. PO_4-P and TP removal efficiencies were significantly improved in reactors where peat was present during operational period as well. However, due to the low influent COD concentrations, the introduction of peat and cattails to the system appeared to increase the effluent COD levels during both periods. The wetland reactors achieved a better overall performance across the reactors during normal operational period compared to start-up period. A more detailed comparison of each individual pollutant is presented in the following sections.

Table 5.2 Mean effluent pollutant concentrations and removal efficiencies in each treatment wetland reactors for start-up period

Parameter	Unit	Influent	Peat + Cattails T1		Cattails T2		Peat T3	
			Effluent Conc.	R %	Effluent Conc.	R %	Effluent Conc.	R %
pH		7.43 (0.41)	6.25 (1.09)		7.12 (0.24)		6.39 (1.27)	
COD	mg/L	14.2 (14.1)	49.2 (39.6)		15.9 (5.7)		44.0 (42.2)	
NH_4-N	mg/L	0.10 (0.08)	0.23 (0.22)		0.09 (0.04)	10%	0.22 (0.22)	
NO_3-N	mg/L	0.83 (0.32)	0.61 (0.26)	26.5%	0.52 (0.20)	37.3%	0.71 (0.31)	19.4%
TN	mg/L	8.75 (2.80)	8.21 (2.11)	6.17%	5.14 (2.58)	41.2%	8.58 (1.56)	0.8%
PO_4-P	mg/L	0.71 (0.13)	0.70 (0.28)	1.4%	0.59 (0.13)	16.9%	0.82 (0.22)	
TP	mg/L	2.90 (1.83)	3.42 (2.29)		2.27 (2.47)	18.2%	3.74 (1.95)	

Notes: Standard deviation of pollutant concentrations is indicated in brackets

Table 5.3 Mean effluent pollutant concentrations and removal efficiencies in each treatment wetland reactors for operational period

Parameter	Unit	Influent	Peat + Cattails T1		Cattails T2		Peat T3	
			Effluent Conc.	R %	Effluent Conc.	R %	Effluent Conc.	R %
pH		8.25 (0.81)	7.55 (0.96)		7.52 (0.92)		6.97 (0.37)	
DO	mg/L	6.10 (0.93)	6.44 (1.56)		5.92 (2.11)		6.32 (1.10)	
TSS	mg/L	4.1 (3.5)	9.8 (6.3)		6.4 (6.3)		17.6 (13.2)	
Alkalinity	mg/L	121.6 (15.9)	80.8 (21.0)		119.8 (37.9)		68.4 (54.9)	
COD	mg/L	12.2 (7.6)	49.0 (13.6)		24.4 (4.8)		49.8 (13.1)	
NH_4-N	mg/L	0.20 (0.32)	0.97 (0.33)		0.47 (0.36)		1.69 (0.53)	
NO_3-N	mg/L	7.93 (2.02)	1.08 (0.88)	86.9%	0.64 (0.42)	92.7%	1.43 (0.87)	81.7%
TN	mg/L	8.29 (1.62)	2.19 (1.49)	70.6%	2.04 (0.78)	75.0%	2.68 (1.43)	64.5%
PO_4-P	mg/L	0.75 (0.14)	0.31 (0.22)	58.7%	0.67 (0.23)	10.7%	0.38 (0.21)	49.3%
TP	mg/L	1.29 (0.33)	0.77 (0.32)	40.3%	1.13 (0.25)	12.4%	0.87 (0.27)	32.6%

Notes: Standard deviation of pollutant concentrations is indicated in brackets

5.3.2 Secondary effluent characteristics

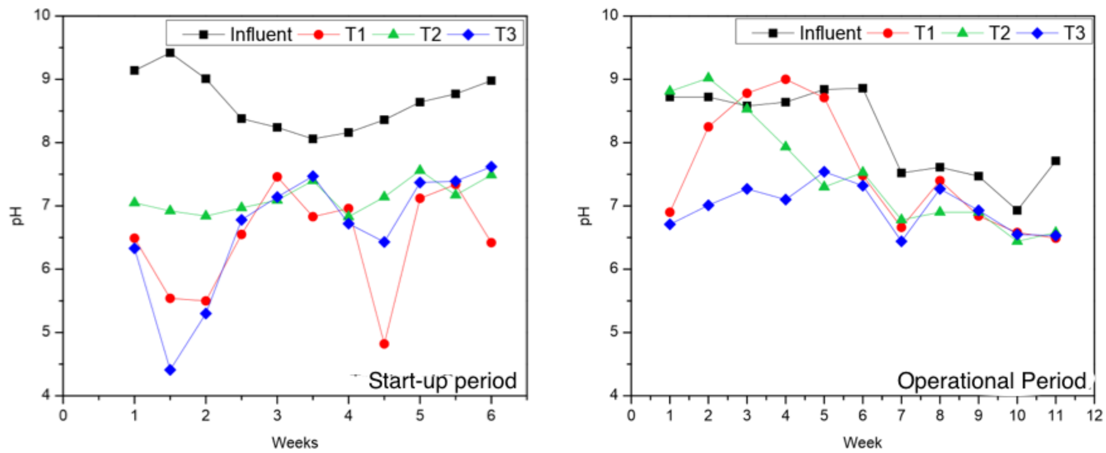
Table 5.2 and Table 5.3 show the influent water quality (secondary effluent from the treatment plant) that entered the experimental system, and a strong difference was noted in pH, NO_3-N, and TP concentrations during start-up and operational period. The higher pH level of the influent during the summer was generally attributed the strong algal activities in the wastewater stabilization ponds that would exhaust the inorganic dissolved carbon and negatively impacted the pH balance in the water. The NO_3-N level was significantly higher during the operational period than during the start-up period, as the nitrification process was not likely as effective during the fall season due to the lower ambient temperature, which would slow down the activity of nitrifying bacteria (Champagne et al., 2017). Although the influent PO_4-P concentrations were similar between seasons, more than double the amount of TP was present during the operational period compared to the start-up period indicating other forms of phosphorus were likely present.

5.3.3 Attenuation of pH

Algal blooms have frequently been reported to occur in the Amherstview WPCP wastewater stabilization pond system during the summer months, and have been identified as the main reason for the elevated pH, and these pH levels have often exceeded the regulatory discharge limit allowed for this system in the past (Wallace et al., 2016). The introduction of a SFCW was identified as a potential solution to resolve this pH issue. In this study, all treatment wetland reactors were noted to reduce the pH to a level below the regulatory discharge limit for the entire experimental period. However, the overall pH level was found to increase during the operational period, mainly due to the increased algal activity in the wastewater stabilization pond, as a result of the elevated ambient temperatures and strong sunlight irradiation (Liu et al., 2016a). The peat substrate played an important role in reducing the mean pH level during the start-up period, as T1 and T3 significantly reduced the pH level in the first season from 7.43 to 6.25 and 6.39, respectively. Peat moss mainly consists of humic and fulvic acids, which can be quickly released under alkaline conditions in aqueous environments and can contribute to the reduction in pH levels. This instant impact was also demonstrated in a previous bench-scale study (Jin et al., 2017b). During the operational period, T3 was found to maintain effluent pH levels below 7, whereas the effluent pH level for T1 was higher (7.55). This could be due to the presence of vegetation, as the operational period experiences a more complete growth of *T. latifolia*, and its growth might have altered the water chemistry.

The pH trends during both treatment periods over time are shown in Figure 5.3. The pH level was reduced in T1 and T3 during the first two weeks of the start-up period. The short-term effect was likely due to the initial release of acidic compounds from the peat, which quickly decreased the pH level below 5.5. After the initial decrease in pH, the pH level in T1 and T3 were generally maintained between 6.5 and 7.5 throughout start-up period. The pH level in T2 was relatively consistent and remained between 7 and 7.5 with less fluctuation compared to T1 and T3 during the start-up period. This was to be expected as there was no external source of acidic compounds entering the system. The starting pH levels of T1 and T3 were similar at the beginning of operational period (pH

~6.8). T3 was found to maintain a relatively stable pH level throughout the operational period, whereas T1 experienced a pH increase up to approximately 9 during Weeks 2-4, but eventually the pH was observed to decrease again to approximately 7. T2 had a similar pH level as the influent at the beginning of operational period. However, the pH was gradually noted to decrease from ~9 to 6.5 towards the end of operational period. It was noted that precipitation greatly affected the influent pH levels, where after a heavy rainfall event, stormwater runoff, which is typically pH neutral, would generally enter the stabilization pond and mitigate the high pH effluents. Several heavy rainfall events occurred after Week 6 during the operational period, which is reflected in the pH trend observed.



(a) (b)

Figure 5.3 (a) pH variation over start-up experimental period; and (b) pH variation over operational experimental period.

5.3.4 Nitrogen removal

Due to the nature of the shallow wastewater stabilization pond, in which aerobic conditions typically prevail, NH_4-N can be easily oxidized and converted to NO_3-N, resulting in a low effluent NH_4-N concentrations. The elevated pH in the stabilization pond could also encourage the volatilization of NH_3 to the atmosphere, which further lower the NH_4-N level. Therefore, the NH_4-N concentration from the secondary effluent was consistently low during the entire experimental period. As a result, further removal of NH_4-N in the following treatment process was not anticipated. In this experiment, the influent NH_4-N concentrations were 0.10 mg/L and 0.20 mg/L for the start-up and operational periods, respectively. Only T2 could further remove the NH_4-N in start-up period, and only a 10% removal efficiency was observed. Effluent NH_4-N concentrations were increased in all other scenarios during both treatment periods. Low NH_4-N removal efficiencies were also reported in other studies where influent concentrations were low. A SF CW study showed that only a 11.8% of NH_4-N removal efficiency was achieved with an influent concentration of 0.88 mg/L (Maine et al., 2017). Another study also observed no positive removal of NH_4-N, when the influent NH_4-N level was below 0.41 mg/L (Hernández-Crespo et al., 2017). The increase in NH_4-N concentration might be due to dissimilatory nitrate reduction to ammonia, which is a reduction process that could reduce NO_2-N and NO_3-N back to NH_4-N under anoxic/reduced environments (Behrendt et al., 2014). In this study, the increase in COD concentrations and high COD/NO_3-N ratio could favor the production of NH_4-N through dissimilatory nitrate reduction. The introduction of peat might also contribute to the high NH_4-N effluent concentrations due to the nitrogen released by peat. Despite the limited ability to further remove NH_4-N from the secondary effluent, all treatments removed NO_3-N and TN during both treatment periods. Maximum NO_3-N and TN removal efficiencies of 37.3% and 41.2% were achieved during the start-up period, and 92.7% and 75.0% during the operational period in T2. During both treatment periods, NO_3-N accounted for most of TN removal in all reactors.

In a typical CW reactor, nitrification-denitrification, anaerobic ammonium oxidation (ANAMMOX) and plant uptake are the three main pathways to remove NO_3-N and TN (Saeed & Sun, 2012). However, the low NH_4-N input and the aerobic conditions present in all reactors promoted by a shallow reactor depth and the vegetative oxygen diffusion, indicated that ANAMMOX would not likely to be the primary route for nitrogen removal. As no vegetation was employed in T3, most of the TN was expected to be removed through the nitrification and denitrification route and a 64.5% of TN removal efficiency indicated that peat could provide adequate TN removal efficiency. However, the introduction of vegetation produced TN removal efficiencies of 41.2% and 75.0% during the start-up and operational periods, respectively. The vegetation not only provided another TN removal route, but most likely also stimulated the biological activity in the reactors. The TN removal efficiency of T1 was always between that of T3 and T2 during both periods. However, T1 had higher NH_4-N concentrations compared to T2, which would suggest the presence of bacteria performing dissimilatory nitrate reduction processes. These bacteria may have competed with denitrifier (heterotrophic bacteria), which in turn would have reduced the overall TN removal efficiency.

5.3.5 Phosphorus removal

The overall phosphorus removal efficiency was low during the start-up period, and only T2 could reduce both PO_4-P and TP concentrations. T1 was only able to decrease PO_4-P concentrations by 1.4%, while T3 exhibited a higher effluent concentration than the influent. The introduction of peat could be responsible for the increase in phosphorus during the start-up period, as the mobile phosphorus could easily have been detached from the peat and released to the water column, which in turn could have contributed to a high phosphorus concentration in the effluent. Decaying plant material was another source of phosphorus that could have contributed to the effluent, but this would be expected to have a lower impact on the reactors than peat, as T2 could reduce both PO_4-P and TP from the reactor during the start-up period. During the operational period, T1 and T3 both outperformed T2, as both PO_4-P and TP concentrations reductions were observed with maximum PO_4-P and TP removal efficiencies of 58.7% and 40.3%, respectively. Substrate plays an important role in the overall retention of phosphorus in CWs, and it is the main component of phosphorus storage. Some researchers have reported that substrates accounted for more than 50% of the TP removal compared to other components, including water, periphyton, and macrophytes (Lai, 2014). Peat is considered to be an excellent phosphorus sink, and it has a strong phosphorus retention ability (Jin et al., 2017b). PO_4-P, which is also known as reactive phosphorus, is the form commonly used by bacteria, plants and algae as a vital nutrient in surface waters. The removal of PO_4-P accounted for more than 80% of the TP removal. One study found that CWs are effective at removing PO_4-P compared to other forms of phosphorus, including organic phosphates, and particulate phosphorus (Ciria et al., 2005)

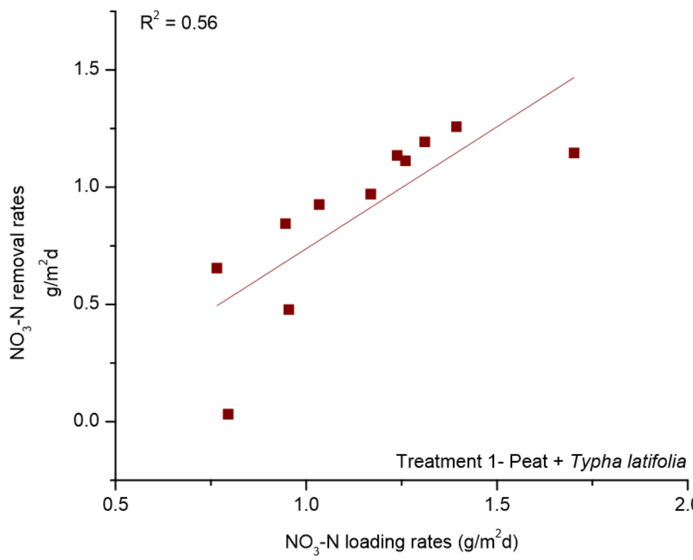
5.3.6 Organics removal

The influent secondary wastewater effluent had a relatively low COD concentration, and all treatment wetland reactors were unable to further reduce COD concentrations. An increase in COD was noted in T2 during the start-up period, whereas T1 and T3 significantly increased the COD concentrations to 49.2 mg/L and 44.0 mg/L, respectively. The COD level was well maintained during the operational period, and only a slightly increase was noted in T3. Although the properties of peat vary based on its location or origin, typically peat has a high organic and carbon content resulting from its formation. Therefore, leaching of carbon will inevitably occur when peat and most of other organic substrates are applied to wetland reactors. This was also reported in other studies when organic substrates were applied to mitigate micro-polluted wastewater

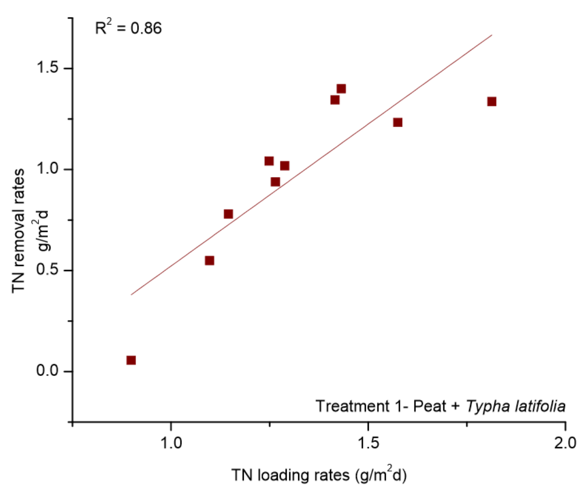
(Saeed & Sun, 2011). Another explanation could be that color-producing organics within peat may transform into intermediate non-colored recalcitrant organic materials. These materials strongly resist further degradation, which would contribute to elevated COD levels (Ong et al., 2009). The low COD removals by peat was also found in other studies that employed a peat-filled substrate filter to treat landfill leachate and municipal wastewater, and only a 17% of COD removal efficiency was recorded when influent COD concentrations were well above 500 mg/L (Kõiv et al., 2009).

5.3.7 Loading rates and removal rates

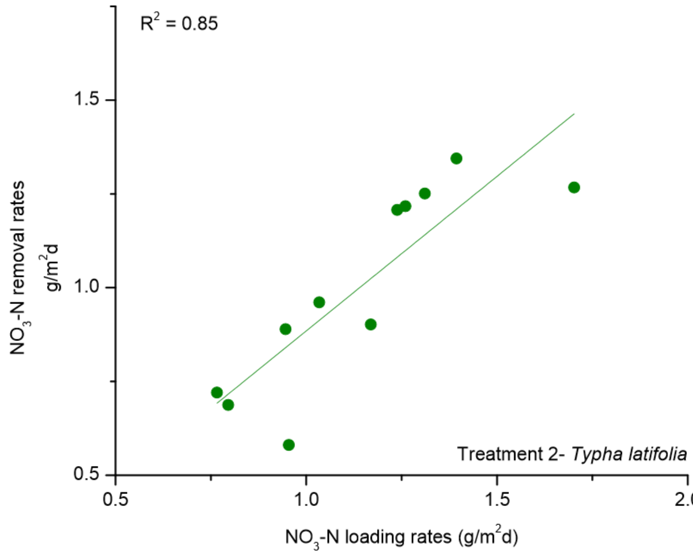
Figure 5.4 shows the correlation plots (indicated by statistical parameter coefficient of determination, R^2) of NO_3-N and TN loading vs. removal rates (g/m^2 d), as wastewater passed through all wetland reactors. As observed in Figure 5.4, both NO_3-N and TN removal rates increased with increases in loading. With the exception of NO_3-N removal in T1, all other treatments had a R^2 value between 0.75 and 0.87. However, the NO_3-N removal rates did not increase when the loading rates of NO_3-N were beyond 1.5 g/m^2d for all wetland reactors. The TN removal rates exhibited similar trends as NO_3-N. A comparison of NO_3-N and TN removal rates also indicated that NO_3-N removal accounted for almost all of the TN removal.


R^2 = 0.56
NO3-N removal rates g/m2d
NO3-N loading rates (g/m2d)
Treatment 1- Peat + *Typha latifolia*
1.5
1.0
0.5
0.0
0.5
1.0
1.5
2.0

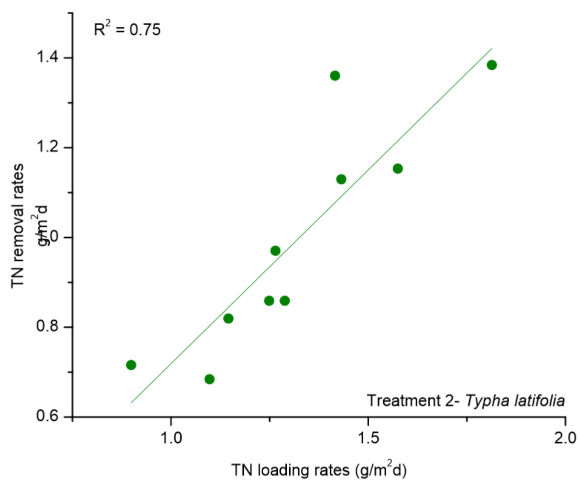
(a)


R^2 = 0.86
TN removal rates g/m2d
TN loading rates (g/m2d)
Treatment 1- Peat + *Typha latifolia*
1.5
1.0
0.5
0.0
1.0
1.5
2.0

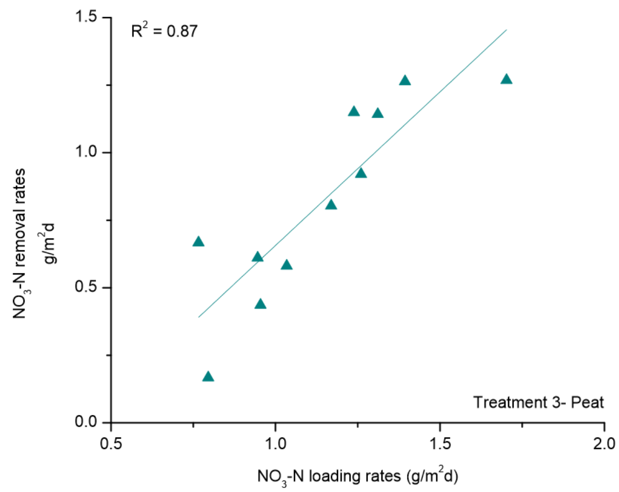
(b)


$R^2 = 0.85$
1.5
1.0
0.5
NO_3-N removal rates
g/m^2d
0.5
1.0
1.5
2.0
NO_3-N loading rates (g/m^2d)
Treatment 2- *Typha latifolia*

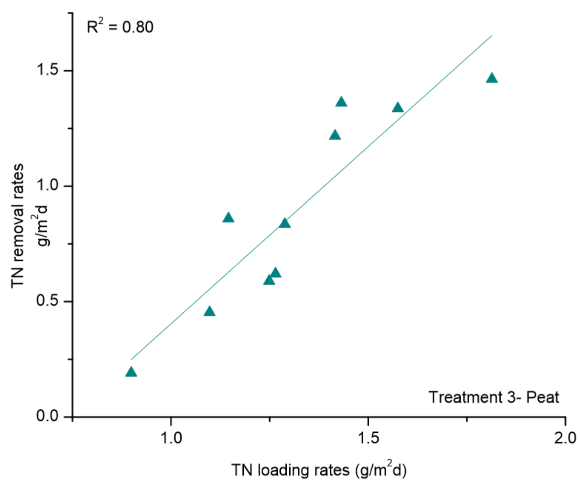
(c)


$R^2 = 0.75$
1.4
1.2
1.0
0.8
0.6
TN removal rates
g/m^2d
1.0
1.5
2.0
TN loading rates (g/m^2d)
Treatment 2- *Typha latifolia*

(d)



(e)



(f)

Figure 5.4 Correlation plots of: T1-NO_3-N (a); T1-TN (b); T2-NO_3-N (c); T2-TN (d); T3-NO_3-N (e); and T3-TN (f) loading rates and removal rates in T1, T2 and T3 over the entire experimental period.

5.3.8 Effects of substrate and vegetation

Table 5.4 indicates the statistical comparison of selected nitrogen and phosphorus removal efficiencies and removal rates (g/m^2 d) between T1 and T2, T1 and T3, and T2 and T3, to evaluate their individual effect on the wetland reactors. Only results from the operational period were employed for analysis using ANOVA and Tukey post-hoc. As observed in Table 4, no significant statistical differences were found between T1 and T3 in terms of removing nitrogen or phosphorus compounds, despite T1 having higher nitrogen removal efficiencies than T3, and vice versa in terms of phosphorus removal efficiencies.

However, the introduction of peat to the wetland system with *T. latifolia* (T1 and T2) had a much more impact than the introduction of *T. latifolia* to a wetland system with peat (T1 and T3), as most of the significant statistical differences ($p < 0.05$) were observed between T1 and T2. Reactors with peat strongly outcompeted the reactors without peat in terms of phosphorus removal efficiencies and removal rates.

