Comparison of two constructed wetland substrates for reducing phosphorus and nitrogen pollution in agricultural runoff

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June, 2008

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Science

Abstract

Phosphorus and nitrogen present in runoff from agricultural land is a primary freshwater pollution source in southern Quebec. The focus of this study was to optimize a constructed wetland for use as a best management practice and the specific aim was to determine if substrate type influences its phosphorus and nitrogen reduction capabilities. The pilot-scale constructed wetland site was located 3 km north of McGill's Macdonald campus in Ste-Anne-de-Bellevue, Quebec, Canada. Three tank replicates filled with sandy clay loam soil, and three with a sandy soil were planted with cattails (*Typha latifolia* L.) and reed canary grass (*Phalaris arundinaceae* L.). From July to September 2007, the tanks were flooded continuously with an artificial runoff wastewater, containing 10 mg N L^{-1} as nitrate 0.3 mg P L^{-1} as orthophosphate. Results show that there was no significant difference in P removal between the two soil types and both retained approximately 41%. The sandy clay loam soil outperformed the sandy soil in N removal, with 63% and 40% retained respectively.

Résumé

Le phosphore et l'azote présents dans les eaux de ruissellement provenant de terres agricoles constituent la source prédominent de pollution des eaux douces dans la partie méridionale du Québec. La présente étude visait à optimiser un marais artificiel en temps que pratique de gestion optimale, et, en particulier, à déterminer si le genre de substrat sous-jacent influence la capacité du marais à réduire phosphore et d'azote dans les eaux. Une série de marais artificiels construits à l'échelle pilote furent situés 3 km au nord du campus Macdonald de l'université McGill, à Sainte Anne-de-Bellevue, Québec, Canada. Des quenouilles (*Typha latifolia* L.) et de l'alpiste roseau (*Phalaris arundinacea* L.) furent plantés dans trois répétitions-réservoirs sous-tendus par un loam sablo-argileux, ainsi que dans trois autres sous-tendus par un sol sableux. De juillet à septembre 2007, les réservoirs furent inondés avec des eaux d'écoulement artificiels, contenant 10 mg N L^{-1} sous forme de nitrates et 0.3 mg P L^{-1} sous forme d'orthophosphate. Aucune différence significative ne fut notée entre les deux types de sol quant à l'élimination du P, les deux ayant retenu environ 41% de celui-ci. Quant à l'élimination de l'azote, le loam sablo-argileux surclassa le sol sableux, retenant 63% de l'azote, comparé à 40%.

This work is dedicated to Colin Yates

Acknowledgements

This study was made possible by the financial support of NSERC and Canada Fund for Innovation. I would first like to extend my deep and sincere thanks to my supervisor Dr. Shiv O. Prasher, not only for his instruction and guidance throughout the entire process, but for his faith in me and this project. I would also like to acknowledge Dr. Suzelle Barrington for lending her invaluable insight and expertise to this project.

A special thanks to Ms. Helene Lalande from the Soil Testing Laboratory in the Natural Resource Sciences Department, who was pivotal in the success of the laboratory work and was so kind during the process. Another special thanks to Kathy Zarayan, our own laboratory technician, whose perseverance and organizational skills were truly valued and respected.

Gratitude is extended to Dr. Roger Cue, who donated his patience and time to help me successfully analyze my results with SAS. Thanks also to Dr. William Hendershot for his valuable discussions about the results.

Recognition and thanks must also go to the summer students who spent long hours in the field, collecting samples and doing maintenance, as this project would not have been nearly as efficient without them: Laurent Huet whose moral support at the very beginning of the project was integral to its success, Miriam Lebeau, whose positive attitude never faltered, and Andreanne Lebrecque who always strove for success no matter the task. Recognition and thanks goes to Marie Manchester as well, who was instrumental in the success of the tracer study and never once complained no matter how hard it was raining. Thanks also to Dr. Yousef Karimi who helped get this project off the ground, and Thejashree Ramalingaiah, fellow grad student.