Table 5.4 Statistical comparison (p values) between removal efficiencies and removal rates across the treatment wetland reactors

Parameter	T1 (Peat + Cattails) and T2 (Cattails)		T1 (Peat + Cattails) and T3 (Peat)		T2 (Cattails) and T3 (Peat)	
	Removal efficiency	Removal rates	Removal efficiency	Removal rates	Removal efficiency	Removal rates
NO_3-N	**0.0003**	**0.0001**	0.2348	0.2359	**0.0366**	**0.0291**
TN	0.6020	0.7752	0.2632	0.2529	0.1718	0.2238
PO_4-P	**0.0431**	**0.0407**	0.4117	0.2846	**0.0451**	**0.0429**
TP	**0.0459**	0.0992	0.4289	0.3544	0.0578	0.0691

Notes: The significant statistical difference ($p < 0.05$) is indicated in bold numbers.

5.3.9 Effects of seasons

Figure 5.5 illustrates the temperature and precipitation variation at the Amherstview WPCP, and Table 5.5 summarizes the data during the entire experimental period. Previous studies have demonstrated that the performance of CWs tends to be reduced under cold climate conditions, especially removal processes involving microorganisms and bacteria. Low nitrogen removal efficiencies by CWs in cold climates have been reported in other studies, and the results from this study mirror their results (Fan et al., 2016). Both NO_3-N and TN had significantly higher removal efficiencies during the operational period than during the start-up period across all reactors. During the start-up period, most of the transplanted *T. latifolia* began to decay due to the climate conditions. Consequently, decaying plant material accumulated in the reactors could release nutrient back into the water column, thereby reducing the removal efficiency. Most of the growth of *T. latifolia* occurred during the operational period which meant the plants required more nutrients to support their growth.

5.3.10 Regulation consideration

This small-scale on-site experiment was designed as a preliminary test for an upcoming pilot-scale SFCW at the Amherstview WPCP. The intention of the construction of a pilot-scale SFCW is to not only increase their rated treatment capacity, but also to further improve the performance of the treatment plant in order to meet increasingly stringent regulatory discharge guidelines. In this experiment, all treatments failed to meet the TP regulatory discharge limits during the startup period. T1 and T3 could meet all regulatory discharge limits during operational period, but T2 was still unable to meet the TP discharge limit. As the secondary biological treatment at the Amherstview WPCP was not designed to remove excess nutrients (phosphorus), the TP concentration in the secondary effluent was still high enough to promote excessive algal growth. The results indicated that employing vegetation alone in a SFCW was not sufficient to reduce phosphorus concentrations to below regulatory discharge limits due to its lack of ability to retain phosphorus. An appropriate substrate in the wetland reactor is required to enhance the phosphorus removal efficiency and reduce phosphorus concentrations below the regulatory discharge limit.

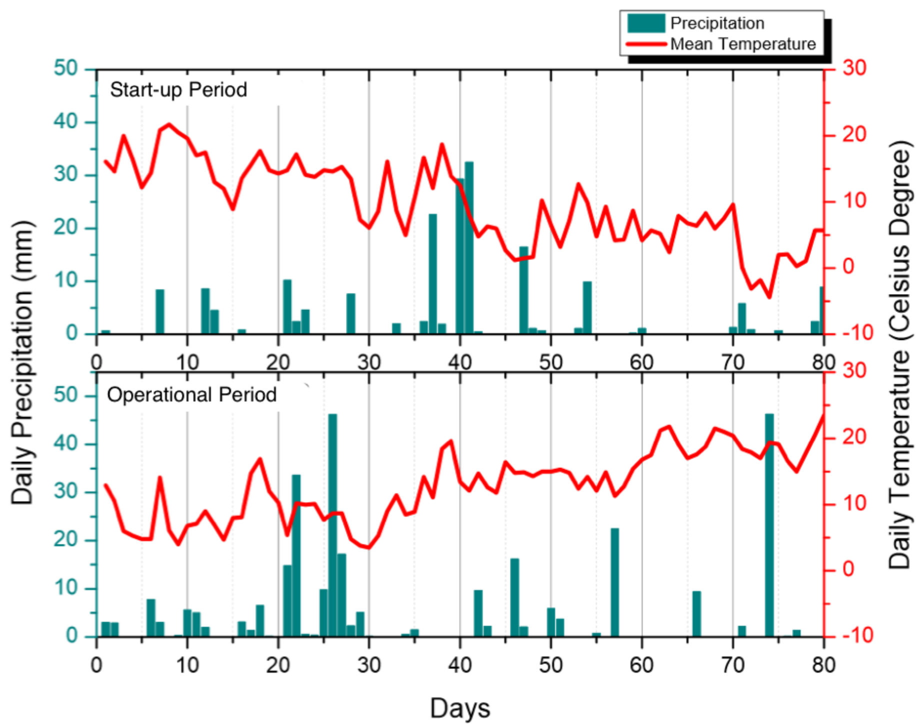


Figure 5.5 Changes in temperature and precipitation at the Amherstview WPCP over the entire experimental period

Table 5.5 Summary of temperature and precipitation data during the entire experimental period

Experiment	Temperature			Precipitation		
Period	Min.	Max.	Average	Min.	Max.	Average
Start-up	-4.4 C°	21.7 C°	9.0 C°	0 mm	32.5 mm	2.9 mm
Operational	3.5 C°	23.5 C°	15.3 C°	0 mm	46.3 mm	2.7 mm

5.4 Conclusion

In this study, T1 and T3 could treat secondary effluent to meet the municipal wastewater regulatory discharge guidelines during the operational period at the Amherstview WPCP. More importantly, they could maintain the pH level below 7.5 throughout the entire experimental period. Effective NO_3-N, TN, and TP removal efficiencies were observed. T2 was not able to meet the phosphorus discharge limit and was only able to reduce the TP level to 1.13 mg/L with a 12.4% of removal efficiency. Nutrient leaching could potentially contribute to the low performance observed during the start-up period. NO_3-N and TN removal efficiencies were more effective under warmer conditions, and the growing season for vegetation enhanced the efficiency through the plant uptake.

When comparing their individual effects on the wetland system, the introduction of peat had a larger impact than the *T. latifolia*. Peat could effectively reduce the elevated pH level and greatly enhanced the phosphorus removal efficiency due to its own physical-chemical properties. However, it also reduced the ability of *T. latifolia* to remove nitrogenous compounds. On the other hand, the presence of *T. latifolia* was found to improve the nitrogen removal efficiency by providing an additional removal route, although in this study, no significant difference was found in either nutrient removal efficiency or removal rate. In the future, a longer acclimation period would be suggested as a requirement to allow the wetland system to acclimatize and reach maximum function.

5.5 References

APHA. (2012). Standard methods for the examination of water and wastewater.

Behrendt, A., Tarre, S., Beliavski, M., Green, M., Klatt, J., de Beer, D., and Stief, P. (2014). Effect of high electron donor supply on dissimilatory nitrate reduction pathways in a bioreactor for nitrate removal. *Bioresource Technology, 171*, 291-297.

Calheiros, C. S. C., Rangel, A. O. S. S., and Castro, P. M. L. (2009). Treatment of industrial wastewater with two-stage constructed wetlands planted with typha latifolia and phragmites australis. *Bioresource Technology, 100*(13), 3205-3213.

Champagne, P., Liu, L., and Howell, M. (2017). 7 - aerobic treatment in cold-climate countries a2 - lee, duu-jong *Current developments in biotechnology and bioengineering* (pp. 161-201): Elsevier.

Ciria, M. P., Solano, M. L., and Soriano, P. (2005). Role of macrophyte typha latifolia in a constructed wetland for wastewater treatment and assessment of its potential as a biomass fuel. *Biosystems Engineering, 92*(4), 535-544.

Clyde, E. J., Champagne, P., Jamieson, H. E., Gorman, C., and Sourial, J. (2016). The use of a passive treatment system for the mitigation of acid mine drainage at the williams brothers mine (california): Pilot-scale study. *Journal of Cleaner Production, 130*(Supplement C), 116-125.

Fan, J., Zhang, J., Ngo, H. H., Guo, W., and Yin, X. (2016). Improving low-temperature performance of surface flow constructed wetlands using potamogeton crispus l. Plant. *Bioresource Technology, 218*, 1257-1260.

Giácoman-Vallejos, G., Ponce-Caballero, C., and Champagne, P. (2015). Pathogen removal from domestic and swine wastewater by experimental constructed wetlands. *Water Science and Technology, 71*(8), 1263.

Gottschall, N., Boutin, C., Crolla, A., Kinsley, C., and Champagne, P. (2007). The role of plants in the removal of nutrients at a constructed wetland treating agricultural (dairy) wastewater, ontario, canada. *Ecological Engineering, 29*(2), 154-163.

Gunes, K. (2007). Restaurant wastewater treatment by constructed wetlands. *CLEAN – Soil, Air, Water, 35*(6), 571-575.

Hernández-Crespo, C., Gargallo, S., Benedito-Durá, V., Nácher-Rodríguez, B., Rodrigo-Alacreu, M. A., and Martín, M. (2017). Performance of surface and subsurface flow constructed wetlands treating eutrophic waters. *Science of The Total Environment, 595*, 584-593.

Herrera-Melián, J. A., González-Bordón, A., Martín-González, M. A., García-Jiménez, P., Carrasco, M., and Araña, J. (2014). Palm tree mulch as substrate for primary treatment wetlands processing high strength urban wastewater. *Journal of Environmental Management, 139*(0), 22-31.

Jácome, J. A., Molina, J., Suárez, J., Mosqueira, G., and Torres, D. (2016). Performance of constructed wetland applied for domestic wastewater treatment: Case study at boimorto (galicia, spain). *Ecological Engineering, 95*, 324-329.

Jin, M., Champagne, P., and Hall, G. (2017). Effects of different substrates in the mitigation of algae-induced high ph wastewaters in a pilot-scale free water surface wetland system. *Water Science and Technology, 75*(1), 1-10.

Kadlec, R. H., and Wallace, S. (2008). *Treatment wetlands* (2nd Edition ed.). CRC press, Florida.

Kasak, K., Mander, Ü., Truu, J., Truu, M., Järveoja, J., Maddison, M., and Teemusk, A. (2015). Alternative filter material removes phosphorus and mitigates greenhouse gas emission in horizontal subsurface flow filters for wastewater treatment. *Ecological Engineering, 77*(0), 242-249.

Kõiv, M., Vohla, C., Mõtlep, R., Liira, M., Kirsimäe, K., and Mander, Ü. (2009). The performance of peat-filled subsurface flow filters treating landfill leachate and municipal wastewater. *Ecological Engineering, 35*(2), 204-212.

Lai, D. Y. F. (2014). Phosphorus fractions and fluxes in the soils of a free surface flow constructed wetland in hong kong. *Ecological Engineering, 73*, 73-79.

Liu, L., Hall, G., and Champagne, P. (2016). Effects of environmental factors on the disinfection performance of a wastewater stabilization pond operated in a temperate climate. *Water, 8*(1), 5.

Liu, M., Wu, S., Chen, L., and Dong, R. (2014). How substrate influences nitrogen transformations in tidal flow constructed wetlands treating high ammonium wastewater? *Ecological Engineering, 73*(0), 478-486.

Lizama Allende, K., Fletcher, T. D., and Sun, G. (2012). The effect of substrate media on the removal of arsenic, boron and iron from an acidic wastewater in planted column reactors. *Chemical Engineering Journal, 179*, 119-130.

Maine, M. A., Hadad, H. R., Sánchez, G. C., Di Luca, G. A., Mufarrege, M. M., Caffaratti, S. E., and Pedro, M. C. (2017). Long-term performance of two free-water surface wetlands for metallurgical effluent treatment. *Ecological Engineering, 98*, 372-377.

Martín, M., Oliver, N., Hernández-Crespo, C., Gargallo, S., and Regidor, M. C. (2013). The use of free water surface constructed wetland to treat the eutrophicated waters of lake l'albufera de valencia (spain). *Ecological Engineering, 50*, 52-61.

Mateus, D. M. R., Vaz, M. M. N., and Pinho, H. J. O. (2012). Fragmented limestone wastes as a constructed wetland substrate for phosphorus removal. *Ecological Engineering, 41*(0), 65-69.

Mawuli, D., Xiaochang, W., Yucong, Z., Yuan, G., Jiaqing, X., and Yaqian, Z. (2015). Characteristics of nitrogen and phosphorus removal by a surface-flow constructed wetland for polluted river water treatment. *Water Science and Technology, 71*(6), 904-912.

Murphy, C., Wallace, S., Knight, R., Cooper, D., and Sellers, T. (2015). Treatment performance of an aerated constructed wetland treating glycol from de-icing operations at a uk airport. *Ecological Engineering, 80*(0), 117-124.

Ong, S.-A., Uchiyama, K., Inadama, D., and Yamagiwa, K. (2009). Simultaneous removal of color, organic compounds and nutrients in azo dye-containing wastewater using up-flow constructed wetland. *Journal of Hazardous Materials, 165*(1), 696-703.

Paing, J., Serdobbel, V., Welschbillig, M., Calvez, M., Gagnon, V., and Chazarenc, F. (2015). Treatment of high organic content wastewater from food-processing industry with the french vertical flow constructed wetland system. *Water Science and Technology, 72*(1), 70-76.

Pandey, M. K., Jenssen, P. D., Krogstad, T., and Jonasson, S. (2013). Comparison of vertical and horizontal flow planted and unplanted subsurface flow wetlands treating municipal wastewater. *Water Science and Technology, 68*(1), 117-123.

Saeed, T., Afrin, R., Muyeed, A. A., and Sun, G. (2012). Treatment of tannery wastewater in a pilot-scale hybrid constructed wetland system in bangladesh. *Chemosphere, 88*(9), 1065-1073.

Saeed, T., Paul, B., Afrin, R., Al-Muyeed, A., and Sun, G. (2016). Floating constructed wetland for the treatment of polluted river water: A pilot scale study on seasonal variation and shock load. *Chemical Engineering Journal, 287*, 62-73.

Saeed, T., and Sun, G. (2011). A comparative study on the removal of nutrients and organic matter in wetland reactors employing organic media. *Chemical Engineering Journal, 171*(2), 439-447.

Saeed, T., and Sun, G. (2012). A review on nitrogen and organics removal mechanisms in subsurface flow constructed wetlands: Dependency on environmental parameters, operating conditions and supporting media. *Journal of Environmental Management, 112*, 429-448.

Saeed, T., and Sun, G. (2013). A lab-scale study of constructed wetlands with sugarcane bagasse and sand media for the treatment of textile wastewater. *Bioresource Technology, 128*, 438-447.

Schierano, M. C., Maine, M. A., and Panigatti, M. C. (2017). Dairy farm wastewater treatment using horizontal subsurface flow wetlands with typha domingensis and different substrates. *Environmental Technology, 38*(2), 192-198.

Sehar, S., Sumera, Naeem, S., Perveen, I., Ali, N., and Ahmed, S. (2015). A comparative study of macrophytes influence on wastewater treatment through subsurface flow hybrid constructed wetland. *Ecological Engineering, 81*(0), 62-69.

Sim, C. H., Quek, B. S., Shutes, R. B., and Goh, K. H. (2013). Management and treatment of landfill leachate by a system of constructed wetlands and ponds in singapore. *Water Science and Technology, 68*(5), 1114-1122.

Speer, S., Champagne, P., and Anderson, B. (2012). Pilot-scale comparison of two hybrid-passive landfill leachate treatment systems operated in a cold climate. *Bioresource Technology, 104*(Supplement C), 119-126.

Speer, S., Champagne, P., Crolla, A., and Kinsley, C. (2009). Hydraulic performance of a mature wetland treating milkhouse wastewater and agricultural runoff. *Water Science and Technology, 59*(12), 2455.

Stefanakis, A. I., Seeger, E., Dorer, C., Sinke, A., and Thullner, M. (2016). Performance of pilot-scale horizontal subsurface flow constructed wetlands treating groundwater contaminated with phenols and petroleum derivatives. *Ecological Engineering, 95*, 514-526.

Toscano, A., Marzo, A., Milani, M., Cirelli, G. L., and Barbagallo, S. (2015). Comparison of removal efficiencies in mediterranean pilot constructed wetlands vegetated with different plant species. *Ecological Engineering, 75*(0), 155-160.

Vymazal, J. (2013a). Emergent plants used in free water surface constructed wetlands: A review. *Ecological Engineering, 61, Part B*(0), 582-592.

Vymazal, J. (2013b). Plants in constructed, restored and created wetlands. *Ecological Engineering, 61*, 501-504.

Wallace, J., Champagne, P., and Hall, G. (2016). Multivariate statistical analysis of water chemistry conditions in three wastewater stabilization ponds with algae blooms and ph fluctuations. *Water Research, 96*(Supplement C), 155-165.

Wallace, J., Champagne, P., and Monnier, A.-C. (2015). Performance evaluation of a hybrid-passive landfill leachate treatment system using multivariate statistical techniques. *Waste Management, 35*(Supplement C), 159-169.

Yin, H., Yan, X., and Gu, X. (2017). Evaluation of thermally-modified calcium-rich attapulgite as a low-cost substrate for rapid phosphorus removal in constructed wetlands. *Water Research, 115*, 329-338.

Zhao, J., Zhao, Y., Xu, Z., Doherty, L., and Liu, R. (2016). Highway runoff treatment by hybrid adsorptive media-baffled subsurface flow constructed wetland. *Ecological Engineering, 91*, 231-239.

Chapter 6

Design and Implementation of a Pilot-scale Free Water Surface Constructed Wetland for Mitigation of High pH Secondary Effluent at the Amherstview WPCP

Abstract: A pilot-scale free water surface constructed wetland was successfully established at the Amherstview WPCP. Three different substrate materials, including peat, topsoil and sludge, and two connection types, including berm connection and open water connection, were employed, and four unique treatment trains, including TB: topsoil + berm connection; SB: sludge + berm connection; PB: peat + berm connection; PO: peat + open water connection, were designed based on previous laboratory bench-scale and on-site small-scale studies to compare treatment performance in terms of pH attenuation and nutrient concentrations from the secondary effluent. Overall, this newly designed FWS CW was highly effective at retaining PO_4-P and TP, and fairly effective at removing NO_3-N and TN. Three out of the four treatment trains could attenuate the pH below regulatory discharge limit (<9.5) except TB, which, in fact, further increase the pH beyond the discharge limit. Peat exhibited the best overall treatment performance. In addition, open water connection outperformed the berm connection for the attenuation of pH, but it encouraged the accumulation of algal biomass. A few operational issues were observed in the first season, and corrective actions have already been implemented to rectify these issues. It is anticipated that the treatment performance of the constructed wetland could further improve when the wetland becomes more mature.

Keywords: Free water surface, constructed wetland, peat, pH, nutrients

6.1 Introduction

Wastewater stabilization ponds (WSPs) have been widely employed in wastewater treatment facilities across North America, as a polishing treatment process for secondary or tertiary effluent, as they can offer a natural treatment process. It has also been recognized as an effective, low-cost, and commercially viable approach for small to medium municipalities (Maynard et al., 1999). It has been shown that WSPs can be very efficient in the removal of organics, solids and pathogenic organisms, which makes them a valuable tool in sustainable development (Kayombo et al., 2002; Mburu et al., 2013). Despite their notably good performance for removing organics and solids, WSPs can exhibit limitations in the removal of nutrients such as nitrogen and phosphorous under high-loading conditions. As a result, eutrophication can occur take place. Secondly, excessive algal growth and strong photosynthetic activity during the summer months can quickly exhaust dissolved inorganic carbon in the water, disturbing the carbon equilibrium. This can lead to elevated effluent pH levels that do not meet regulatory discharge limits due to the absence of inorganic carbon (Jin et al., 2017b; Wallace et al., 2016).

Natural wetlands are often referred to as the “Earth’s kidneys”. They can filter the water to remove nutrients, thus reducing potential harmful effects of eutrophication such as algal blooms and hypoxia (Kadlec & Wallace, 2008). They also provide other ecosystem services such as flood control, recreational opportunities and carbon sequestration that can yield significant economic value. Constructed wetlands (CWs), on the other hand, are a wastewater treatment technology that intends to mimic the function of natural wetlands, but do so in a more controlled environment. There has been a growing interest in integrating CWs as part of the wastewater treatment strategies, especially for small, rural and/or remote communities, due to their simple maintenance requirements and low capital and operating costs. Generally, there are two main types of CW depending on the flow: surface flow (Abe et al., 2014; Hsueh et al., 2014; Martín et al., 2013) and subsurface flow (horizontal or vertical) (Abou-Elela & Hellal, 2012; Jong & Tang, 2015; Narvaez et al., 2011; Schierano et al., 2017; Stefanakis et al., 2016). CWs have been demonstrated to be able to treat a variety of conventional wastewater pollutants (e.g. nitrogen, phosphorus, heavy metals,) (Hernández-Crespo et al., 2017; Luo et al., 2017; Maine et al., 2017) as well as emerging constituents of concerns (e.g. pharmaceutical,) (Hijosa-Valsero et al., 2016). Appropriate hydraulic and pollutant loading rates and thriving vegetation communities are key to providing effective treatment for a variety of pollutants in each of these wetland systems (Browne & Jenssen, 2005; Weerakoon et al., 2013). Multiple wetland systems combining one, two or three of these wetland configurations are commonly used to address with more complex pollutants, and the sequence of these wetlands must be carefully evaluated to achieve the specified objectives (Avila et al., 2013; Saeed et al., 2012; Sehar et al., 2015b). The flexibility of the CW systems makes them ideal for both newly designed wastewater treatment plants as well as for upgrading existing treatment systems.

As described in the previous chapters, the Amherstview Water Pollution Control Plant (WPCP) is a municipal wastewater treatment plant operated by Loyalist Township in Ontario, Canada. It employs a secondary activated sludge treatment process and three polishing facultative WSPs, to treat an average of 3,500 m^3/day of municipal wastewater. Eutrophication frequently occurs in the three WSPs during the summer, resulting in algal blooms and a consequent elevated pH effluent. Previous bench-scale and small-scale on-site studies have demonstrated that free water surface (FWS) CWs with an appropriate substrate selection and hydraulic control, could hinder the excessive growth of algae and potentially mitigate the high pH effluent in their treatment ponds (Jin et al., 2017a; Jin et al., 2017b).

Hence, this chapter describes the design and initial performance of the newly designed pilot-scale FWS CW, which operates year-round under temperate climate conditions. This constructed wetland is the final treatment process at the Amherstview WPCP, prior to effluent discharge to the Bayview Bog. Prior to construction of the wetland, the WPCP could meet all regulatory discharge regulations by Ministry of the Environment and Climate Change (MOECC), with the exception of occasional effluent pH exceedances (pH > discharge limit of 9.5) through the summer operation. With the addition of the FWS CW, it was expected that this combined passive wastewater polishing system would mitigate the pH issue. As well, the projected population and industrial growth are expected to exceed the capacity of the existing WSP system in the next few years. Therefore, the introduction of the CW could increase the rated capacity of the existing treatment system to enhance the treatment performance of the WPCP in the long run.

6.2 Design of the pilot-scale constructed wetland

The intention of the design of the pilot-scale FWS CW was to provide additional treatment to existing WSP system to mitigate the elevated pH and nutrient concentrations in the secondary effluent of the Amherstview WPCP, as well as to compare the treatment performance of different wetland configurations (e.g. substrates, cell connection). Hence, four different wetland configurations with different substrate materials and different treatment cell connections were incorporated in this design. The manual of Constructed Wetlands Treatment of Municipal Wastewaters published by United States Environmental Protection Agency (USEPA) and United States National Risk Management Research Laboratory were used as the guidelines during the design process (USEPA, 2000).

6.2.1 Overall design

This newly developed CW is a FWS CW and was constructed within the current footprint of WSP #4 (Figure 6.1). The wetland mainly consists of a distribution ditch, twelve individual treatment cells forming four treatment trains, a collection ditch, internal berms, external berms, and a water distribution and collection system. The conceptual design is shown in Figure 6.2, and the detailed AutoCAD drawings of the design of the wetland are shown in the appendix. The distribution ditch, connected to the effluent of WSP #1 (Figure 6.1) by a 300 mm pipe, was designed to allow sufficient mixing of the wastewater prior to entering the individual treatment trains. There are four individual treatment trains each approximately the length of WSP #4 (~240 m) and each divided by either an internal berm or deep open water zone. The purpose of the four flow paths was to allow for the construction of four unique cell configurations for use in a proof-of-concept, pilot-scale study. Since the current footprint of WSP #4 (Figure 6.1) was not rectangular, the actual size of each cell and each treatment train was slightly different. However, the aspect ratio of each cell was approximately constant. The effluent of all treatment trains was combined in the collection ditch prior to discharge. The collection ditch was designed to minimize cell short-circuiting and stimulate transverse mixing at the end of the cell's length. The flow rate of each cell was ~25% of the total flow rate to the wetland and, thus, the theoretical hydraulic retention time (HRT) for each flow path was equal to that of the final design. The theoretical HRT was designed for 2.5 days, as extended theoretical HRT could promote the unnecessary algae growth in treatment cells. Upon the completion of the pilot study, the intention was that the cell design with optimal treatment performance would applied to the other 3 flow paths.

Figure 6.1 Satellite image of Amherstview WPCP before the construction of CW from Google Earth (2014 May)

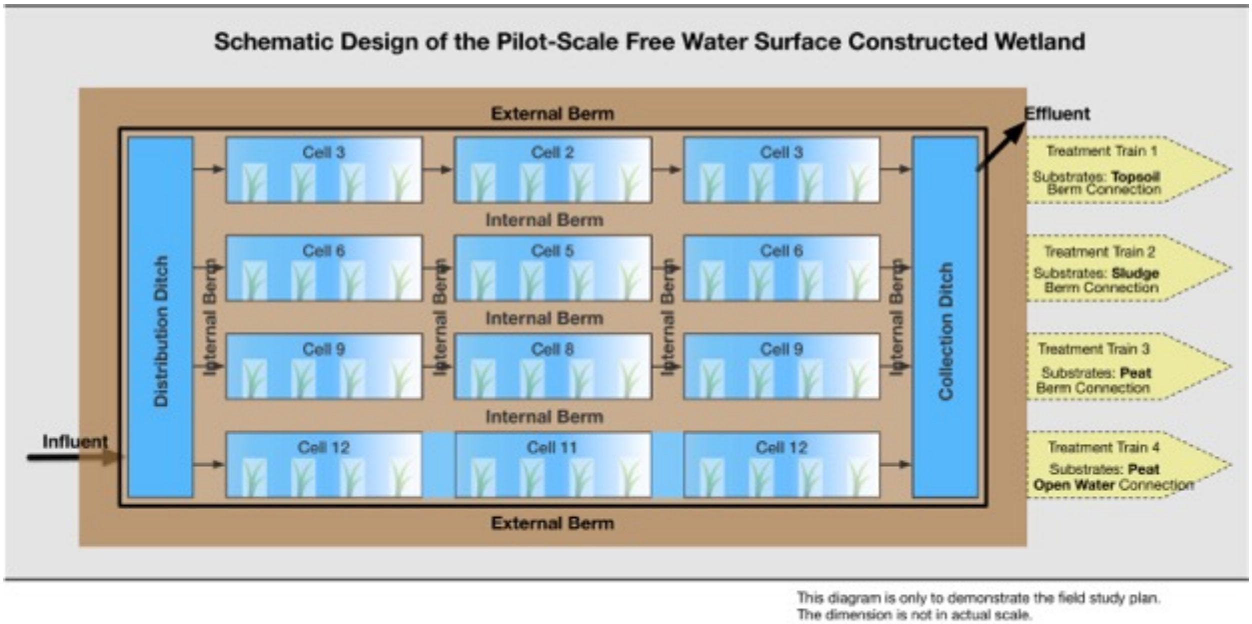


Figure 6.2 The schematic design of the pilot-scale free water surface flow constructed wetland at the Amherstview WPCP

6.2.2 Treatment trains

Each treatment train consisted of three similar treatment cells. Each treatment cell was roughly 80 m x 25 m. Hence, one treatment train provided a surface area of approximately 6,000 m^2 with a total treatment area of approximately 24,000 m^2 (2.4 ha) in total, with the aspect ratio of each treatment cell roughly 3.4:1, conforming to the USEPA guidelines of between 3:1 and 5:1. The substrate material in each treatment cell was 20 cm in depth with a free water level of 40 cm. Given that FWS systems are preceded by WSP #2 and WSP #1 (Figure 6.1), which seasonally produces high total suspended solids (TSS) concentrations, each treatment cell consisted an inlet and outlet deep-water zone to allow TSS to settle. This feature increased the distribution and mixing efficiency in the wetland as well. It is believed that a substantial portion of the incoming settleable and suspended solids can be removed with the addition of an inlet and outlet deep-water zone (Kadlec & Wallace, 2008). The deep zone allowed for a 100 cm water column depth, which was believed to be sufficient to prevent the encroachment of vegetation (USEPA, 2000).

Three different wetland substrate materials, peat, topsoil and sludge, were employed in the CW. Topsoil and peat were tested in the previous bench-scale (Jin et al., 2017b) and on-site small-scale studies (Jin et al., 2017a), and their pH and nutrients attenuation capacity have been demonstrated. Sludge was originally from the bottom of the pre-existing WSP #4 (Figure 6.1) and was also employed in one treatment train. The sludge could promote the growth of vegetation as well as retain nutrients. Topsoil was employed in the Treatment Train 1, sludge was employed in the Treatment Train 2 and peat was employed in the Treatment Train 3 and 4 as indicated in Figure 6.2.

6.2.3 Internal berm vs. open water connection

Treatment cells in same treatment train were connected either by internal berm or deep open water zone. Treatment Trains 1, 2, and 3 were connected by internal berms as shown in Figure 6.3. The water exited one cell through a perforated pipe that extended through the internal berm and exited in the next cell, where it was then distributed by a perforated pipe to distribute the water flow throughout the width of the next cell. The width of the internal berm was 100 cm and the free board was designed to be at least 60 cm. The slope of the berms was at least 3:1. The actual internal berms are illustrated in Figure 6.4.

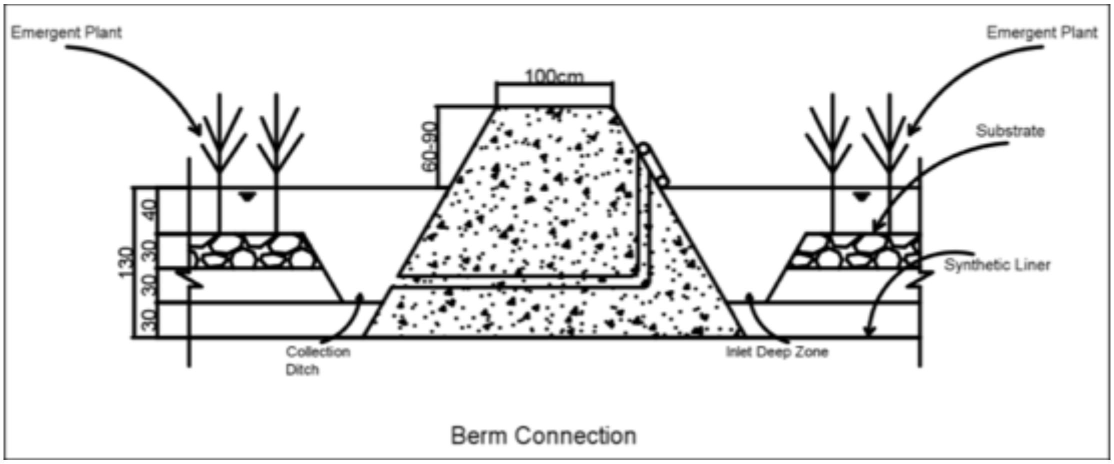


Figure 6.3 CAD drawing shows schematic design of an internal berm separating adjacent cells in the same flow train

(a) (b)

Figure 6.4 (a) Internal berm between the final treatment cell and collection ditch; (b) Internal berm between treatment cells.

Unlike Treatment Trains 1, 2, and 3, Treatment Train 4 did not include an internal berm between the cells. Instead, the cells were connected by two deep open water zones. The schematic design is shown in Figure 6.5, and the actual open water zone is shown in Figure 6.6. The purpose of the deep-water zones in theory was to: allow for lateral mixing; allow for increased aeration; provide near constant head across the flow path; and increase detention time.

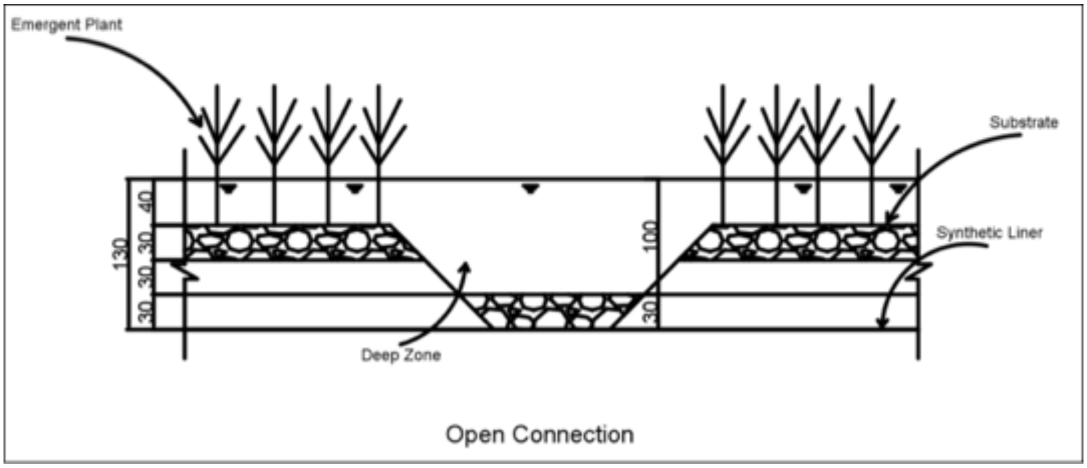


Figure 6.5 A schematic of the open water cell-to-cell connection

Figure 6.6 The deep open water zone in the treatment cell before operation

6.2.4 External berm

Figure 6.7 below shows the external berm design. The existing external berms of WSP #4 (Figure 6.1) was designed to remain intact and act as the external berms of the new CW. The major difference between the internal and external berm were the width, where external berms were 300 cm wide and allowed for individual and vehicle access. The free board of external berm was also at least 60 cm.

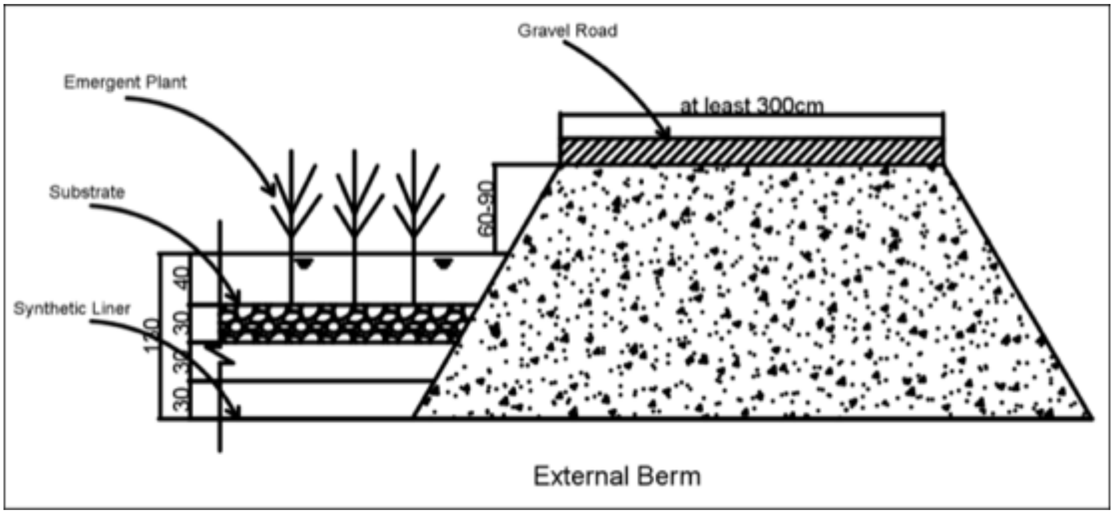


Figure 6.7 A schematic of the pre-existing external berm

6.3 Construction of the constructed wetland

The construction of the CW commenced by decommissioning the existing WSP #4 during the summer of 2015. Wastewater in the WSP #4 (Figure 6.1) was gradually drained and no additional wastewater was allowed to enter this WSP. During this period, the wastewater at the Amherstview WPCP was discharged through a bypass pipe, which connected the effluent point of WSP #1 (Figure 6.1) directly to the discharge point of the treatment plant. Contractor was hired in this project from summer 2015 to summer 2016 to perform the civil construction of the wetland. They were responsible for the levelling and grading of the pond bottom, removing bedrock, establishing internal berms, installing connections and perforated pipes, and distributing substrate materials. The construction process is outlined in Figure 6.8, and different stages of construction are shown in Figure 6.9.

Typha latifolia (*T. Latifolia*), a locally available emergent wetland plant that widely used in CW (Vymazal, 2013a), was selected as the primary vegetation for the new wetland. *T.*

Latifolia plants were collected and revegetated from the Bayview Bog, which is a natural wetland partially owned by the Cataraqui Region Conservation Authority (CRCA) Figure 6.10 (a). A transplanting permit application was submitted to CRCA by Queen's University and the Loyalist Township, and was approved in August 2016 Figure 6.10 (b). The transplanting activity took place from August 2016 to October 2016 by graduate and undergraduate students from Queen's University and employees from the Loyalist Township. A backhoe was supplied by Loyalist Township to remove the adult *T. Latifolia* from the Bayview Bog site. Next, the *T. Latifolia* was transferred to a pickup truck and delivered to the Amherstview WPCP by Loyalist Township. The *T. Latifolia* were stored on the south side of the CW, and waterproof polyethylene tarps were used to cover the *T. Latifolia* to maintain the moisture and protect the plants prior to planting. The healthy and viable shoots of *T. Latifolia* were identified and selected on each day of planting. These selected plants were transported to individual treatment cells by a wheel barrel and planted. A 1 m distance between the edge of the substrates and the first row of plants was maintained along each side of the cell to prevent vegetation encroachment. The density of the plants was set to 4 shoot per square meter.

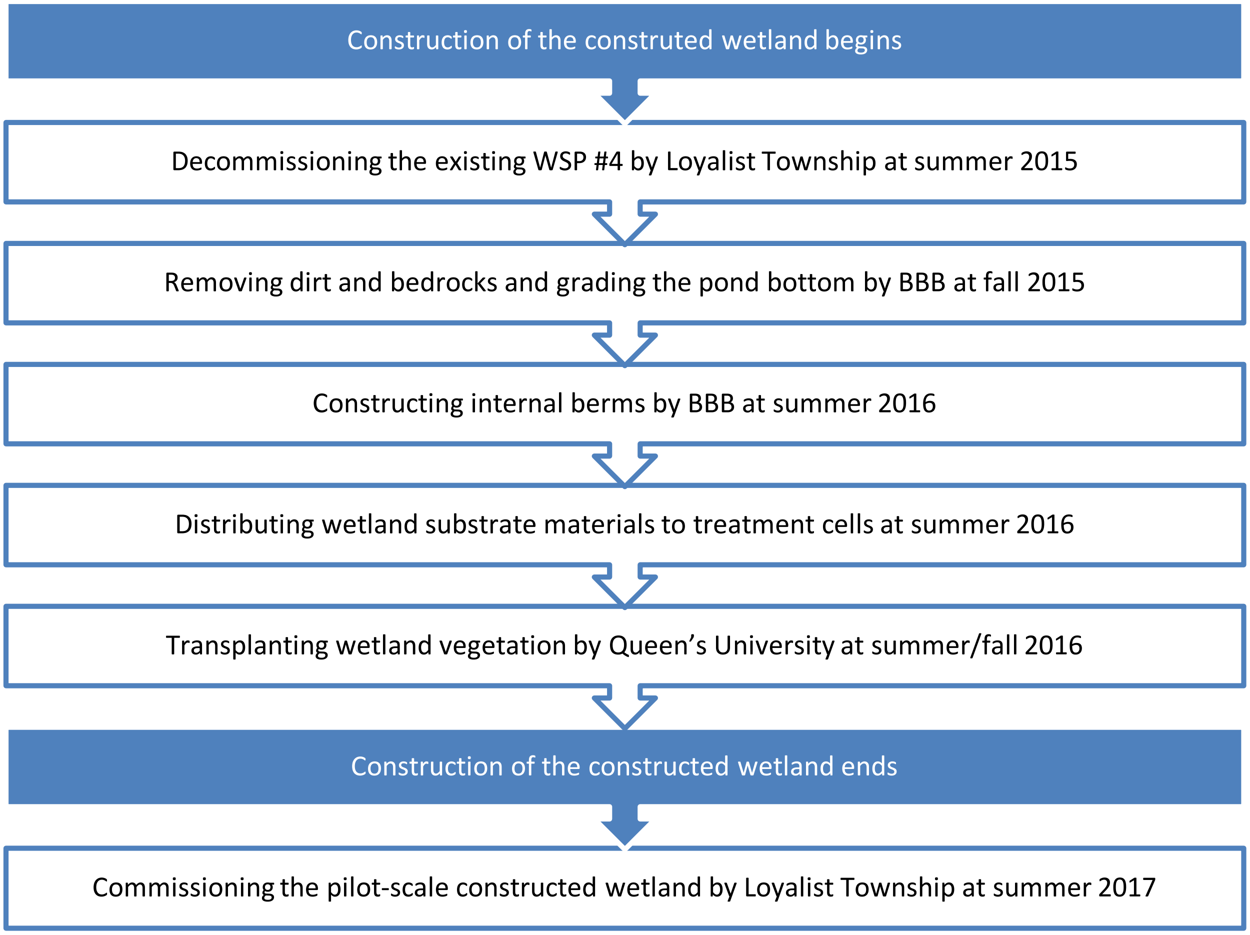
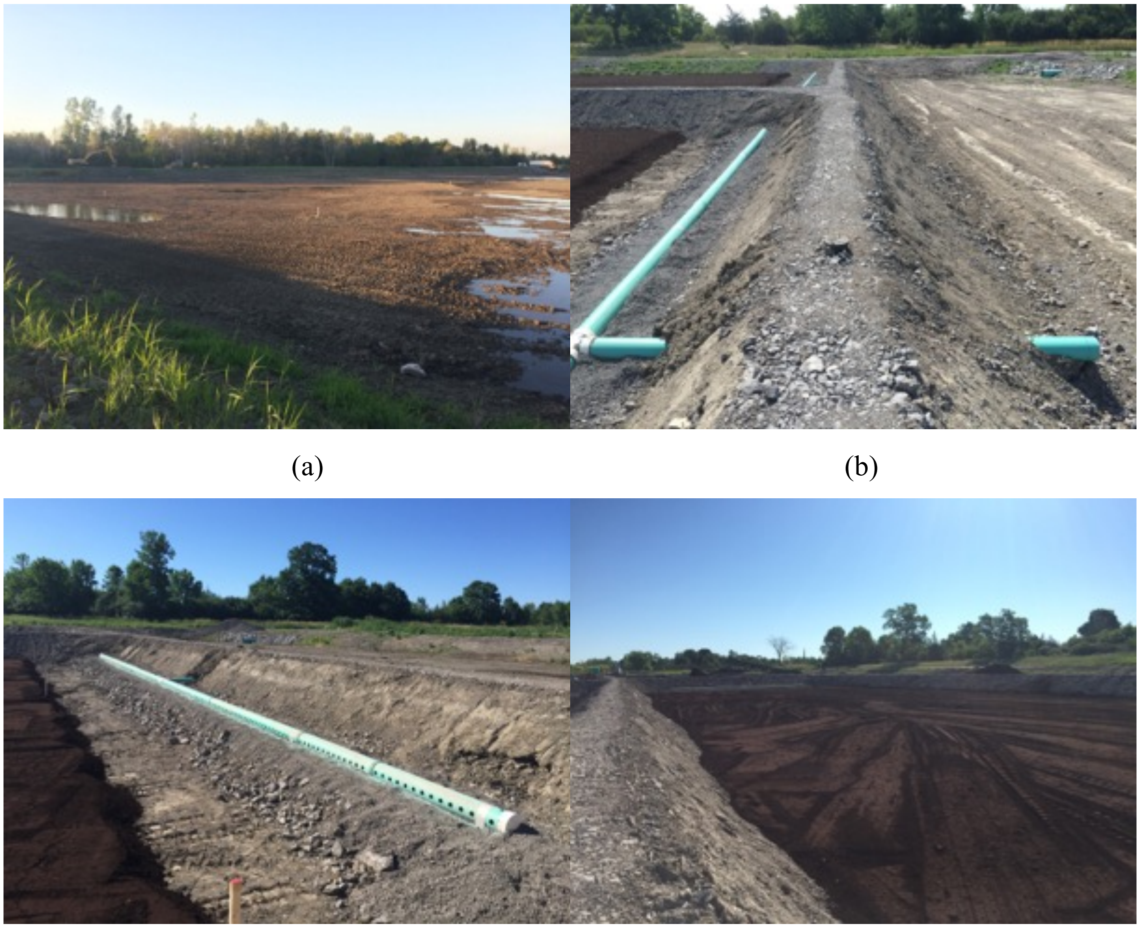


Figure 6.8 The process of the construction of the pilot-scale constructed wetland at the Amherstview WPCP



(a) (b)

(c) (d)

Figure 6.9 (a) The Decommissioned the existing WSP #4; (b) Collection ditch and treatment cell connected by internal berm; (c) Installed perforated pipe to distribute the wastewater to the treatment cell; (d) The open water connection treatment train with substrate peat.

However, transplanting adult *T. Latifolia* on topsoil and sludge was difficult due to the properties of these two substrate materials. The compacted topsoil surface was too difficult to shovel, and the sludge surface is too sticky for people to access on foot. Hence, seeding the *T. Latifolia* instead of transplanting of adult shoot was used as an alternative method to allow the vegetation to grow in the inner parts of those treatment cells. A transplanting map is shown in Figure 6.11. The seeds were collected from the same site as where the adult *T. Latifolia* were collected. Those seeds were placed in a leaf blower to spread the seeds across those treatment cells. The seeds were spread from both sides and ends of the treatment cell to maximize coverage.

(a) (b)

Figure 6.10 (a) Bayview bog natural wetland site near the Amherstview WPCP with *T. Latifolia*; (b) Professors from Queen's University and project coordinator from Loyalist Township meeting with CRCA staff to discuss the transplanting permit.