A heartfelt thanks goes to my partner Dean Parchomchuk for his undying support throughout this whole process. From digging soil in the middle of winter to drawing the site diagrams, he was always willing to help. And a final thank you to my parents, for their constant moral support.

Contribution of the authors

Charlotte Yates, a Master's student in the Bioresource Engineering department, was the primary investigator and writer for both papers. She was responsible for the design, execution and interpretation of the experiments presented here.

Dr. Shiv Prasher, Professor in the Bioresource Engineering department and professional engineer, assisted Charlotte with the experimental design, technical components of the experiments, and data interpretation. He facilitated the work at Macdonald campus and played a supervisory role throughout the entire project.

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1. Chapter 1- Introduction

1.1. The Problem

Globally, irrigation and fertilization of agricultural lands is placing increasing pressure on water quality and availability. Food production, with its attendant problem of phosphorus and nitrogen runoff into fresh water, is one of the largest contributors to declining water quality. The threat that agricultural nonpoint source pollution poses to freshwater reserves is eutrophication, a process whereby oxygen is depleted from the water, leading to outbreaks of potentially toxic blue-green algae. The algae ultimately renders the water unfit to support aquatic life, and unusable for human activities. Agriculture as a source of pollutants, and the social issues governing land and water use, are at the heart of the vastly complex issue of water quality deterioration around the world.

In North America, phosphorus, and nitrogen to a lesser extent, have been deemed the primary cause of surface water quality deterioration (USEPA, 1998; MENV, 2002), with an estimated 70% of the phosphorus entering lakes in Quebec coming from agricultural nonpoint sources. A particularly sensitive watershed in Quebec is Missisquoi Bay, located on the northeast corner of Lake Champlain, where 79% of the phosphorus loads entering is coming from the 26% of the watershed that is used for agriculture (Michaud *et al.*, 2005). Lake Champlain is one of the largest lakes in North America and is shared between the province of Quebec and the states of Vermont and New York. The three stakeholder groups recently signed an agreement establishing phosphorus load reduction goals to be realized by 2009 (MENV, 2002). In order to reduce the P concentration of Pike River, its main tributary on the Quebec side of the border, it is estimated that an annual reduction of 28 tons of phosphorus is necessary (Adhikari *et al.*, 2007).

1.2. Justification

Agricultural best management practices aimed at controlling nonpoint sources of phosphorus and nitrogen are classified in into two main groups: (1) prevention- at the level of soil management in terms of fertilizing and tillage practices to reduce loss, and (2) correction- through the reduction of nutrients from water leaving the field via filtration structures (Kronvang *et al.*, 2005). One such filtration structure is the constructed wetland. Constructed wetlands can be used in a wide variety of applications to treat waste water; and their use in treating agricultural nonpoint source pollution specifically, is gaining interest (Braskerud, 2002a). Constructed wetlands are an interesting nutrient mitigation strategy because of the low capital investment required for development and because they operate on the basis of harnessing processes endemic to natural wetlands.

One of the challenges in designing a constructed wetland is aligning it with the local conditions in order to maximize its efficiency. In other words, constructed wetlands must be designed specifically for outcomes needed in each region in which they are to be implemented.

This thesis is concerned with testing a pilot-scale constructed wetland to assess its efficiency at reducing phosphorus and nitrogen from agricultural runoff typical in Quebec. More specifically, we were interested in the influence on phosphorus and nitrogen retention within the wetland by two different soil substrates common in southern Quebec, in an effort to optimize the design as a best management practice in Quebec.

1.3. Site location

Field measurements were made at the pilot-scale, surface-flow constructed wetland research site, located 3km north of McGill University's Macdonald Campus in Ste-Anne-de-Bellevue, Quebec, Canada. The site consisted of six open ditch-style tanks; three filled with a sandy soil and the other three with a sandy clay loam field soil (Figure 1.1).