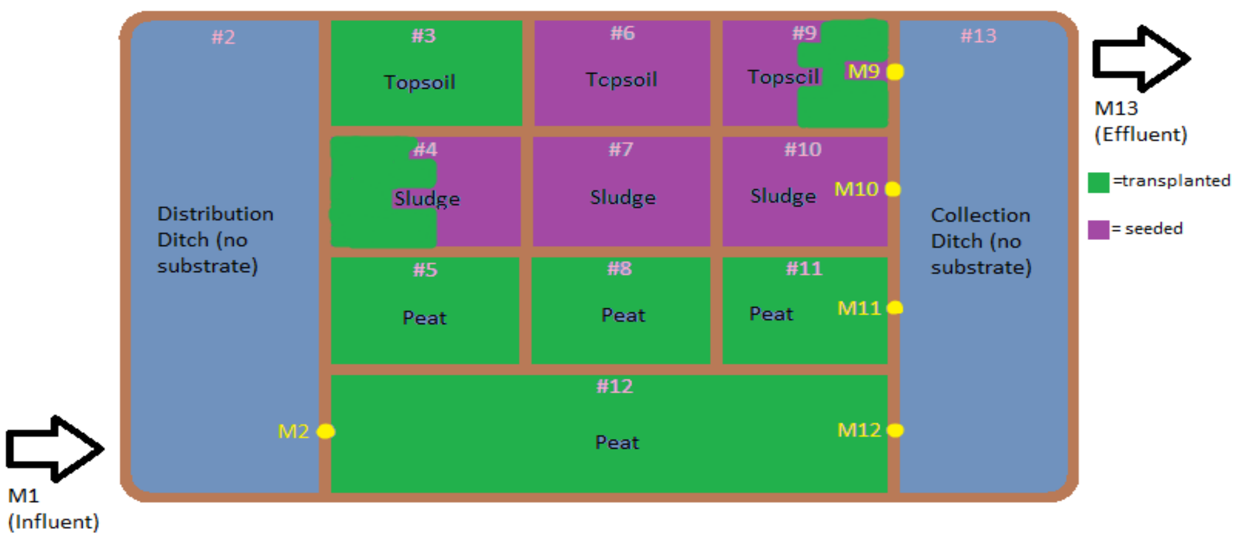


Figure 6.11 Map of transplanting and seeding of *T. Latifolia* in pilot-scale constructed wetland

6.4 Materials and methods

6.4.1 Monitoring program

A preliminary monitoring program was established after the initial operation of the CW. Samples were collected on a weekly basis (May 3rd and June 14th, 2017) from the wetland influent, effluent of the distribution ditch, effluent from each treatment train, and the final effluent as illustrated in Figure 6.12. Due to the unusual rainfall events and operational issues occurred during the initial stage of operation, only two months data was collected and analyzed. A retractable pole with a pitcher attached to the end was used to collect water sample from each sampling point. At each sampling point, approximately 3.5 L was collected by the retractable pole and transferred into a utility bucket. Then, a HydroLab DS5 probe was used to measure water temperature, pH, ORP, Salinity, total dissolved solids, DO, and Chlorophyll-a (Chl-a) on-site in the bucket. Next, a small portion of the sample (approximately 250 ml) was transferred to a labeled 300 ml sampling bottle for storage, and transported to the laboratory at Queen's for further analyses. All samples were stored in a cooler at 4° C prior to laboratory testing.

Samples were analyzed for pH, nitrate nitrogen (NO_3-N), ammonium nitrogen (NH_4-N), total nitrogen (TN), phosphate (PO_4-P), total phosphorous (TP), alkalinity, chemical oxygen demand (COD), and TSS. NO_3-N and alkalinity tests were done using the low range TNTplus vial test (0.2-13.5mg/L NO_3-N) and TNTplus vial test (25 - 400mg/L $CaCO_3$), respectively. TN, TP, and COD were all measured using Hach test kits, and TSS were measured using the standard method (APHA, 2012). PO_4-P and NH_4-N tests were done using the stannous chloride and Nessler's reagent Standard Methods, respectively.

All nutrient testing was conducted in duplicate to ensure accuracy, and error bars representing standard deviation are displayed on each graph to depict the level of accuracy. Parameters of interest and detailed analytical methods are listed in Table 6.1.

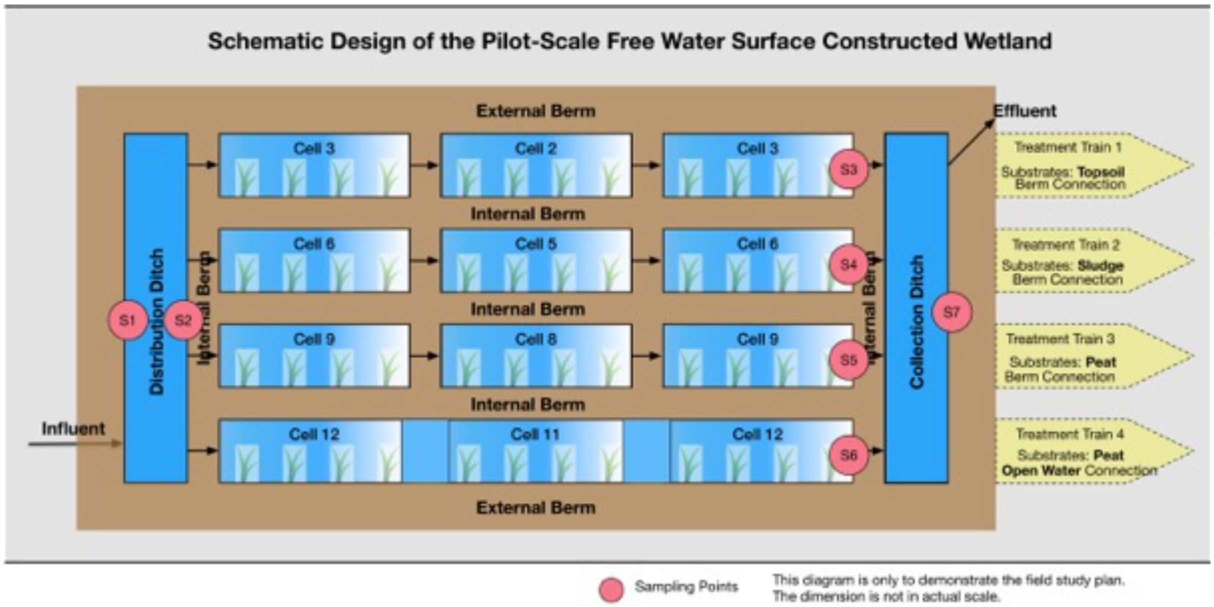


Figure 6.12. Constructed wetland configuration. Please note that the pink circles indicate the sampling points.

Table 6.1 Parameters of interest for summer 2017 free water surface flow constructed wetland effluent monitoring at the Amherstview WPCP

Parameter	Frequency	Location	Method
pH	Weekly	On-site	Hydrolab® DS5 Probe
Temperature	Weekly	On-site	Hydrolab® DS5 Probe
ORP	Weekly	On-site	Hydrolab® DS5 Probe
DO	Weekly	On-site	Hydrolab® DS5 Probe
Salinity	Weekly	On-site	Hydrolab® DS5 Probe
Total Dissolved Solids	Weekly	On-site	Hydrolab® DS5 Probe
Total Suspended Solids	Weekly	Laboratory	APHA Standard Method 2540D
Ammonium (as N)	Weekly	Laboratory	Nessler's reagent Standard Methods
Nitrate (as N)	Weekly	Laboratory	Dimethylphenol Method Hach Method 10206
Total Nitrogen	Weekly	Laboratory	Persulfate Digestion Method Hach Method 10071
Orthophosphate	Weekly	Laboratory	Stannous chloride method
Total Phosphorous	Weekly	Laboratory	USEPA PhosVer®3 with Acid Persulfate Digestion Method Hach Method 8190
COD	Weekly	Laboratory	APHA Standard Method 5220D and U.S. EPA Reactor Digestion Method, Hach Method 8000

6.4.2 Statistical analysis

In order to compare the treatment performance of the different treatment trains in the CW, parametric and non-parametric statistical analyses were performed using Microsoft EXCEL. The following indicators were used to evaluate wastewater treatment performance, including removal efficiency (R, %), and removal rates (RR, g/m^2d) as defined by Equation 6.1 and Equation 6.2, respectively.

Equation 6.1

$$RE\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

Equation 6.2

$$RR\ (g/\ m^2 d) = \frac{(C_0 - C_t) \times Q}{A}$$

Where, RE was the removal efficiency (%), RR was the removal rates (g/m^2d), C_0 was the influent concentration (mg/L), C_t was the effluent concentration (mg/L), Q was the flow rate (m^3/d) and, A was the area of reactors (m^2)

Prior to statistical analysis, the data was tested for normality using probability plots. Any probability plots that showed signs of abnormality were analyzed for skewness and kurtosis by using the skewness and kurtosis coefficients, where any data with skewness or kurtosis coefficients greater than 2 or less than -2 were deemed not to show normality. To determine whether there were statistically significant differences between samples, a single factor analysis of variance (ANOVA) test was used. When the ANOVA test indicated statistical significance ($p < 0.05$), a post-hoc test was then used to determine which samples had statistically significant differences. The post-hoc test involved running a two sample *t*-test assuming equal variances for each set of samples and comparing the *p* value obtained to the Bonferroni corrected *p* value of 0.0083. If the p value obtained was lower than the Bonferroni corrected *p* value, the difference between the samples was considered to be statistically significant. Pearson correlation coefficients were calculated for each treatment train.

6.5 Results and discussions

6.5.1 Overall performance

The mean concentrations of constituents of interest for each sampling point in the CW are shown in Table 6.2 (standard deviations are shown in parentheses), and the removal efficiencies of select parameters are shown in Table 6.3. Overall, the results showed that the wetland was highly effective at retaining PO_4-P and TP and moderately effective at removing NO_3-N and TN. Three of four treatment trains could attenuate the pH, and alkalinity levels were noticeably decreased as well. COD, NH_4-N and TSS concentrations were found to increase throughout the system, which was attributed to the generally low influent constituent concentrations and the fact that the substrates used were organic in nature and would be expected to leach some constituents.

Table 6.2 Mean (St. dev.) concentrations of constituents of interest in the CW

Parameters	Unit	Influent	Distribution Ditch	Train 1 Effluent Topsoil, B	Train 2 Effluent Sludge, B	Train 3 Effluent Peat, B	Train 4 Effluent Peat, O
pH	-	9.45 (0.50)	9.55 (0.73)	9.73 (0.73)	9.33 (0.41)	9.40 (0.53)	9.16 (0.47)
DO	mg/L	17.82 (2.19)	21.79 (7.39)	17.42 (6.08)	16.65 (2.82)	15.11 (4.41)	12.65 (6.01)
ORP	mg/L	138.88 (45.85)	103.04 (42.72)	132.56 (26.32)	148.33 (14.82)	140.10 (29.63)	146.15 (18.85)
Salinity	mg/L	0.32 (0.02)	0.32 (0.02)	0.24 (0.12)	0.24 (0.11)	0.17 (0.12)	0.23 (0.08)
Alkalinity	mg/L	102.96 (11.91)	105.21 (12.93)	48.18 (38.27)	79.50 (14.29)	84.04 (12.08)	71.07 (18.13)
TDS	mg/L	0.40 (0.00)	0.40 (0.01)	0.30 (0.15)	0.31 (0.13)	0.24 (0.15)	0.28 (0.08)
TSS	mg/L	4.33 (1.70)	3.00 (4.00)	11.00 (7.65)	76.80 (127.06)	3.00 (4.12)	12.50 (12.84)
COD	mg/L	16.50 (5.68)	16.58 (9.62)	30.83 (8.80)	22.00 (5.60)	27.00 (16.21)	31.92 (17.33)
NH_4-N	mg/L	0.37 (0.17)	0.59 (0.50)	0.73 (0.70)	0.74 (0.41)	0.92 (0.82)	0.83 (0.77)
NO_3-N	mg/L	4.64 (1.34)	3.75 (1.67)	2.93 (1.54)	3.14 (1.68)	2.27 (1.21)	2.86 (2.01)
TN	mg/L	6.23 (1.68)	4.95 (0.84)	4.75 (1.10)	4.69 (1.08)	3.35 (1.19)	4.21 (1.73)
PO_4-P	mg/L	0.58 (0.27)	0.61 (0.47)	0.12 (0.16)	0.38 (0.34)	0.13 (0.14)	0.17 (0.15)
TP	mg/L	0.92 (0.31)	1.01 (0.67)	0.39 (0.22)	0.60 (0.34)	0.46 (0.17)	0.45 (0.15)
Chl-a	mg/L	0.58 (0.18)	0.57 (0.41)	1.97 (1.25)	1.65 (0.95)	1.70 (1.44)	6.74 (6.30)

B – Berm connection, O- Open water connection

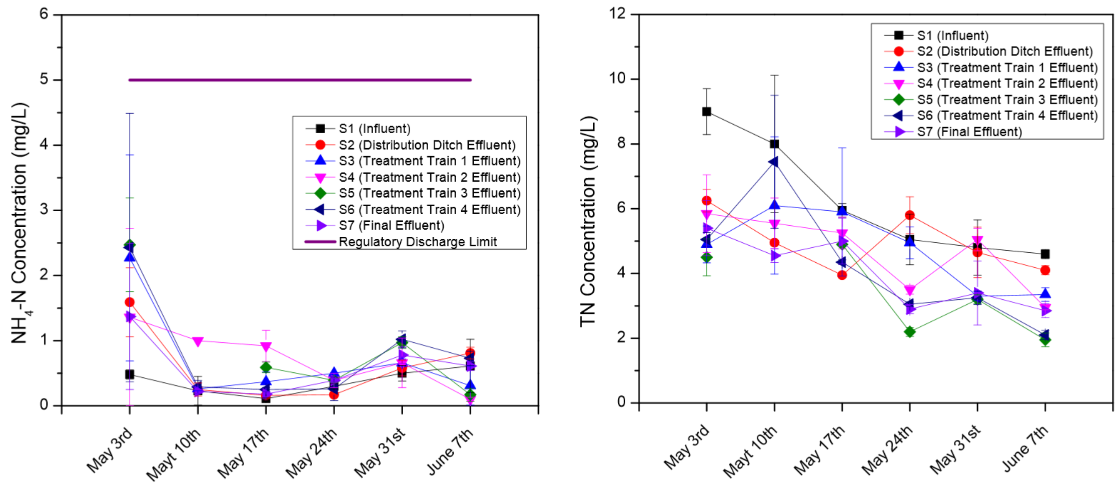
Table 6.3 Removal efficiencies (RE) across the wetland for select parameters (%)

Parameter	Train 1 Effluent Topsoil, B	Train 2 Effluent Sludge, B	Train 3 Effluent Peat, B	Train 4 Effluent Peat, O
Alkalinity	53.21	22.78	18.37	30.97
NO_3-N	36.81	32.33	51.00	38.35
TN	23.80	24.73	46.26	32.49
PO_4-P	79.94	34.48	76.92	70.66
TP	58.19	34.84	50.26	51.49

B – Berm connection, O- Open water connection

6.5.2 Effluent concentrations

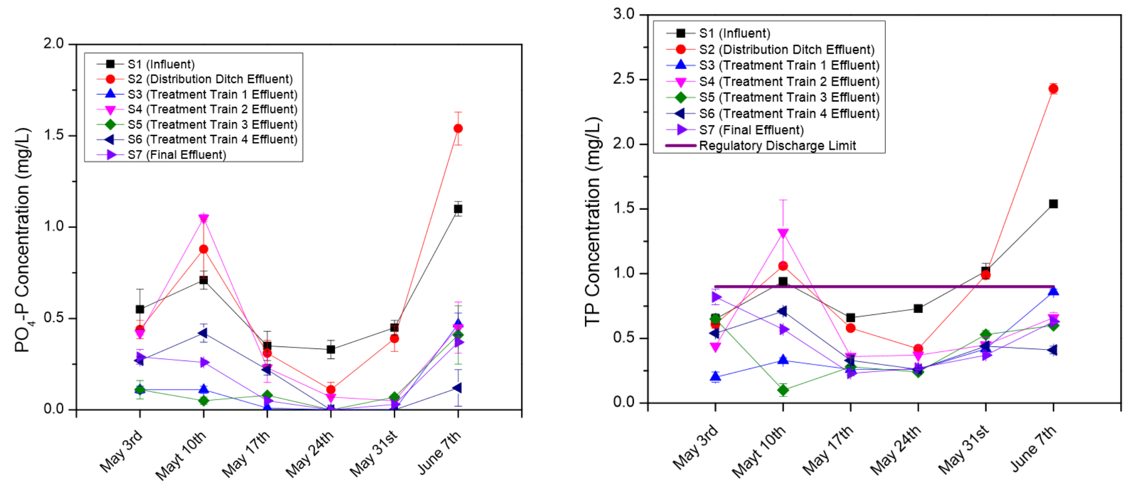
As can be seen from Figure 6.13, NH_4-N levels were always well below the regulatory discharge limit despite the fact that the effluent concentrations increased throughout the wetland. Some of the fluctuations observed were attributed to the presence of algae and other macrophytes, which use NH_4-N as their preferred nitrogen source. These would not have been as well established in early May as in subsequent months. The NH_4-N decrease observed later in the season could also be partially associated with higher temperatures, which would enhance biological uptake that would have been observed later in the season. NO_3-N levels were found to decrease steadily from May to June, likely due to the increase in algal biomass and the growth of *T. Latifolia* throughout the system during this period. TN concentrations decreased from May to June as well, which was attributed to the decrease in NO_3-N levels as well as the effect of algae and plant growth on other nitrogenous compounds.



(a) (b)

Figure 6.13 (a) Effluent NH_4-N concentration at each sampling point during the entire experimental period and the regulatory discharge limit of NH_4-N at the Amherstview WPCP; (b) Effluent NO_3-N concentration at each sampling point during the entire experimental period and the regulatory discharge limit of NH_4-N at the Amherstview WPCP

PO_4-P levels remained fairly constant throughout the operational period. Levels spiked on May 10th and June 7th, (Figure 6.14), which was associated with high wind and rainfall events that resulted in high sediment levels during those weeks. PO_4-P was found to decrease appreciatively from the influent to the effluent, as well as across treatment trains. Treatment Train 1 was found to be the most effective at removing PO_4-P, showing a statistically significant difference with the influent (α = 0.05). Similar to PO_4-P, TP concentrations were relatively constant aside from the increases noted on May 10th and June 7th (Figure 6.14). As noted for PO_4-P concentrations, these spikes could likely be attributed to high sediment levels during those weeks. TP concentrations were consistently below the regulatory discharge limit, and the only treatment train effluent to exceed the regulatory discharge limit was Treatment Train 2.



(a) (b)

Figure 6.14 (a) Effluent PO_4-P concentrations at each sampling point during the entire experimental period; (b) Effluent TP concentrations at each sampling point during the experimental period and the regulatory discharge limit of TP at the Amherstview WPCP

As can be seen in Figure 6.15, all TSS final effluent concentrations were below the regulatory discharge limit of 25 mg/L for the duration of the operational period with the exception of Treatment Trains 2 and 4 that produced effluents above the limit on May 10^{th}. The spike in TSS levels during the week of May 10^{th} could likely be attributed to the presence of algae and plant matter. In general, TSS levels increased from influent to effluent, which was likely due to a combination of unconsolidated organic substrates and algal or plant matter entering the water column. It should be noted that TSS levels were found to decrease throughout the study period, which could be attributed to the settling of solids resulting from the extended HRT.

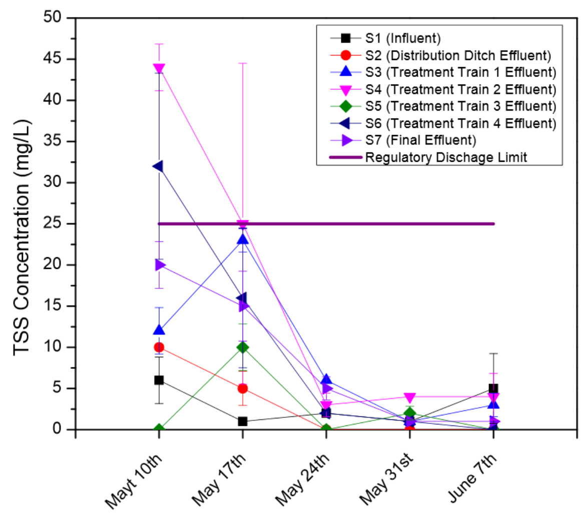


Figure 6.15 Effluent TSS concentrations at each sampling point during the experimental period and the regulatory discharge limit of TP at the Amherstview WPCP

6.5.3 Effects of substrate

The result from treatment train 1 (topsoil), 2 (sludge), and 3 (peat) were used to compare the treatment performance of different substrates below.

6.5.3.1 Topsoil

Topsoil is a conventional substrate material for FWS CW (Maine et al., 2017; Wu et al., 2017). The benefits of using topsoil are that it is relatively inexpensive and versatile, and can support the growth of most vegetation. However, as most types of soils are not well adapted to the wastewater constituents, the treatment provided by soil is typically limited. In this study, the Treatment Train 1 (topsoil) was the only treatment train that could not attenuate the pH to below the regulatory discharge limit (Table 6.4). Topsoil also had the highest Chl-a concentrations throughout the monitoring period. Unlike sludge and peat, where organic and inorganic acids could be liberated from the substrate to mitigate the pH, it was expected that the pH attenuation capacity from topsoil would be limited.

However, topsoil was surprisingly good at removing phosphorous constituents compared to the other substrates, with removal efficiencies of PO_4-P and TP of 79.94% and 58.19%, respectively. A similar TP removal efficiency of 52.8% with an influent concentration of 0.889 mg/L was also reported by Maine et al. (2017), where a 1.5 m layer of topsoil was used as a substrate in their FWS CW. Wu et al. (2017) discovered that phosphorous was mainly retained in the roots and above-ground part of emergent plants. This could be demonstrated by the large number of *T. Latifolia* in the treatment cells. Phosphorous consumption by algae is another pathway to retain PO_4-P and TP concentrations. The highest Chl-a concentrations were recorded in topsoil Treatment Train 1.

Table 6.4 Treatment objective and regulatory discharge limit at the Amherstview WPCP

Regulatory discharge limit at the Amherstview WPCP		
Parameters	Objective	Discharge limit
pH	N/A	6.0 - 9.5
cBOD5	10 mg/L	15 mg/L
TSS	15 mg/L	25 mg/L
NH_4-N	2.0 mg/L	3.0 mg/L
TP	0.7 mg/L	0.9 mg/L
E. coli	N/A	100 cfu/100ml

6.5.3.2 Sludge

Sludge is not a conventional substrate material for FWS CW, but researchers have begun to investigate its potential use (Korboulewsky et al., 2012; Xiaohong et al., 2015; Zhao et al., 2011). Most wastewater treatment plants in North America produce sludge, and most of the sludge is sent to the local farms as a free or inexpensive fertilizer. Reusing the sludge can not only reduce the logistical cost of delivering the sludge, but also reduce the cost of establishing a CW. As can be seen from Table 6.2, the Treatment Train 2 (sludge) showed the best performance best in terms of pH attenuation, and COD and Chl-a removal. The pH level was attenuated from 9.55 to 9.33. Increased organic concentration is always an issue when employing organic substrates in CW. However, the sludge maintained the effluent COD concentration below 25 mg/L. Most of other studies, which employed organic substrates, will not meet the regulatory discharge limit (Gunes, 2007; Herrera-Melián et al., 2014). The sludge used in this study was from the bottom of the pre-existing WSP #4, and the effluent organic concentration of WSP #4 was <25 mg/L. Hence, it was expected that the sludge would not contribute to effluent COD concentrations. (Korboulewsky et al., 2012)

6.5.3.3 Peat

In previous studies, peat was shown to exhibit an excellent pH attenuation capacity in both bench-scale and small-scale on-site experiments (Jin et al., 2017a; Jin et al., 2017b). However, the high pH attenuation capacity was not observed in the pilot-scale study, as the pH level was only reduced from 9.55 to 9.40. This might have been due to the poor hydraulic performance of the treatment cells, as wastewater was retained at the final treatment cell in the treatment train due to the steep designed slope. Hence, there was less contact time between wastewater and peat in the first two treatment cells, which essentially limited the pH attenuation capacity provided by peat. In addition, less contact time between substrate peat and wastewater also resulted in a relatively low effluent COD concentration compared to the bench-scale and small-scale experiments. Typically, peat as a substrate, would be expected to potentially release organics and nutrients back to the wastewaters during the start-up stage of operation, due to its high organic and nutrient concentrations (Gunes, 2007). Leaching organics and nutrients were observed both in the previous bench-scale and small-scale studies (Jin et al., 2017a; Jin et al., 2017b). However, in this study, there was no sign of leaching of either nitrogenous or phosphorous compounds, as peat could further reduce those compounds. Increased effluent COD concentrations were still observed, but this did not necessarily imply that BOD, which is regulated by the MOECC, would exceed the regulatory discharge limit as well. In fact, BOD was regularly monitored by the operator of the Amherstview WPCP, with the effluent values consistently below 5 mg/L.

ANOVA tests were carried out to compare the treatment performance of the different substrates Table 6.5. The ANOVA results showed that there was no statistically significant difference between those treatment trains in terms of treatment performance for pH, organics, nutrients, and Chl-a. This could be due to the fact that the FWS CW was not fully mature and also be due to the extreme weather conditions (e.g. stormwater event) that were experienced during the treatment season and could have easily affected the treatment performance of the immature. Although, large amounts of new *T. Latifolia* were established in the treatment cells, the average height of these *T. Latifolia* was only 30 cm and the treatment provided by these *T. Latifolia* was considered to be limited.

Table 6.5 ANOVA test result among treatment train 1, 2, and 3

Parameter	**pH**	**Alkalinity**	**COD**	**NH_4-N**	**NO_3-N**	**PO_4-P**	**TP**	**Chl-a**
p value	0.466	0.105	0.435	0.926	0.756	0.148	0.380	0.730

6.5.4 Effects of treatment cell connection

Different treatment cell connections were used to assess their effect on treatment performance. Berm connections were applied in Treatment Train 3, while deep open water zones were used in Treatment Train 4. Despite having the same substrate, the pH attenuation capacity was quite different. Treatment Train 4 could attenuate the pH level from 9.55 down to 9.16. Chl-a effluent concentrations in Treatment Train 4 were statistically significantly different than in Treatment Train 3, along with slight increases in TSS and COD. The difference in treatment performance could be attributed to the hydraulic performance of different connections, as the contact time and area between the substrate and wastewater could be different. As noted earlier, the slope of the bottom of the treatment cells were relatively steep. Hence, most of the wastewater in the treatment trains was retained in the final treatment cell. However, since there was no physical barrier in the deep open water zone connection, more substrate materials could have come in contact with the wastewater, thereby facilitating further treatment. In addition, perforated pipe clogging due to the algal biomass, was observed in other treatment trains. The wastewater distribution and mixing in Treatment Train 4 was considerably better compared to the other berm-connected treatment trains and this could have resulted in a better overall performance.

6.6 Challenges and lesson learned

6.6.1 Berm fails

Berms, especially internal berms, are an important part of the wetland system, and both the design and construction must be performed correctly to prevent the failure of the system. Damaged berms could be dangerous. USEPA recommendation for the slope of the internal berms was to provide a ratio of at least 3:1. However, the slope of the internal berms at the Amherstview WPCP were at a ratio of 2:1. Steep berms can cause problems when trying to maintain the treatment cells due to the difficulty of access. In addition, the relatively high free board created by the steep berms could pose potential safety hazards to people walking on the berms. Most importantly, steep berms contributed to the berm erosion. Although, the wastewater is mainly driven by wind and the flowrate is relatively low, it can still cause severe erosion during the storm water events (Figure 6.16), when the increased wastewater level combined with strong winds severely damaged the berms. Hence, hydroseeding or similar procedures would be encouraged to apply to mitigate this issue.

Figure 6.16 Internal berms show the sign of erosion after a stormwater event

6.6.2 Vegetation transplantation

As vegetation plays an important role in a CW, vegetation transplantation is a vital process to ensure the expected treatment performance. Previous literatures suggested that manually transplanting adult shoot was the most practical approach to ensure good treatment performance in the first few treatment seasons (Brown & Bedford, 1997). However, transplanting adult plant shoots is time consuming and labor intensive. Surprisingly, spreading *T. Latifolia* seeds using a leaf blower in the early spring, seemed to be a more effective and promising approach in this project. In the spring 2017, *T. Latifolia* seeds were spread to the treatment cells, which was substantially easier than transplanting adult plant shoots. Two months later, there were quite a few new sprouts shooting out from the substrate layers. Those sprouts grew rapidly into new shoots to a height of approximately 50 cm in spring and summer 2017. Nearly 100% coverage of *T. Latifolia* was observed in the vegetated treatment cells (Figure 6.17). One thing that was observed was that controlling water level played a vital role in terms of *T. Latifolia* growth performance. The water level should always below the top of *T. Latifolia* to promote the continuous growth, and submerging *T. Latifolia* below the water level could actually hinder the maturation process.

Figure 6.17 The growth of *T. Latifolia* in the treatment cells of the constructed wetland after seeding in spring 2017.

6.6.3 Flow control structure

The perforated pipes employed in the CW were designed to evenly distribute the wastewater and to facilitate flow mixing. It also allowed more oxygen to enter the CW promoting aerobic biological processes. However, due to the significantly amount of filamentous algae in the WSPs prior to the CW during the summer months, these were transported over to the CW, clogging the perforated pipes Figure 6.18. In the future, a protective mesh or other protective method should be implemented to prevent this clogging.

Figure 6.18 Clogging issue by algae biomass of using perforated pipe

6.7 Conclusion

A pilot-scale FWS CW was designed and implemented to mitigate the elevated pH of the secondary effluents at the Amherstview WPCP. The FWS CW was designed based on the previous bench-scale and small-scale studies as well as the USEPA design manual. Four unique treatment train designs were implemented to compare the treatment performance of different substrates, with the intention of transforming the best design to the remaining treatment trains when implementing the full-scale CW.

Overall, this newly designed FWS CW performed well during its first treatment season and three out of four treatment train designs could attenuate the pH. The results showed that the CW was highly effective at retaining PO_4-P and TP, and fairly effective at removing NO_3-N and TN. Slight increases of COD, NH_4-N and TSS were occasionally observed, but the effluent concentrations were able to meet the regulatory discharge limits set by the MOECC. When comparing the treatment performance of substrates, peat showed the best overall performance. There was no sign of nutrient leaching in this pilot-scale study. The open water connection performed better than the berm connection treatment train when the same peat substrate was employed. Despite of exhibiting effective removing efficiencies for nitrogenous and phosphorous compounds, the pH attenuation capacity was not as high as anticipated in the berm connection treatment train.

A few issues arose during the start-up of this newly implemented CW, including the failure of a few internal berms and clogging of perforated pipes. Actions have already been taken to rectify these issues. The treatment from the vegetation was limited at this early stage of the operation. It is anticipated that the treatment performance will further improve as the constructed wetland matures and more vegetation is established in the treatment cells.

6.8 References

Abe, K., Komada, M., Ookuma, A., Itahashi, S., and Banzai, K. (2014). Purification performance of a shallow free-water-surface constructed wetland receiving secondary effluent for about 5 years. *Ecological Engineering, 69*(0), 126-133.

Abou-Elela, S. I., Golinielli, G., Abou-Taleb, E. M., and Hellal, M. S. (2013). Municipal wastewater treatment in horizontal and vertical flows constructed wetlands. *Ecological Engineering, 61*, 460-468.

Abou-Elela, S. I., and Hellal, M. S. (2012). Municipal wastewater treatment using vertical flow constructed wetlands planted with canna, phragmites and cyprus. *Ecological Engineering, 47*, 209-213.

Aguirre, P., Ojeda, E., GarcÍa, J., BarragÁn, J., and Mujeriego, R. (2005). Effect of water depth on the removal of organic matter in horizontal subsurface flow constructed wetlands. *Journal of Environmental Science and Health, Part A, 40*(6-7), 1457-1466.

Akratos, C. S., and Tsihrintzis, V. A. (2007). Effect of temperature, hrt, vegetation and porous media on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands. *Ecological Engineering, 29*(2), 173-191.

Al-Layla, M. A., and Middlebrooks, E. J. (1975). Effect of temperature on algal removal from wastewater stabilization ponds by alum coagulation. *Water Research, 9*(10), 873-879.

Al-Qasmi, M., Raut, N., Talebi, S., Al-Rajhi, S., and Al-Barwani, T. (2012). *A review of effect of light on microalgae growth.* Paper Proceedings from the Proceedings of the world congress on engineering.

Amini Khoeyi, Z., Seyfabadi, J., and Ramezanpour, Z. (2012). Effect of light intensity and photoperiod on biomass and fatty acid composition of the microalgae, chlorella vulgaris. *Aquaculture International, 20*(1), 41-49.

APHA. (2012). Standard methods for the examination of water and wastewater.

Arroyo, P., Ansola, G., and Miera, L. E. S. d. (2013). Effects of substrate, vegetation and flow on arsenic and zinc removal efficiency and microbial diversity in constructed wetlands. *Ecological Engineering, 51*, 95-103.

Aslam, M. M., Malik, M., Baig, M. A., Qazi, I. A., and Iqbal, J. (2007). Treatment performances of compost-based and gravel-based vertical flow wetlands operated identically for refinery wastewater treatment in pakistan. *Ecological Engineering, 30*(1), 34-42.

Avila, C., Matamoros, V., Reyes-Contreras, C., Pina, B., Casado, M., Mita, L., Rivetti, C., Barata, C., Garcia, J., and Bayona, J. M. (2013). Attenuation of emerging organic contaminants in a hybrid constructed wetland system under different hydraulic loading rates and their associated toxicological effects in wastewater. *Sci Total Environ, 470-471C*, 1272-1280.

Babatunde, A. O., Zhao, Y. Q., Burke, A. M., Morris, M. A., and Hanrahan, J. P. (2009). Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. *Environmental Pollution, 157*(10), 2830-2836.

Babatunde, A. O., Zhao, Y. Q., Doyle, R. J., Rackard, S. M., Kumar, J. L. G., and Hu, Y. S. (2011). Performance evaluation and prediction for a pilot two-stage on-site constructed wetland system employing dewatered alum sludge as main substrate. *Bioresource Technology, 102*(10), 5645-5652.

Bai, L., Wang, C., Huang, C., He, L., and Pei, Y. (2014). Reuse of drinking water treatment residuals as a substrate in constructed wetlands for sewage tertiary treatment. *Ecological Engineering, 70*(0), 295-303.

Barca, C., Gérente, C., Meyer, D., Chazarenc, F., and Andrès, Y. (2012). Phosphate removal from synthetic and real wastewater using steel slags produced in europe. *Water Research, 46*(7), 2376-2384.

Bare, W. F. R., Jones, N. B., and Middlebrooks, E. J. (1975). Algae removal using dissolved air flotation. *Journal (Water Pollution Control Federation), 47*(1), 153-169.

Barsanti, L., and Gualtieri, P. (2014). *Algae: Anatomy, biochemistry, and biotechnology*. CRC press.

Behrendt, A., Tarre, S., Beliavski, M., Green, M., Klatt, J., de Beer, D., and Stief, P. (2014). Effect of high electron donor supply on dissimilatory nitrate reduction pathways in a bioreactor for nitrate removal. *Bioresource Technology, 171*, 291-297.

Beutel, M. W., Whritenour, V., and Brouillard, E. (2013). Fecal coliform removal in a lightly loaded surface-flow constructed treatment wetland polishing agricultural runoff. *Water Sci Technol, 68*(4), 909-915.

Białowiec, A., Janczukowicz, W., and Randerson, P. F. (2011). Nitrogen removal from wastewater in vertical flow constructed wetlands containing lwa/gravel layers and reed vegetation. *Ecological Engineering, 37*(6), 897-902.

Blanco, I., Molle, P., Sáenz de Miera, L. E., and Ansola, G. (2016). Basic oxygen furnace steel slag aggregates for phosphorus treatment. Evaluation of its potential use as a substrate in constructed wetlands. *Water Research, 89*, 355-365.

Blomqvist, P., Jansson, M., Drakare, S., Bergström, A. K., and Brydsten, L. (2001). Effects of additions of doc on pelagic biota in a clearwater system: Results from a whole lake experiment in northern sweden. *Microbial Ecology, 42*(3), 383-394.

Borde, X., Guieysse, B. t., Delgado, O., Muñoz, R., Hatti-Kaul, R., Nugier-Chauvin, C., Patin, H., and Mattiasson, B. (2003). Synergistic relationships in algal–bacterial microcosms for the treatment of aromatic pollutants. *Bioresource Technology, 86*(3), 293-300.

Brown, S. C., and Bedford, B. L. (1997). Restoration of wetland vegetation with transplanted wetland soil: An experimental study. *Wetlands, 17*(3), 424-437.

Browne, W., and Jenssen, P. D. (2005). Exceeding tertiary standards with a pond/reed bed system in norway. *Water Science and Technology, 51*(9), 299.

Bruch, I., Fritsche, J., Bänninger, D., Alewell, U., Sendelov, M., Hürlimann, H., Hasselbach, R., and Alewell, C. (2011). Improving the treatment efficiency of constructed wetlands with zeolite-containing filter sands. *Bioresource Technology, 102*(2), 937-941.

Calheiros, C. S. C., Rangel, A. O. S. S., and Castro, P. M. L. (2009). Treatment of industrial wastewater with two-stage constructed wetlands planted with typha latifolia and phragmites australis. *Bioresource Technology, 100*(13), 3205-3213.

Wastewater systems effluent regulations (2012). (SOR/2012-139). edn, Environmental Canada.

Cao, W., Wang, Y., Sun, L., Jiang, J., and Zhang, Y. (2016). Removal of nitrogenous compounds from polluted river water by floating constructed wetlands using rice straw and ceramsite as substrates under low temperature conditions. *Ecological Engineering, 88*, 77-81.

Champagne, P., Liu, L., and Howell, M. (2017). 7 - aerobic treatment in cold-climate countries a2 - lee, duu-jong *Current developments in biotechnology and bioengineering* (pp. 161-201): Elsevier.

Chen, T. Y., Kao, C. M., Yeh, T. Y., Chien, H. Y., and Chao, A. C. (2006). Application of a constructed wetland for industrial wastewater treatment: A pilot-scale study. *Chemosphere, 64*(3), 497-502.

Chen, X., Kong, H., Wu, D., Wang, X., and Lin, Y. (2009). Phosphate removal and recovery through crystallization of hydroxyapatite using xonotlite as seed crystal. *Journal of Environmental Sciences, 21*(5), 575-580.

Chyan, J.-M., Senoro, D.-B., Lin, C.-J., Chen, P.-J., and Chen, I. M. (2013). A novel biofilm carrier for pollutant removal in a constructed wetland based on waste rubber tire chips. *International Biodeterioration & Biodegradation, 85*, 638-645.

Ciria, M. P., Solano, M. L., and Soriano, P. (2005). Role of macrophyte typha latifolia in a constructed wetland for wastewater treatment and assessment of its potential as a biomass fuel. *Biosystems Engineering, 92*(4), 535-544.

Clyde, E. J., Champagne, P., Jamieson, H. E., Gorman, C., and Sourial, J. (2016). The use of a passive treatment system for the mitigation of acid mine drainage at the williams brothers mine (california): Pilot-scale study. *Journal of Cleaner Production, 130*(Supplement C), 116-125.

Cole, J. J., Likens, G. E., and Strayer, D. L. (1982). Photosynthetically produced dissolved organic carbon: An important carbon source for planktonic bacteria1. *Limnology and Oceanography, 27*(6), 1080-1090.

Coles, J. F., and Jones, R. C. (2000). Effect of temperature on photosynthesis-light response and growth of four phytoplankton species isolated from a tidal freshwater river. *Journal of Phycology, 36*(1), 7-16.

Collison, R. S., and Grismer, M. E. (2013). Nitrogen and cod removal from domestic and synthetic wastewater in subsurface-flow constructed wetlands. *Water Environment Research, 85*(9), 855-862.

Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., Lancelot, C., and Likens, G. E. (2009). Controlling eutrophication: Nitrogen and phosphorus. *Science, 323*(5917), 1014-1015.

Cooper, P. (1999). A review of the design and performance of vertical-flow and hybrid reed bed treatment systems. *Water Science and Technology, 40*(3), 1.

Crites, R., and Technobanoglous, G. (1998). *Small and decentralized wastewater management systems*. McGraw-Hill.

Cui, L., Ouyang, Y., Gu, W., Yang, W., and Xu, Q. (2013). Evaluation of nutrient removal efficiency and microbial enzyme activity in a baffled subsurface-flow constructed wetland system. *Bioresource Technology, 146*, 656-662.

Currie, D. J., and Kalff, J. (1984). A comparison of the abilities of freshwater algae and bacteria to acquire and retain phosphorus. *Limnology and Oceanography, 29*(2), 298-310.

Daigger, G. T., and Boltz, J. P. (2011). Trickling filter and trickling filter-suspended growth process design and operation: A state-of-the-art review. *Water Environment Research, 83*(5), 388-404.

Degerholm, J., Gundersen, K., Bergman, B., and Söderbäck, E. (2006). *Phosphorus-limited growth dynamics in two baltic sea cyanobacteria, nodularia sp. And aphanizomenon sp* (Vol. 58).

Deng, Y., Wu, M., Zhang, H., Zheng, L., Acosta, Y., and Hsu, T.-T. D. (2017). Addressing harmful algal blooms (habs) impacts with ferrate(vi): Simultaneous removal of algal cells and toxins for drinking water treatment. *Chemosphere, 186*(Supplement C), 757-761.

Despland, L. M., Clark, M. W., Vancov, T., and Aragno, M. (2014). Nutrient removal and microbial communities' development in a young unplanted constructed wetland using bauxsol™ pellets to treat wastewater. *Science of The Total Environment, 484*, 167-175.

Dorman, L., Castle, J. W., and Rodgers Jr, J. H. (2009). Performance of a pilot-scale constructed wetland system for treating simulated ash basin water. *Chemosphere, 75*(7), 939-947.

Dotro, G., Castro, S., Tujchneider, O., Piovano, N., Paris, M., Faggi, A., Palazolo, P., Larsen, D., and Fitch, M. (2012). Performance of pilot-scale constructed wetlands for secondary treatment of chromium-bearing tannery wastewaters. *J Hazard Mater, 239-240*, 142-151.

Drakare, S. (2002). Competition between picoplanktonic cyanobacteria and heterotrophic bacteria along crossed gradients of glucose and phosphate. *Microbial Ecology, 44*(4), 327-335.

Dreybrodt, W., Buhmann, D., Michaelis, J., and Usdowski, E. (1992). Geochemically controlled calcite precipitation by co2 outgassing: Field measurements of precipitation rates in comparison to theoretical predictions. *Chemical Geology, 97*(3–4), 285-294.

Drizo, A., Frost, C. A., Grace, J., and Smith, K. A. (2000). Phosphate and ammonium distribution in a pilot-scale constructed wetland with horizontal subsurface flow using shale as a substrate. *Water Research, 34*(9), 2483-2490.

Elser, J. J., and Kimmel, B. L. (1985). Nutrient availability for phytoplankton production in a multiple-impoundment series. *Canadian Journal of Fisheries and Aquatic Sciences, 42*(8), 1359-1370.

Elser, J. J., Marzolf, E. R., and Goldman, C. R. (1990). Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of north america: A review and critique of experimental enrichments. *Canadian Journal of Fisheries and Aquatic Sciences, 47*(7), 1468-1477.

Fan, J., Zhang, J., Ngo, H. H., Guo, W., and Yin, X. (2016). Improving low-temperature performance of surface flow constructed wetlands using potamogeton crispus l. Plant. *Bioresource Technology, 218*, 1257-1260.

Fei, Z., Juan, W., Yanran, D., Dongfang, X., Shuiping, C., and Hongjiu, J. (2015). Performance evaluation of wastewater treatment using horizontal subsurface flow constructed wetlands optimized by micro-aeration and substrate selection. *Water Science & Technology, 71*(9), 1317-1324.

García, J., Aguirre, P., Barragán, J., Mujeriego, R., Matamoros, V., and Bayona, J. M. (2005). Effect of key design parameters on the efficiency of horizontal subsurface flow constructed wetlands. *Ecological Engineering, 25*(4), 405-418.

García-Villada, L., Rico, M., Altamirano, M., Sánchez-Martín, L., López-Rodas, V., and Costas, E. (2004). Occurrence of copper resistant mutants in the toxic cyanobacteria microcystis aeruginosa: Characterisation and future implications in the use of copper sulphate as algaecide. *Water Research, 38*(8), 2207-2213.

Giácoman-Vallejos, G., Ponce-Caballero, C., and Champagne, P. (2015). Pathogen removal from domestic and swine wastewater by experimental constructed wetlands. *Water Science and Technology, 71*(8), 1263.

Goldman, C. R. (1981). Lake tahoe: Two decades of change in a nitrogen deficient oligotrophic lake. *Verh. Int. Ver. Limnol, 21*, 45-70.

Gottschall, N., Boutin, C., Crolla, A., Kinsley, C., and Champagne, P. (2007). The role of plants in the removal of nutrients at a constructed wetland treating agricultural (dairy) wastewater, ontario, canada. *Ecological Engineering, 29*(2), 154-163.

Gray, S., Kinross, J., Read, P., and Marland, A. (2000). The nutrient assimilative capacity of maerl as a substrate in constructed wetland systems for waste treatment. *Water Research, 34*(8), 2183-2190.

Gschlößl, T., Steinmann, C., Schleypen, P., and Melzer, A. (1998). Constructed wetlands for effluent polishing of lagoons. *Water Research, 32*(9), 2639-2645.

Guan, B., Yao, X., Jiang, J., Tian, Z., An, S., Gu, B., and Cai, Y. (2009). Phosphorus removal ability of three inexpensive substrates: Physicochemical properties and application. *Ecological Engineering, 35*(4), 576-581.

Gunes, K. (2007). Restaurant wastewater treatment by constructed wetlands. *CLEAN – Soil, Air, Water, 35*(6), 571-575.

He, X., Liu, Y.-L., Conklin, A., Westrick, J., Weavers, L. K., Dionysiou, D. D., Lenhart, J. J., Mouser, P. J., Szlag, D., and Walker, H. W. (2016). Toxic cyanobacteria and drinking water: Impacts, detection, and treatment. *Harmful Algae, 54*(Supplement C), 174-193.

Heng, L., Jun, N., Wen-jie, H., and Guibai, L. (2009). Algae removal by ultrasonic irradiation–coagulation. *Desalination, 239*(1), 191-197.

Hernández-Crespo, C., Gargallo, S., Benedito-Durá, V., Nácher-Rodríguez, B., Rodrigo-Alacreu, M. A., and Martín, M. (2017). Performance of surface and subsurface flow constructed wetlands treating eutrophic waters. *Science of The Total Environment, 595*, 584-593.

Herrera-Melián, J. A., González-Bordón, A., Martín-González, M. A., García-Jiménez, P., Carrasco, M., and Araña, J. (2014). Palm tree mulch as substrate for primary treatment wetlands processing high strength urban wastewater. *Journal of Environmental Management, 139*(0), 22-31.

Hijosa-Valsero, M., Reyes-Contreras, C., Domínguez, C., Bécares, E., and Bayona, J. M. (2016). Behaviour of pharmaceuticals and personal care products in constructed wetland compartments: Influent, effluent, pore water, substrate and plant roots. *Chemosphere, 145*, 508-517.

Hosetti, B., and Frost, S. (1998). A review of the control of biological waste treatment in stabilization ponds. *Critical Reviews in Environmental Science and Technology, 28*(2), 193-218.

Hsueh, M. L., Yang, L., Hsieh, L. Y., and Lin, H. J. (2014). Nitrogen removal along the treatment cells of a free-water surface constructed wetland in subtropical taiwan. *Ecological Engineering, 73*(0), 579-587.

Hu, Y., Zhao, Y., Zhao, X., and Kumar, J. L. G. (2012). High rate nitrogen removal in an alum sludge-based intermittent aeration constructed wetland. *Environmental Science and Technology, 46*(8), 4583-4590.

Huang, J., Gao, X., Balch, G., Wootton, B., Jørgensen, S. E., and Anderson, B. (2015). Modelling of vertical subsurface flow constructed wetlands for treatment of domestic sewage and stormwater runoff by subwet 2.0. *Ecological Engineering, 74*, 8-12.

Huang, X., Liu, C., Wang, Z., Gao, C., Zhu, G., and Liu, L. (2013). The effects of different substrates on ammonium removal in constructed wetlands: A comparison of their physicochemical characteristics and ammonium-oxidizing prokaryotic communities. *CLEAN – Soil, Air, Water, 41*(3), 283-290.

IPCC. (2013). Fifth assessment report: Climate change 2013: The physical science basis.

Jácome, J. A., Molina, J., Suárez, J., Mosqueira, G., and Torres, D. (2016). Performance of constructed wetland applied for domestic wastewater treatment: Case study at boimorto (galicia, spain). *Ecological Engineering, 95*, 324-329.

Jäger, C. G., Hagemann, J., and Borchardt, D. (2017). Can nutrient pathways and biotic interactions control eutrophication in riverine ecosystems? Evidence from a model driven mesocosm experiment. *Water Research, 115*(Supplement C), 162-171.

Jansson, M., Bergström, A.-K., Blomqvist, P., Isaksson, A., and Jonsson, A. (1999). Impact of allochthonous organic carbon on microbial food web carbon dynamics and structure in lake örträsket. *Archiv für Hydrobiologie, 144*(4), 409-428.

Jiang, C., Jia, L., Zhang, B., He, Y., and Kirumba, G. (2014). Comparison of quartz sand, anthracite, shale and biological ceramsite for adsorptive removal of phosphorus from aqueous solution. *Journal of Environmental Sciences, 26*(2), 466-477.

Jin, M., Carlos, J., McConnell, R., Hall, G., and Champagne, P. (2017a). Peat as substrate for small-scale constructed wetlands polishing secondary effluents from municipal wastewater treatment plant. *Water, 9*(12).

Jin, M., Champagne, P., and Hall, G. (2017b). Effects of different substrates in the mitigation of algae-induced high ph wastewaters in a pilot-scale free water surface wetland system. *Water Science and Technology, 75*(1), 1-10.

Johnk, K. D., Huisman, J. E. F., Sharples, J., Sommeijer, B. E. N., Visser, P. M., and Stroom, J. M. (2008). Summer heatwaves promote blooms of harmful cyanobacteria. *Global Change Biology, 14*(3), 495-512.

Jong, J. (1976). Purification of wastewater with the aid of rush or reed ponds. *Biological Control of Water Pollution. J. Tourbier & Rw Pierson, Jr., eds*.

Jong, V. S. W., and Tang, F. E. (2015). The use of palm kernel shell (pks) as substrate material in vertical-flow engineered wetlands for septage treatment in malaysia. *Water Science & Technology, 72*(1), 84-91.

Kaasik, A., Vohla, C., Mõtlep, R., Mander, Ü., and Kirsimäe, K. (2008). Hydrated calcareous oil-shale ash as potential filter media for phosphorus removal in constructed wetlands. *Water Research, 42*(4–5), 1315-1323.

Kadlec, R. H., Burgoon, P. S., and Henderson, M. E. (1997). Integrated natural systems for treating potato processing wastewater. *Water Science and Technology, 35*(5), 263-270.

Kadlec, R. H., and Wallace, S. (2008). *Treatment wetlands* (2nd Edition ed.). CRC press, Florida.

Kasak, K., Mander, Ü., Truu, J., Truu, M., Järveoja, J., Maddison, M., and Teemusk, A. (2015). Alternative filter material removes phosphorus and mitigates greenhouse gas emission in horizontal subsurface flow filters for wastewater treatment. *Ecological Engineering, 77*(0), 242-249.

Kayombo, S., Mbwette, T. S. A., Mayo, A. W., Katima, J. H. Y., and Jørgensen, S. E. (2002). Diurnal cycles of variation of physical–chemical parameters in waste stabilization ponds. *Ecological Engineering, 18*(3), 287-291.

Kelly, J., Champagne, P., and Michel, F. (2007). Assessment of metal attenuation in a natural wetland system impacted by alkaline mine tailings, cobalt, ontario, canada. *Mine Water and the Environment, 26*(3), 181-190.

Kietlińska, A., and Renman, G. (2005). An evaluation of reactive filter media for treating landfill leachate. *Chemosphere, 61*(7), 933-940.

Klug, J. L. (2005). Bacterial response to dissolved organic matter affects resource availability for algae. *Canadian Journal of Fisheries and Aquatic Sciences, 62*(2), 472-481.

Knowles, P., Dotro, G., Nivala, J., and García, J. (2011). Clogging in subsurface-flow treatment wetlands: Occurrence and contributing factors. *Ecological Engineering, 37*(2), 99-112.

Kõiv, M., Kriipsalu, M., and Mander, Ü. (2006). After treatment of landfill leachate in peat filters. *WIT Transactions on Ecology and the Environment, 89*.

Kõiv, M., Liira, M., Mander, Ü., Mõtlep, R., Vohla, C., and Kirsimäe, K. (2010). Phosphorus removal using ca-rich hydrated oil shale ash as filter material – the effect of different phosphorus loadings and wastewater compositions. *Water Research, 44*(18), 5232-5239.

Kõiv, M., Vohla, C., Mõtlep, R., Liira, M., Kirsimäe, K., and Mander, Ü. (2009). The performance of peat-filled subsurface flow filters treating landfill leachate and municipal wastewater. *Ecological Engineering, 35*(2), 204-212.

Korboulewsky, N., Wang, R., and Baldy, V. (2012). Purification processes involved in sludge treatment by a vertical flow wetland system: Focus on the role of the substrate and plants on n and p removal. *Bioresource Technology, 105*, 9-14.

Lai, D. Y. F. (2014). Phosphorus fractions and fluxes in the soils of a free surface flow constructed wetland in hong kong. *Ecological Engineering, 73*, 73-79.

Lai, D. Y. F., and Lam, K. C. (2009). Phosphorus sorption by sediments in a subtropical constructed wetland receiving stormwater runoff. *Ecological Engineering, 35*(5), 735-743.

Lantzke, I., Heritage, A., Pistillo, G., and Mitchell, D. (1998). Phosphorus removal rates in bucket size planted wetlands with a vertical hydraulic flow. *Water Research, 32*(4), 1280-1286.

Li, C., Dong, Y., Lei, Y., Wu, D., and Xu, P. (2015). Removal of low concentration nutrients in hydroponic wetlands integrated with zeolite and calcium silicate hydrate functional substrates. *Ecological Engineering, 82*, 442-450.

Li, C., Yu, H., Tabassum, S., Li, L., Wu, D., Zhang, Z., Kong, H., and Xu, P. (2017). Effect of calcium silicate hydrates (csh) on phosphorus immobilization and speciation in shallow lake sediment. *Chemical Engineering Journal, 317*, 844-853.

Li, H., Chi, Z., Yan, B., Cheng, L., and Li, J. (2016). Nitrogen removal in wood chip combined substrate baffled subsurface-flow constructed wetlands: Impact of matrix arrangement and intermittent aeration. *Environmental Science and Pollution Research*, 1-7.

Li, H., Li, Y., Gong, Z., and Li, X. (2013). Performance study of vertical flow constructed wetlands for phosphorus removal with water quenched slag as a substrate. *Ecological Engineering, 53*, 39-45.

Li, J., Wen, Y., Zhou, Q., Xingjie, Z., Li, X., Yang, S., and Lin, T. (2008). Influence of vegetation and substrate on the removal and transformation of dissolved organic matter in horizontal subsurface-flow constructed wetlands. *Bioresource Technology, 99*(11), 4990-4996.

Liu, L., Hall, G., and Champagne, P. (2016a). Effects of environmental factors on the disinfection performance of a wastewater stabilization pond operated in a temperate climate. *Water, 8*(1), 5.

Liu, M., Wu, S., Chen, L., and Dong, R. (2014). How substrate influences nitrogen transformations in tidal flow constructed wetlands treating high ammonium wastewater? *Ecological Engineering, 73*(0), 478-486.

Liu, X., Huang, S., Tang, T., Liu, X., and Scholz, M. (2012). Growth characteristics and nutrient removal capability of plants in subsurface vertical flow constructed wetlands. *Ecological Engineering, 44*, 189-198.

Liu, Y., Cao, X., Yu, Z., Song, X., and Qiu, L. (2016b). Controlling harmful algae blooms using aluminum-modified clay. *Marine Pollution Bulletin, 103*(1), 211-219.

Lizama Allende, K., Fletcher, T. D., and Sun, G. (2012). The effect of substrate media on the removal of arsenic, boron and iron from an acidic wastewater in planted column reactors. *Chemical Engineering Journal, 179*, 119-130.

Lotito, A. M., De Sanctis, M., Di Iaconi, C., and Bergna, G. (2014). Textile wastewater treatment: Aerobic granular sludge vs activated sludge systems. *Water Research, 54*(0), 337-346.

Lüderitz, V., and Gerlach, F. (2002). Phosphorus removal in different constructed wetlands. *Acta Biotechnologica, 22*(1-2), 91-99.

Luo, P., Liu, F., Liu, X., Wu, X., Yao, R., Chen, L., Li, X., Xiao, R., and Wu, J. (2017). Phosphorus removal from lagoon-pretreated swine wastewater by pilot-scale surface flow constructed wetlands planted with myriophyllum aquaticum. *Science of The Total Environment, 576*, 490-497.

LÜrling, M., Eshetu, F., Faassen, E. J., Kosten, S., and Huszar, V. L. M. (2013). Comparison of cyanobacterial and green algal growth rates at different temperatures. *Freshwater Biology, 58*(3), 552-559.

Ma, J., and Liu, W. (2002). Effectiveness and mechanism of potassium ferrate(vi) preoxidation for algae removal by coagulation. *Water Research, 36*(4), 871-878.

Maassarani, R., Champagne, P., and Hall, G. (2015). *Modelling the effects of varying climate on a waste stailization pond in canadian high arctic.* (Master), Queen's University.

Maine, M. A., Hadad, H. R., Sánchez, G. C., Di Luca, G. A., Mufarrege, M. M., Caffaratti, S. E., and Pedro, M. C. (2017). Long-term performance of two free-water surface wetlands for metallurgical effluent treatment. *Ecological Engineering, 98*, 372-377.

Mara, D. (1996). Waste stabilization ponds: Effluent quality requirements and implications for process design. *Water Science and Technology, 33*(7), 23-31.

Martín, M., Oliver, N., Hernández-Crespo, C., Gargallo, S., and Regidor, M. C. (2013). The use of free water surface constructed wetland to treat the eutrophicated waters of lake l'albufera de valencia (spain). *Ecological Engineering, 50*, 52-61.

Mateus, D. M. R., Vaz, M. M. N., and Pinho, H. J. O. (2012). Fragmented limestone wastes as a constructed wetland substrate for phosphorus removal. *Ecological Engineering, 41*(0), 65-69.

Mawuli, D., Xiaochang, W., Yucong, Z., Yuan, G., Jiaqing, X., and Yaqian, Z. (2015). Characteristics of nitrogen and phosphorus removal by a surface-flow constructed wetland for polluted river water treatment. *Water Science and Technology, 71*(6), 904-912.

Mayes, W. M., and Younger, P. L. (2006). Buffering of alkaline steel slag leachate across a natural wetland. *Environmental Science and Technology, 40*(4), 1237-1243.

Maynard, H. E., Ouki, S. K., and Williams, S. C. (1999). Tertiary lagoons: A review of removal mecnisms and performance. *Water Research, 33*(1), 1-13.

Mburu, N., Tebitendwa, S. M., van Bruggen, J. J. A., Rousseau, D. P. L., and Lens, P. N. L. (2013). Performance comparison and economics analysis of waste stabilization ponds and horizontal subsurface flow constructed wetlands treating domestic wastewater: A case study of the juja sewage treatment works. *Journal of Environmental Management, 128*, 220-225.

Michalak, A. M., Anderson, E. J., Beletsky, D., Boland, S., Bosch, N. S., Bridgeman, T. B., Chaffin, J. D., Cho, K., Confesor, R., Daloğlu, I., DePinto, J. V., Evans, M. A., Fahnenstiel, G. L., He, L., Ho, J. C., Jenkins, L., Johengen, T. H., Kuo, K. C., LaPorte, E., Liu, X., McWilliams, M. R., Moore, M. R., Posselt, D. J., Richards, R. P., Scavia, D., Steiner, A. L., Verhamme, E., Wright, D. M., and Zagorski, M. A. (2013). Record-setting algal bloom in lake erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proceedings of the National Academy of Sciences of the United States of America, 110*(16), 6448-6452.

Miguel, A., Meffe, R., Leal, M., González-Naranjo, V., Martínez-Hernández, V., Lillo, J., Martín, I., Salas, J. J., and Bustamante, I. (2014). Treating municipal wastewater through a vegetation filter with a short-rotation poplar species. *Ecological Engineering, 73*(0), 560-568.

Muñoz, R., and Guieysse, B. (2006). Algal–bacterial processes for the treatment of hazardous contaminants: A review. *Water Research, 40*(15), 2799-2815.

Murphy, C., Wallace, S., Knight, R., Cooper, D., and Sellers, T. (2015). Treatment performance of an aerated constructed wetland treating glycol from de-icing operations at a uk airport. *Ecological Engineering, 80*(0), 117-124.

Narvaez, L., Cunill, C., Caceres, R., and Marfa, O. (2011). Design and monitoring of horizontal subsurface-flow constructed wetlands for treating nursery leachates. *Bioresource Technology, 102*(11), 6414-6420.

Nishimura, H., Nakajima, M., and Kumagai, M. (1984). Exchange of oxygen and carbon dioxide across the water surface during algal blooms in a pond. *Water Research, 18*(3), 345-350.

Nivala, J., Knowles, P., Dotro, G., García, J., and Wallace, S. (2012). Clogging in subsurface-flow treatment wetlands: Measurement, modeling and management. *Water Res, 46*(6), 1625-1640.

Ong, S.-A., Uchiyama, K., Inadama, D., and Yamagiwa, K. (2009). Simultaneous removal of color, organic compounds and nutrients in azo dye-containing wastewater using up-flow constructed wetland. *Journal of Hazardous Materials, 165*(1), 696-703.

Paing, J., Serdobbel, V., Welschbillig, M., Calvez, M., Gagnon, V., and Chazarenc, F. (2015). Treatment of high organic content wastewater from food-processing industry with the french vertical flow constructed wetland system. *Water Science and Technology, 72*(1), 70-76.

Pandey, M. K., Jenssen, P. D., Krogstad, T., and Jonasson, S. (2013). Comparison of vertical and horizontal flow planted and unplanted subsurface flow wetlands treating municipal wastewater. *Water Science and Technology, 68*(1), 117-123.

Pavlineri, N., Skoulikidis, N. T., and Tsihrintzis, V. A. (2017). Constructed floating wetlands: A review of research, design, operation and management aspects, and data meta-analysis. *Chemical Engineering Journal, 308*, 1120-1132.

Peng, J., Song, Y., Liu, Z., Gao, H., and Yu, H. (2012). Performance of a novel circular-flow corridor wetland toward the treatment of simulated high-strength swine wastewater. *Ecological Engineering, 49*, 1-9.

Pietro, K. C., and Ivanoff, D. (2015). Comparison of long-term phosphorus removal performance of two large-scale constructed wetlands in south florida, u.S.A. *Ecological Engineering, 79*(0), 143-157.

Pipes, W. O. (1962). Ph variation and bod removal in stabilization ponds. *Journal (Water Pollution Control Federation), 34*(11), 1140-1150.

Pries, J. (1996). *Constructed wetland treatment systems in canada.* Paper Proceedings from the Constructed wetlands in cold climates. Proceedings of the symposium held at the Niagara-on-the-Lake, Ontario, Canada.

Proctor, D. M., Fehling, K. A., Shay, E. C., Wittenborn, J. L., Green, J. J., Avent, C., Bigham, R. D., Connolly, M., Lee, B., Shepker, T. O., and Zak, M. A. (2000). Physical and chemical characteristics of blast furnace, basic oxygen furnace, and electric arc furnace steel industry slags. *Environmental Science and Technology, 34*(8), 1576-1582.

Qin, B., Zhu, G., Gao, G., Zhang, Y., Li, W., Paerl, H. W., and Carmichael, W. W. (2010). A drinking water crisis in lake taihu, china: Linkage to climatic variability and lake management. *Environmental Management, 45*(1), 105-112.

Raven, J. A., and Geider, R. J. (1988). Temperature and algal growth. *New Phytologist, 110*(4), 441-461.

Reinoso, R., Torres, L. A., and Bécares, E. (2008). Efficiency of natural systems for removal of bacteria and pathogenic parasites from wastewater. *Science of The Total Environment, 395*(2–3), 80-86.

Roadcap, G. S., Kelly, W. R., and Bethke, C. M. (2005). Geochemistry of extremely alkaline (ph > 12) ground water in slag-fill aquifers. *Ground Water, 43*(6), 806-816.

Rodríguez, E., Onstad, G. D., Kull, T. P. J., Metcalf, J. S., Acero, J. L., and von G., U. (2007). Oxidative elimination of cyanotoxins: Comparison of ozone, chlorine, chlorine dioxide and permanganate. *Water Research, 41*(15), 3381-3393.

Saeed, T., Afrin, R., Muyeed, A. A., and Sun, G. (2012). Treatment of tannery wastewater in a pilot-scale hybrid constructed wetland system in bangladesh. *Chemosphere, 88*(9), 1065-1073.

Saeed, T., Paul, B., Afrin, R., Al-Muyeed, A., and Sun, G. (2016). Floating constructed wetland for the treatment of polluted river water: A pilot scale study on seasonal variation and shock load *Chemical Engineering Journal* (Vol. 287, pp. 62-73).

Saeed, T., and Sun, G. (2011). A comparative study on the removal of nutrients and organic matter in wetland reactors employing organic media. *Chemical Engineering Journal, 171*(2), 439-447.

Saeed, T., and Sun, G. (2012). A review on nitrogen and organics removal mechanisms in subsurface flow constructed wetlands: Dependency on environmental parameters, operating conditions and supporting media. *Journal of Environmental Management, 112*, 429-448.

Saeed, T., and Sun, G. (2013). A lab-scale study of constructed wetlands with sugarcane bagasse and sand media for the treatment of textile wastewater. *Bioresource Technology, 128*, 438-447.

Sapkota, D. P., and Bavor, H. J. (1994). Gravel media filtration as a constructed wetland component for the reduction of suspended solids from maturation pond effluent. *Water Science and Technology, 29*(4), 55-66.

Schierano, M. C., Maine, M. A., and Panigatti, M. C. (2017). Dairy farm wastewater treatment using horizontal subsurface flow wetlands with typha domingensis and different substrates. *Environmental Technology, 38*(2), 192-198.

Schindler, D. W. (1988). Experimental studies of chemical stressors on whole lake ecosystems. *Internationale Vereinigung fuer Theoretische und Angewandte Limnologie Verhandlungen IVTLAP, 23*(1).

Schindler, D. W., Hecky, R. E., and McCullough, G. K. (2012). The rapid eutrophication of lake winnipeg: Greening under global change. *Journal of Great Lakes Research, 38*(Supplement 3), 6-13.

Schippers, P., Lürling, M., and Scheffer, M. (2004). Increase of atmospheric co2 promotes phytoplankton productivity. *Ecology Letters, 7*(6), 446-451.

Schramke, J. A. (1992). Neutralization of alkaline coal fly ash leachates by co2(g). *Applied Geochemistry, 7*(5), 481-492.

Sehar, S., Sumera, Naeem, S., Perveen, I., Ali, N., and Ahmed, S. (2015a). A comparative study of macrophytes influence on wastewater treatment through subsurface flow hybrid constructed wetland. *Ecological Engineering, 81*, 62-69.

Sehar, S., Sumera, Naeem, S., Perveen, I., Ali, N., and Ahmed, S. (2015b). A comparative study of macrophytes influence on wastewater treatment through subsurface flow hybrid constructed wetland. *Ecological Engineering, 81*(0), 62-69.

Seidel, K. (1953). Pflanzungen zwischen gewassern und land. *Mitteilungen Max-Planck Gesselschaft*, 17-20.

Senzia, M. A., Mashauri, D. A., and Mayo, A. W. (2003). Suitability of constructed wetlands and waste stabilisation ponds in wastewater treatment: Nitrogen transformation and removal. *Physics and Chemistry of the Earth, Parts A/B/C, 28*(20–27), 1117-1124.

Shen, Q., Zhu, J., Cheng, L., Zhang, J., Zhang, Z., and Xu, X. (2011). Enhanced algae removal by drinking water treatment of chlorination coupled with coagulation. *Desalination, 271*(1–3), 236-240.

Shi, W., Bi, L., and Pan, G. (2016). Effect of algal flocculation on dissolved organic matters using cationic starch modified soils. *Journal of Environmental Sciences, 45*(Supplement C), 177-184.

Shun, Y., McKelvie, I. D., and Hart, B. T. (1994). Determination of alkaline phosphatase-hydrolyzable phosphorus in natural water systems by enzymatic flow injection. *Limnology and Oceanography, 39*(8), 1993-2000.

Sim, C. H., Quek, B. S., Shutes, R. B., and Goh, K. H. (2013). Management and treatment of landfill leachate by a system of constructed wetlands and ponds in singapore. *Water Science and Technology, 68*(5), 1114-1122.

Snoeyink, V. L., and Jenkins, D. (1980). *Water chemistry*. Wiley, New York.

Speer, S., Champagne, P., and Anderson, B. (2011). Treatability study of two hybrid-passive treatment systems for landfill leachate operated at cold temperature. *Water Quality Research Journal of Canada, 46*(3), 230.

Speer, S., Champagne, P., and Anderson, B. (2012). Pilot-scale comparison of two hybrid-passive landfill leachate treatment systems operated in a cold climate. *Bioresource Technology, 104*(Supplement C), 119-126.

Speer, S., Champagne, P., Crolla, A., and Kinsley, C. (2009). Hydraulic performance of a mature wetland treating milkhouse wastewater and agricultural runoff. *Water Science and Technology, 59*(12), 2455.

Stefanakis, A. I., Akratos, C. S., Gikas, G. D., and Tsihrintzis, V. A. (2009). Effluent quality improvement of two pilot-scale, horizontal subsurface flow constructed wetlands using natural zeolite (clinoptilolite). *Microporous and Mesoporous Materials, 124*(1–3), 131-143.

Stefanakis, A. I., Seeger, E., Dorer, C., Sinke, A., and Thullner, M. (2016). Performance of pilot-scale horizontal subsurface flow constructed wetlands treating groundwater contaminated with phenols and petroleum derivatives. *Ecological Engineering, 95*, 514-526.

Stefanakis, A. I., and Tsihrintzis, V. A. (2012a). Effects of loading, resting period, temperature, porous media, vegetation and aeration on performance of pilot-scale vertical flow constructed wetlands. *Chemical Engineering Journal, 181–182*, 416-430.

Stefanakis, A. I., and Tsihrintzis, V. A. (2012b). Use of zeolite and bauxite as filter media treating the effluent of vertical flow constructed wetlands. *Microporous and Mesoporous Materials, 155*, 106-116.

Steinmann, C. R., Weinhart, S., and Melzer, A. (2003). A combined system of lagoon and constructed wetland for an effective wastewater treatment. *Water Research, 37*(9), 2035-2042.

Su, C., and Puls, R. W. (2007). Removal of added nitrate in cotton burr compost, mulch compost, and peat: Mechanisms and potential use for groundwater nitrate remediation. *Chemosphere, 66*(1), 91-98.

Sun, X.-X., Choi, J.-K., and Kim, E.-K. (2004a). A preliminary study on the mechanism of harmful algal bloom mitigation by use of sophorolipid treatment. *Journal of Experimental Marine Biology and Ecology, 304*(1), 35-49.

Sun, X.-X., Han, K.-N., Choi, J.-K., and Kim, E.-K. (2004b). Screening of surfactants for harmful algal blooms mitigation. *Marine Pollution Bulletin, 48*(9), 937-945.

Tang, X. Q., Huang, S. L., and Scholz, M. (2009). Comparison of phosphorus removal between vertical subsurface flow constructed wetlands with different substrates. *Water and Environment Journal, 23*(3), 180-188.

Tao, W., and Wang, J. (2009). Effects of vegetation, limestone and aeration on nitritation, anammox and denitrification in wetland treatment systems. *Ecological Engineering, 35*(5), 836-842.

Tee, H.-C., Lim, P.-E., Seng, C.-E., and Nawi, M.-A. M. (2012a). Newly developed baffled subsurface-flow constructed wetland for the enhancement of nitrogen removal. *Bioresource Technology, 104*, 235-242.

Tee, H. C., Lim, P. E., Seng, C. E., and Nawi, M. A. (2012b). Newly developed baffled subsurface-flow constructed wetland for the enhancement of nitrogen removal. *Bioresource Technology, 104*, 235-242.

Tee, H. C., Seng, C. E., Noor, A. M., and Lim, P. E. (2009). Performance comparison of constructed wetlands with gravel- and rice husk-based media for phenol and nitrogen removal. *Science of The Total Environment, 407*(11), 3563-3571.

Toscano, A., Marzo, A., Milani, M., Cirelli, G. L., and Barbagallo, S. (2015). Comparison of removal efficiencies in mediterranean pilot constructed wetlands vegetated with different plant species. *Ecological Engineering, 75*(0), 155-160.

Constructed wetlands treatment of municipal wastewaters (2000). (EPA/625/R-99/010). edn, National Risk Management Research Laboratory, Cincinnati, Ohio, 45268.

Vymazal, J. (2005). Constructed wetlands for wastewater treatment. *Ecological Engineering, 25*(5), 475-477.

Vymazal, J. (2008). Constructed wetlands, subsurface flow. In Sven Erik JørgensenBrian D. Fath (Ed.), *Encyclopedia of ecology* (pp. 748-764). Oxford: Academic Press.

Vymazal, J. (2013a). Emergent plants used in free water surface constructed wetlands: A review. *Ecological Engineering, 61, Part B*(0), 582-592.

Vymazal, J. (2013b). Plants in constructed, restored and created wetlands. *Ecological Engineering, 61*, 501-504.

Vymazal, J. (2014). Constructed wetlands for treatment of industrial wastewaters: A review. *Ecological Engineering, 73*, 724-751.

Wallace, J., Champagne, P., and Hall, G. (2016). Multivariate statistical analysis of water chemistry conditions in three wastewater stabilization ponds with algae blooms and ph fluctuations. *Water Research, 96*(Supplement C), 155-165.

Wallace, J., Champagne, P., and Monnier, A.-C. (2015). Performance evaluation of a hybrid-passive landfill leachate treatment system using multivariate statistical techniques. *Waste Management, 35*(Supplement C), 159-169.

Wang, R., Korboulewsky, N., Prudent, P., Domeizel, M., Rolando, C., and Bonin, G. (2010). Feasibility of using an organic substrate in a wetland system treating sewage sludge: Impact of plant species. *Bioresource Technology, 101*(1), 51-57.

Wang, X., Bai, X., Qiu, J., and Wang, B. (2005). Municipal wastewater treatment with pond constructed wetland system: A case study. *Water Science & Technology, 51*(12), 325-329.

Wang, Z., Dong, J., Liu, L., Zhu, G., and Liu, C. (2013). Study of oyster shell as a potential substrate for constructed wetlands. *Water Sci Technol, 67*(10), 2265-2272.

Weerakoon, G. M. P. R., Jinadasa, K. B. S. N., Herath, G. B. B., Mowjood, M. I. M., and van Bruggen, J. J. A. (2013). Impact of the hydraulic loading rate on pollutants removal in tropical horizontal subsurface flow constructed wetlands. *Ecological Engineering, 61*, 154-160.

Werker, A. G., Dougherty, J. M., McHenry, J. L., and Van Loon, W. A. (2002). Treatment variability for wetland wastewater treatment design in cold climates. *Ecological Engineering, 19*(1), 1-11.

Wittgren, H. B., and Mæhlum, T. (1997). Wastewater treatment wetlands in cold climates. *Water Science and Technology, 35*(5), 45-53.

Wu, H., Fan, J., Zhang, J., Ngo, H. H., Guo, W., Liang, S., Lv, J., Lu, S., Wu, W., and Wu, S. (2016). Intensified organics and nitrogen removal in the intermittent-aerated constructed wetland using a novel sludge-ceramsite as substrate. *Bioresource Technology, 210*, 101-107.

Wu, H., Zhang, J., Guo, W., Liang, S., and Fan, J. (2017). Secondary effluent purification by a large-scale multi-stage surface-flow constructed wetland: A case study in northern china. *Bioresource Technology*.

Wu, H., Zhang, J., Ngo, H. H., Guo, W., Hu, Z., Liang, S., Fan, J., and Liu, H. (2015). A review on the sustainability of constructed wetlands for wastewater treatment: Design and operation. *Bioresource Technology, 175*(0), 594-601.

Wu, J., He, F., Xu, D., Wang, R., Zhang, X., Xiao, E., and Wu, Z. (2011). Phosphorus removal by laboratory-scale unvegetated vertical-flow constructed wetland systems using anthracite, steel slag and related blends as substrate. *Water Science and Technology, 63*(11), 2719.

Wu, Y., Kerr, P. G., Hu, Z., and Yang, L. (2010). Removal of cyanobacterial bloom from a biopond–wetland system and the associated response of zoobenthic diversity. *Bioresource Technology, 101*(11), 3903-3908.

Xiaohong, Z., Yaqian, Z., Wenke, W., Yongzhe, Y., Babatunde, A., Yuansheng, H., and Kumar, L. (2015). Key issues to consider when using alum sludge as substrate in constructed wetland. *Water Science & Technology, 71*(12), 1775-1782.

Xu, G., Zou, J., and Li, G. (2008). Ceramsite made with water and wastewater sludge and its characteristics affected by sio2 and al2o3. *Environmental Science and Technology, 42*(19), 7417-7423.

Yalcuk, A., and Ugurlu, A. (2009). Comparison of horizontal and vertical constructed wetland systems for landfill leachate treatment. *Bioresource Technology, 100*(9), 2521-2526.

Yan, X., Xu, X., Wang, M., Wang, G., Wu, S., Li, Z., Sun, H., Shi, A., and Yang, Y. (2017). Climate warming and cyanobacteria blooms: Looks at their relationships from a new perspective. *Water Research*.

Yeh, N., Yeh, P., and Chang, Y.-H. (2015). Artificial floating islands for environmental improvement. *Renewable and Sustainable Energy Reviews, 47*, 616-622.

Yen, H. Y., and Chou, J. H. (2016). Water purification by oyster shell bio-medium in a recirculating aquaponic system. *Ecological Engineering, 95*, 229-236.

Yin, H., Yan, X., and Gu, X. (2017). Evaluation of thermally-modified calcium-rich attapulgite as a low-cost substrate for rapid phosphorus removal in constructed wetlands. *Water Research, 115*, 329-338.

Yun, Y., Zhou, X., Li, Z., Uddin, S. M. N., and Bai, X. (2015). Comparative research on phosphorus removal by pilot-scale vertical flow constructed wetlands using steel slag and modified steel slag as substrates. *Water Science and Technology, 71*(7), 996-1003.

Zhang, G., Wang, B. O., Zhang, P., Wang, L. I., and Wang, H. U. I. (2006). Removal of algae by sonication-coagulation. *Journal of Environmental Science and Health, Part A, 41*(7), 1379-1390.

Zhao, J., Zhao, Y., Xu, Z., Doherty, L., and Liu, R. (2016). Highway runoff treatment by hybrid adsorptive media-baffled subsurface flow constructed wetland. *Ecological Engineering, 91*, 231-239.

Zhao, Y. Q., Babatunde, A. O., Hu, Y. S., Kumar, J. L. G., and Zhao, X. H. (2011). Pilot field-scale demonstration of a novel alum sludge-based constructed wetland system for enhanced wastewater treatment. *Process Biochemistry, 46*(1), 278-283.

Zhao, Y. Q., Zhao, X. H., and Babatunde, A. O. (2009). Use of dewatered alum sludge as main substrate in treatment reed bed receiving agricultural wastewater: Long-term trial. *Bioresource Technology, 100*(2), 644-648.

Zhou, Z.-X., Yu, R.-C., and Zhou, M.-J. (2017). Resolving the complex relationship between harmful algal blooms and environmental factors in the coastal waters adjacent to the changjiang river estuary. *Harmful Algae, 62*(Supplement C), 60-72.

Zurita, F., De Anda, J., and Belmont, M. A. (2009). Treatment of domestic wastewater and production of commercial flowers in vertical and horizontal subsurface-flow constructed wetlands. *Ecological Engineering, 35*(5), 861-869.

Chapter 7

Conclusions and Contributions

7.1 Conclusions from experimental results

Wastewater stabilization ponds have been recognized as a sustainable wastewater treatment technology and are widely employed at municipal wastewater treatment plants by municipalities across North America. However, elevated nutrient concentrations and extended retention times may lead to excessive growth of undesired algae. Algal blooms can occur in wastewater stabilization ponds and subsequently affect downstream water quality. The Amherstview Water Pollution Control Plant, which is operated by Loyalist Township, is one of the municipal wastewater treatment facilities in Eastern Ontario that frequently experiences algal blooms in their wastewater stabilization ponds. As a result, effluent with elevated pH above the regulatory discharge limits frequently occurs. Hence, a mitigation method was required by the Ministry of the Environment and Climate Change to ensure compliance with the regulatory discharge limit for pH (6.5<pH<9.5).

Constructed wetlands have been shown to be an ideal sustainable wastewater treatment technology that may mitigate the elevated pH effluents. Constructed wetlands can not only stabilize the system pH, but may also provide enhanced nutrient removal. Generally, there are two main types of constructed wetland depending on the flow (e.g. surface flow and subsurface flow) are available, and most studies were only focused on evaluation of the treatment performance of subsurface flow constructed wetlands due to their superior treatment ability compared to surface flow constructed wetlands. However, surface flow constructed wetlands are inexpensive to establish and more cost-effective to operate. The maintenance and operational costs are significantly lower than subsurface flow constructed wetlands, which make them ideal for small, rural and/or remote communities. Hence, the primary objectives of this study were to investigate the substrate materials and optimal operational conditions for the mitigation of elevated pH effluent a surface flow constructed wetland in the laboratory. This was accomplished using a bench-scale study on the suitability of different substrates for pH attenuation, a pilot-scale study to test the treatment performance of a small-scale free water surface flow constructed wetland system on-site using authentic wastewater from the Amherstview WPCP and to design and implement a pilot-scale free water surface flow constructed wetland at the Amherstview WPCP.

The feasibility of using substrate materials such as topsoil, organic mulch, peat, and gravel, for the mitigation of high pH synthetic wastewater was investigated in a two phases study in Chapter 4. A short-term assessment (Phase 1) of four substrates followed by a long-term assessment (Phase 2) of the two most promising substrates were undertaken. The Phase 1 assessment showed that all substrates had the ability to attenuate the pH of synthetic wastewater from above 10.5 to below 9.5, which is the upper limit of the regulatory discharge guidelines. Among these substrates, peat was found to substantially reduce the pH level to 7.7, and also showed a 53.7% reduction in TP. Gravel produced the effluent with low alkalinity level that is not ideal for pH stabilization, and leaching organic and nutrients back to water column were the biggest concern of using organic mulch from the experiment results. Hence, peat and topsoil were selected for the Phase 2 study. In Phase 2, operational conditions including organic loading rates and hydraulic retention times were examined for their influence on pH attenuation. The results indicated that organic loading rates had more impact on pH when compared to hydraulic retention times but an increased organic loading rate and extended hydraulic retention time combination could enhance the attenuation of pH.

In chapter 5, three small-scale, on-site free water surface constructed wetland reactors were designed to evaluate their treatment performance of secondary effluent at the Amherstview WPCP. Three different wetland configurations of peat substrate with no vegetation, *Typha latifolia* vegetation alone and peat and *T. latifolia* together, were tested for a period of a year. For a hydraulic retention time of 2.5 days, the results showed that all reactors could attenuate the pH level during both the start-up and operational periods. Nutrients removal was only observed during the operational period. Peat exhibited effective removal of NO_3-N, TN, and phosphorous. The addition of *T. latifolia* could further enhance the NO_3-N and TN removal efficiencies. However, employing *T. latifolia* alone did not yield effluents that meet the regulatory discharge guidelines for phosphorous (1.0 mg/L).

Chapter 6 described the design of a pilot-scale surface flow constructed wetland at the Amherstview WPCP and the treatment performance in the first treatment season. This newly designed constructed wetland contains four unique treatment trains with three different substrate materials and two inter-cell connections. The design of the wetland was guided by the studies conducted in Chapters 4 and 5, as well as the USEPA constructed wetland design manual. Overall, the wetland was highly effective at removing PO_4-P and TP, and fairly effective at removing NO_3-N and TN. Three out of four treatment trains were found to attenuate high pH level influent to the level below the regulatory discharge guidelines (pH<9.5). The fourth treatment train with topsoil was unable to attenuate the pH to below 9.5. Peat exhibited the best overall treatment performance. In addition, open water connection outperformed the berm connection for the attenuation of pH.

7.2 Original contributions

The results of this project have not only demonstrated that free water surface constructed wetlands can successfully be employed to attenuate not only high pH level influent, but also provide further treatment in terms of nutrients removal. The substrate materials that ideal for pH attenuation in free water surface constructed wetlands were thoroughly investigated both in the laboratory and in the field. Comparison of substrates and operational conditions in the laboratory and further evaluation of ideal substrates and vegetation in the field, provide important and useful information for the design of the pilot-scale constructed wetlands that are suitable for Canadian environmental and climate conditions.

Peat is a readily available and relatively inexpensive material mainly used for gardening in North America. Few studies have reported on the use of peat as a substrate material in constructed wetland applications, with most studies only applying peat in highly concentrated wastewater. Employing peat for treating secondary effluent in constructed wetland was seldom investigated. In this project, peat was thoroughly investigated as a substrate in free water surface constructed wetlands both in the laboratory and in the field with respect to its potential to attenuate pH and nutrient concentrations.

A novel pilot-scale free water surface constructed wetland with four unique treatment trains was designed and operated at the Amherstview Water Pollution Control Plant, Amherstview, Ontario. The operational conditions were optimized with appropriate substrate materials and hydraulic conditions to attenuate secondary effluents with high pH and nutrient concentrations. The results of this project will serve as a guide for other Canadian municipalities with WSPs, which are experiencing water quality issues, such as high pH levels, due to algae and other contributing factors. The information will provide a framework, at the bench-scale, pilot and full-scale, for other researchers who wish to apply constructed wetlands to wastewater treatment scenarios for other water quality issues.

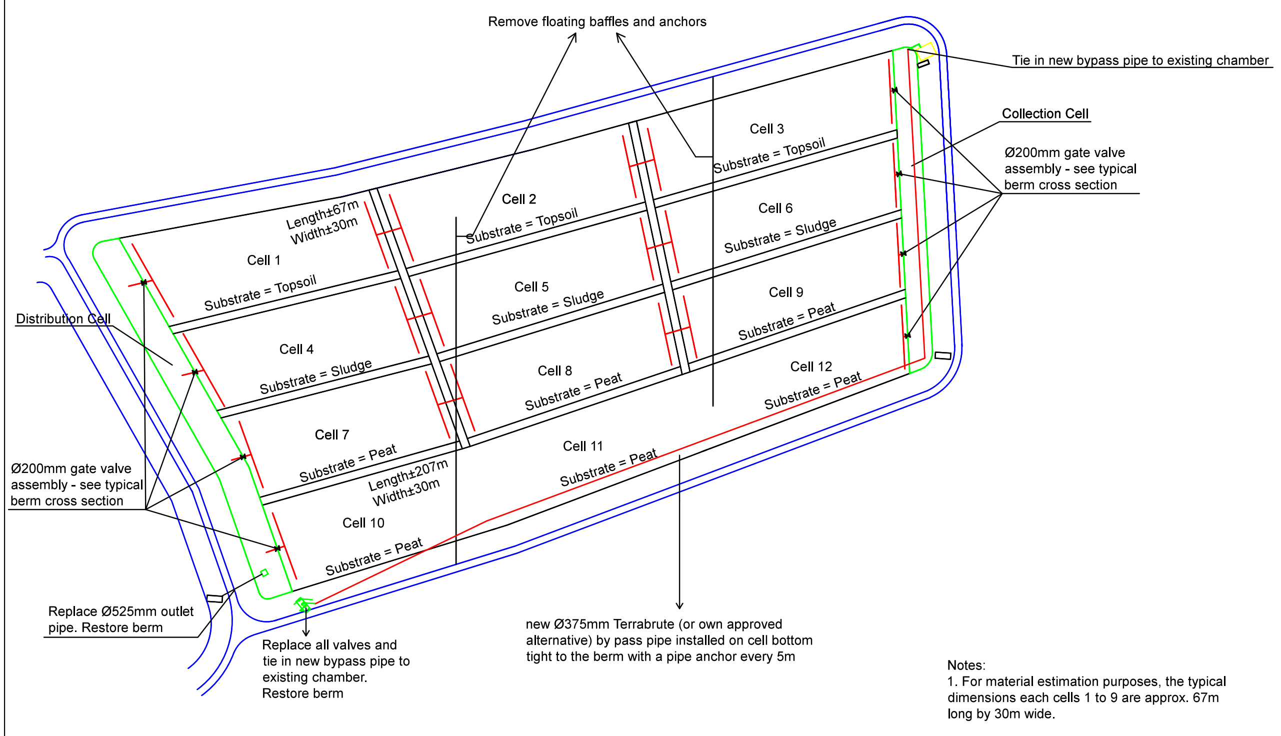
7.3 Future Works

In this project, substrate had been demonstrated as an integral part of the CW system, and played an important role on pH attenuation and nutrients removal. During the bench-scale study, peat demonstrated the best pH attenuation and overall performance. However, characterization of peat could be improved by conducting element analysis and measuring cation-exchange capacity. Peat humification, as a proxy or indicator of the degree of breakdown or decomposition of peat, can also be assessed by using a 10-point von Post scale to provide a detail characterization.

Despite the system was able to attenuate the high pH secondary effluent during the first treatment season, long-term monitoring of the system is required to further evaluate the effectiveness of the pilot-scale wetland system. Besides the substrates and vegetation, hydraulic conditions can significantly affect the performance of the wetland. Hence, a tracer study is necessary to have a better understanding of the hydraulic conditions in the current system. As a natural attenuation system, biological processes play a vital role in terms of the removal of organics and nutrients. Microbial analysis on the species and the number of microorganisms that exist in the pilot-scale constructed wetland system would be helpful to further understand the process of pH attenuation as well as the removal of nutrients.

Appendix A

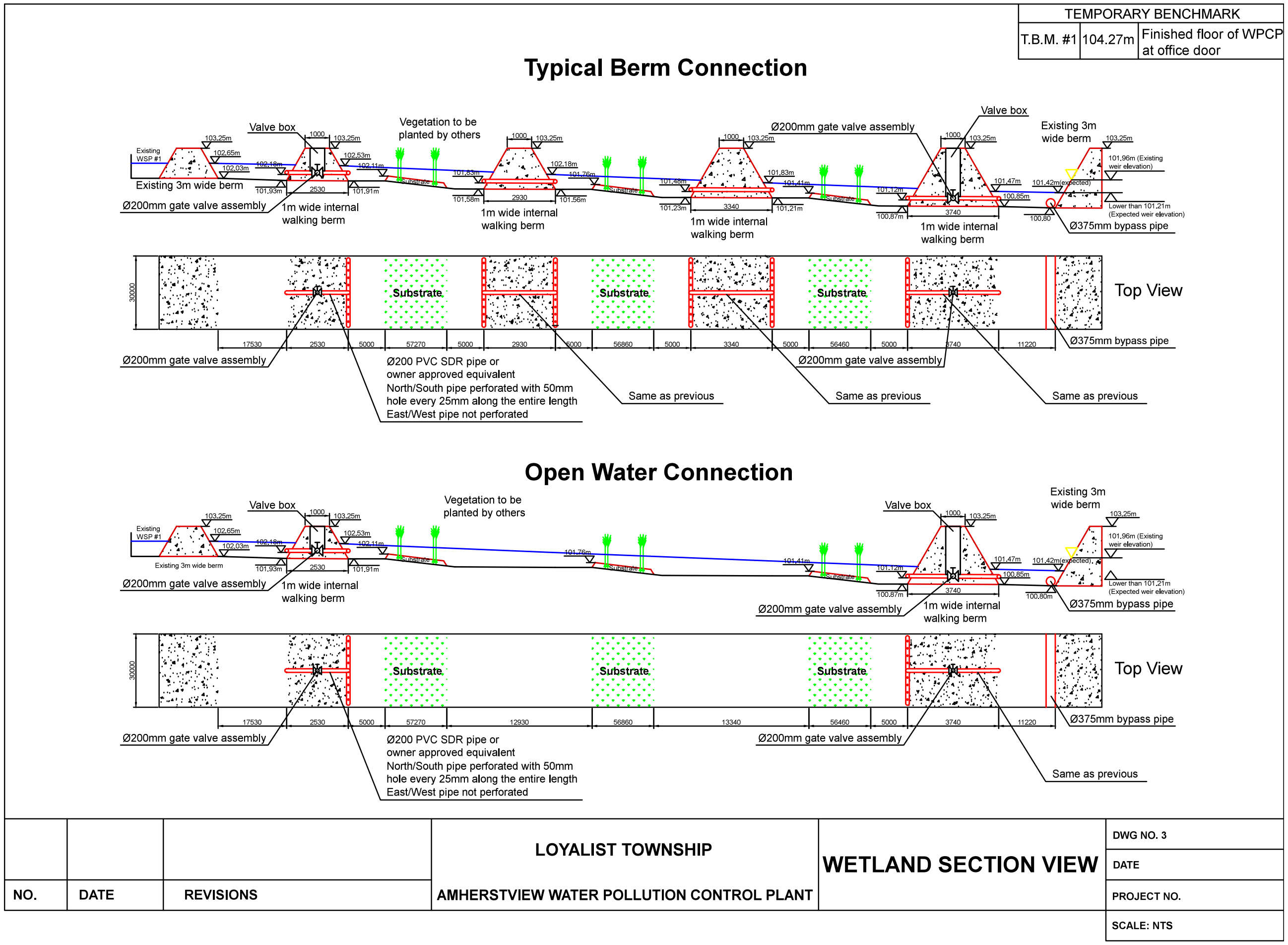
The overview AutoCAD design drawing of the pilot-scale free water surface flow constructed wetland at the Amherstview WPCP



NO.	DATE	REVISIONS	LOYALIST TOWNSHIP AMHERSTVIEW WATER POLLUTION CONTROL PLANT	WETLAND OVERVIEW PLAN	DWG NO. 2 DATE Project NO. Scale: NTS

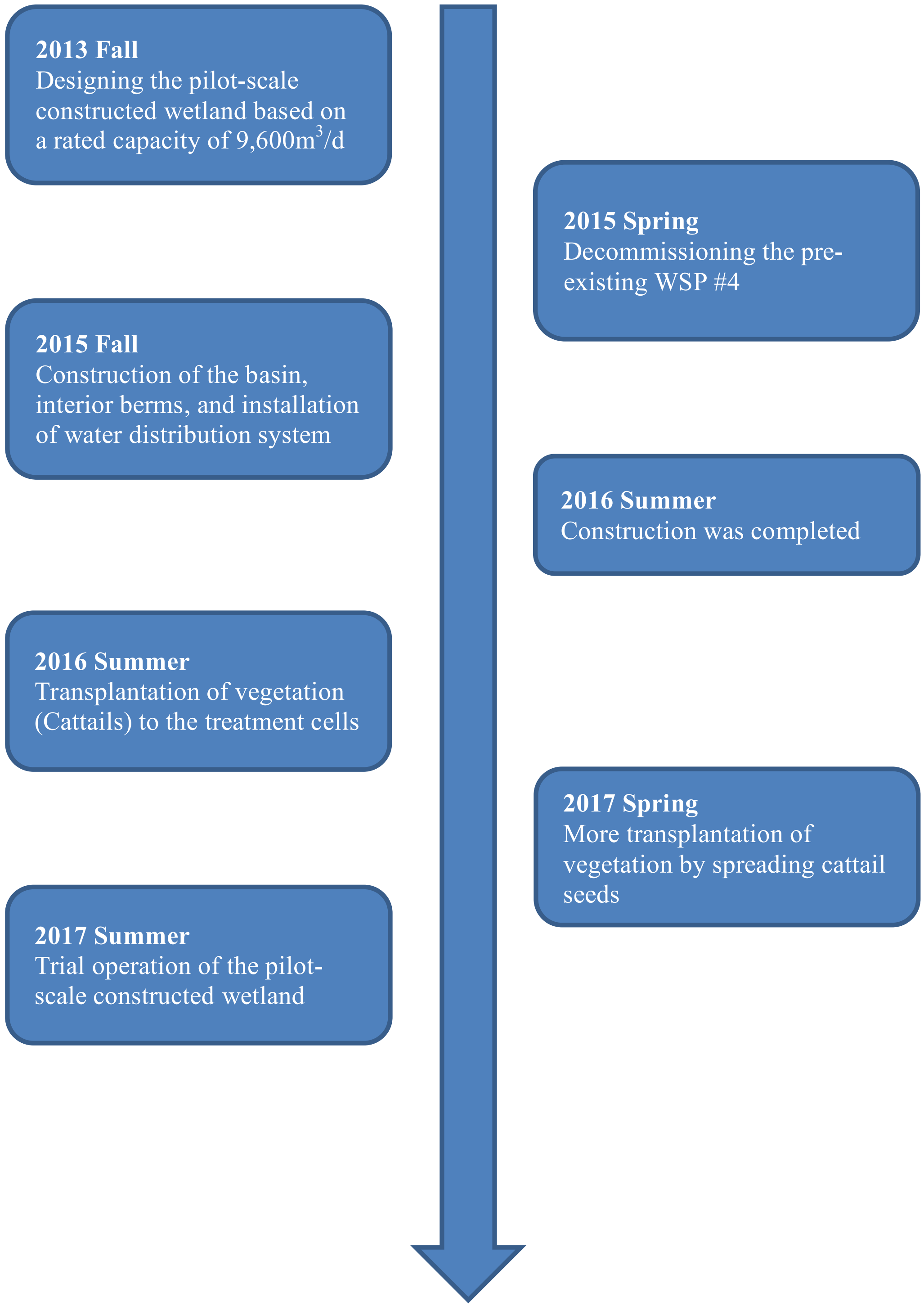
Appendix B

The section view AutoCAD drawings of the individual treatment train of both berm connection and open water connection



Appendix C

The timeline of the development and construction of the pilot-scale constructed wetland



Appendix D

Pilot-scale Constructed Wetland Photos

Figure D.1 Aerial image of pilot-scale constructed wetland at the Amherstview WPCP (1)

Figure D.2 Aerial image of pilot-scale constructed wetland at the Amherstview WPCP (2)

Appendix E

Application of vegetation transplantation

Project Overview

In Canada, there are more than 3,500 wastewater treatment facilities, ranging from small municipal system to large urban facilities. The use of waste stabilization ponds (WSPs) as part of a treatment regime is one of the least energy and operationally intensive treatment options available; however, WSPs can have performance concerns during certain parts of the year due to raised temperatures and high light levels, which may lead to effluent quality that does not meet regulatory discharge requirements set by Ministry of the Environmental and Climate Change (MOECC). The Corporation of Loyalist Township Utilities Unit (LTU) is one such municipality with a combined primary, secondary and WSP treatment system that is experiencing periods of elevated algae and pH levels which exceed regulatory requirements for the discharge of treated effluent into the environment.

A natural attenuation surface flow constructed wetland systems is proposed to augment the performance of existing WSPs by using native cattail species in order to attenuate high pH level in the effluent of the WPCP. This project is designed to shed new light on the mechanisms combining to create the conditions conducive for algal and pH increases while at the same time providing the evidence-base to guide effective planning and installation of constructed wetlands.

Project Status

A surface flow constructed wetland, with distinct treatment cell and trains (cells in series), is currently in its construction phase in the final treatment cell (WSP#4) at the Amherstview Wastewater Pollution Control Plant (WPCP) (Figure #1). A schematic of the constructed wetland is shown in figure 2.

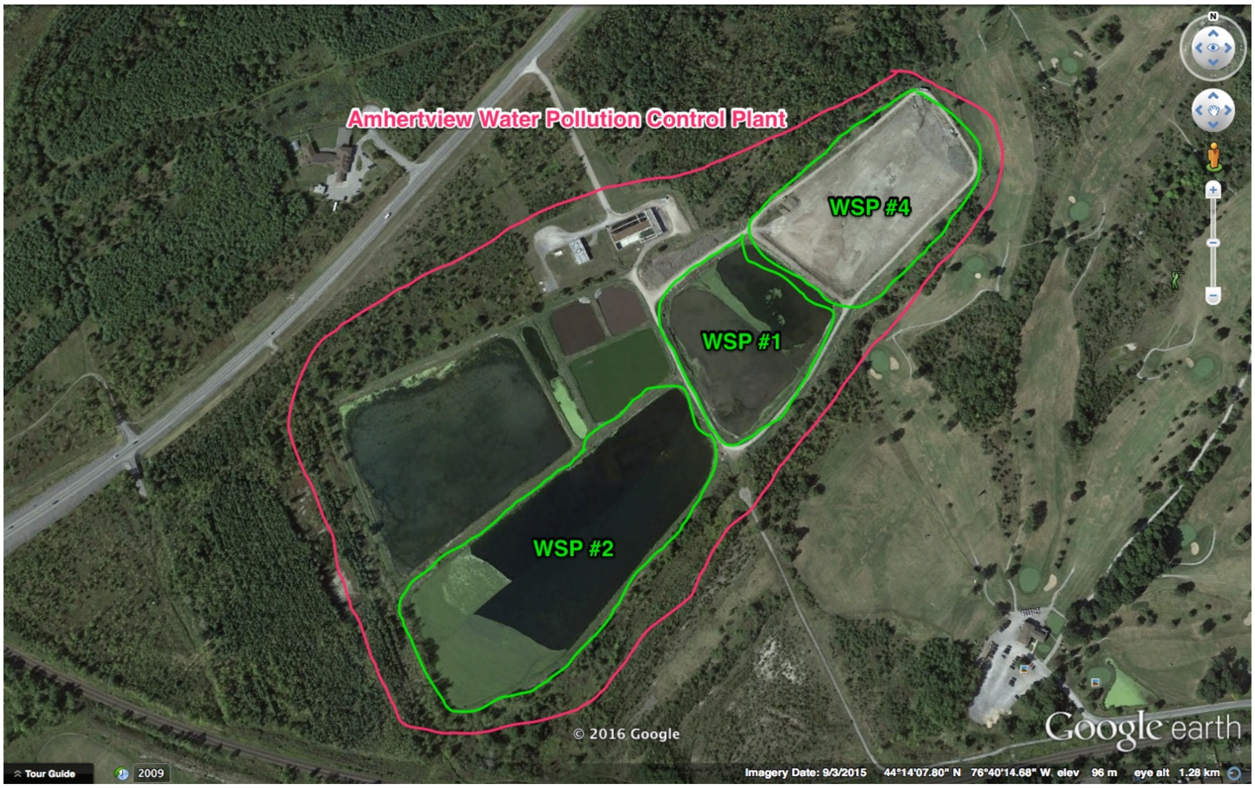


Figure E.3 Current layout of the Amherstview WPCP

The size of each wetland treatment cell is roughly 70m x 30m, with vegetation covering roughly 60m x 30m. One train of cells will provide a treatment area of approximately 6300 m^2 with a total potential treatment area of approximately 25200 m^2. The planting substrate in each cell will be 20cm in height and the free surface water will be 40 cm in height, for a combined height of 60 cm. The substrate materials for each treatment train are shown in the yellow box along with the type of connection of the cells in Figure 2. A distribution ditch is placed in front of the treatment cells in order to allow uniform distribution of influent to the treatment cells through the perforated pipe. A collection ditch is also designed to mix the effluent before final discharge.

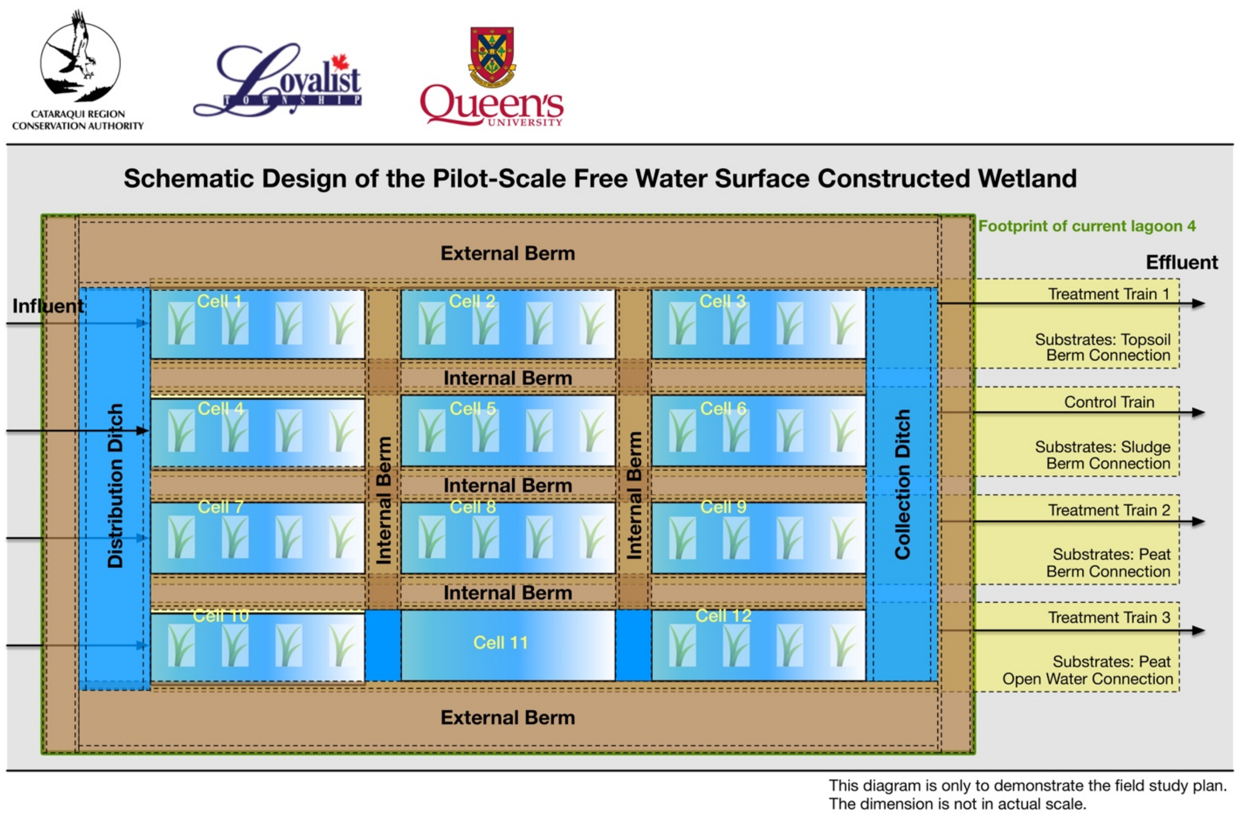


Figure E.4 Schematic Design of the Surface Flow Constructed Wetland

Collection and Transplantation of Plants

Cattails are a common wetland plant in the region and they are also widely used constructed wetland applications to provide additional treatment for municipal wastewater. The plants proposed for this constructed wetland come from a nearby wetland, resulting in donor material locally adapted to the conditions present at the

WPCP. Utilizing locally available cattails is important due to their acclimatization which may help in survivability of the plants after transplantation.

The proposed site to remove the cattails is located at the north-west corner of Taylor-Kidd Blvd at Coronation Blvd adjacent to the road allowance for Coronation Blvd across the Bayview Bog Wetland. The proposed area to remove the cattails are shown in both Figures 3 and 4. The total area of cattails removal will be approximately 450m wide by 6m deep, with a total area of approximately 2700m^2.

A backhoe or excavator provided by LTU will be used to remove the cattails and the harvested cattails will be transported to the WPCP by an LTU pickup or dump truck. Students from Queen's University will sort, prepare and plant the cattails in the constructed wetland.

There are twelve treatment cells in the constructed wetland and eleven of them are planned to be planted with cattails. The vegetation area of each treatment cell is approximately 60m x 30m (1800m^2) as mentioned above. The total vegetation area will be approximately 20,000m^2. The vegetation density is designed to be four rhizomes per square meters with a total of approximately 80,000 rhizomes of cattails required for this project. The density may be reduced depending the ultimate site conditions during planting. Both seeds broadcasting and rhizomes transplantation will be utilized. If the amount of cattails removed from CRCA property is not sufficient for this project, cattails from private land on the north side of the Coronation Blvd will be considered as a potential source. In that event, CRCA, Loyalist Township and Queen's University will contact the owner of that property to discuss the project and seek permission to remove plants.

Figure E.5 Location of the Amherstivew WPCP and the proposed cattail collection area

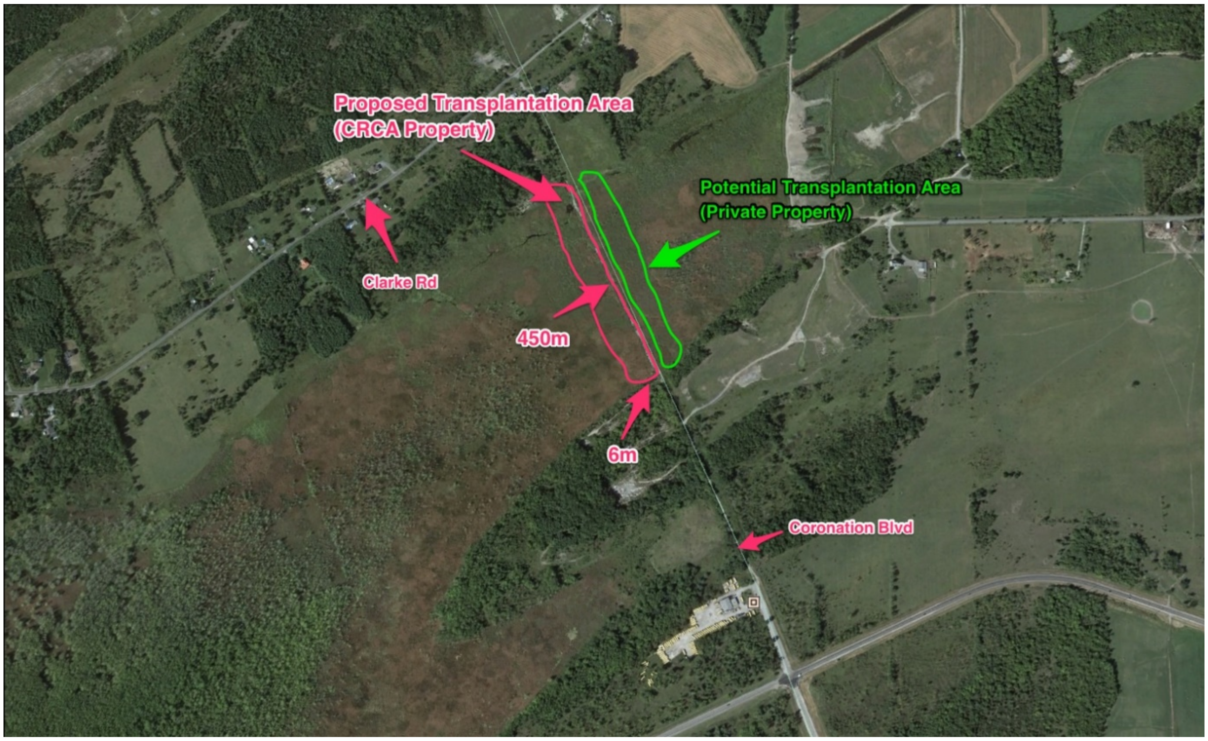


Figure E.6 Location of the cattail collection points within the Bayview Bog Wetland

Schedule

The proposed work is planned to begin during the month of July, 2016. This will occur once construction is complete. Planting is anticipated to take 2 to 3 weeks.

Benefits

The Bayview Bog Wetland contains a variety of fish species. In a 2008 survey, 14 different fish species were noted with the Bayview Bog Complex (Figure 5). Opening channels along the road allowance for Coronation Blvd will likely create habitat for many of these fish species, which otherwise may not inhabit the densely populated cattail areas. In addition, the creation of open water may also encourage aquatic bird species to use the area.

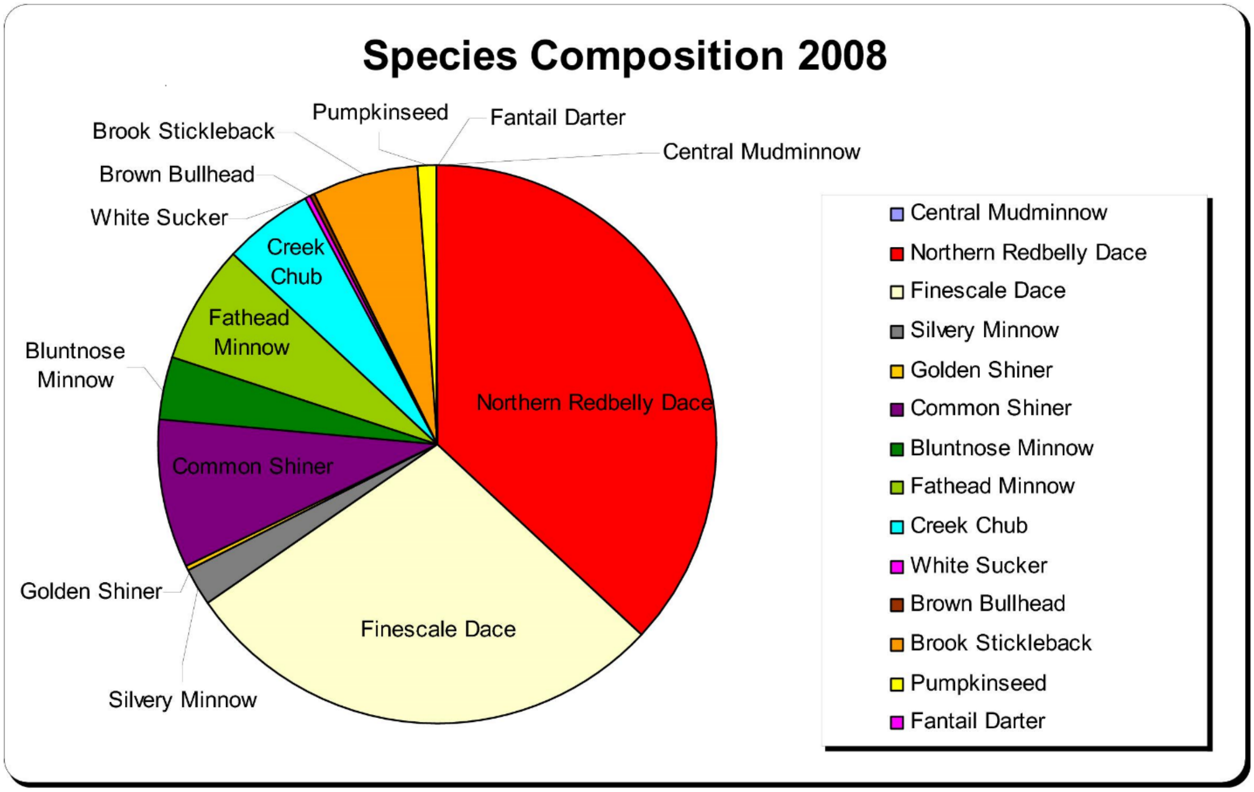


Figure E.7 Fish species noted in the Bayview Bog during a 2008 field survey