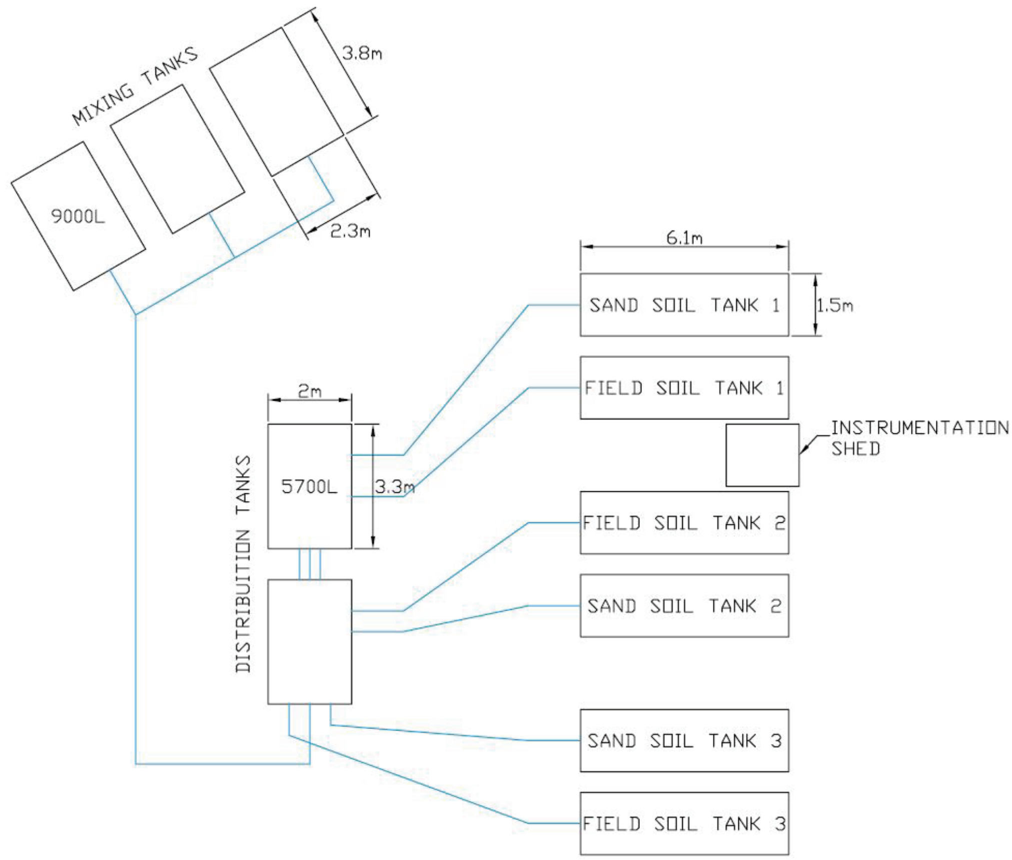

Figure 1.1. Constructed wetland research site diagram. (Not to scale).

Each treatment tank was planted with reed canary grass (*Phalaris arundinaceae* L.) and cattails (*Typha latifolia* L.), and the water flowed from the deep zone, through the shallow vegetated section to the outlet (Figure 1.2).

A simulated agricultural runoff solution containing 0.3 mg P L^{-1} as dissolved phosphorus and 10 mg N L^{-1} as nitrate, was flooded through the system continuously for three months. Measurements were taken to assess the efficiency of the load reduction and discern the processes by which this occurred. The P concentration of 0.3 mg L^{-1} was chosen because it was 10 times greater than the threshold level of 0.03 mg TP L^{-1} permitted to enter surface waters as determined by the Quebec Ministry of Environment (2001). Levels found in non point source agricultural runoff in Southern Quebec have been found above the 0.3 mg L^{-1} (Eastman, 2008). The nitrogen concentration of 10 mg N L^{-1} was chosen because it is the maximum allowable concentration in drinking water, however it has been shown to be ecologically harmful at concentrations as low as 0.4 mg N L^{-1} in marine environments (Casey and Klaine, 2001).

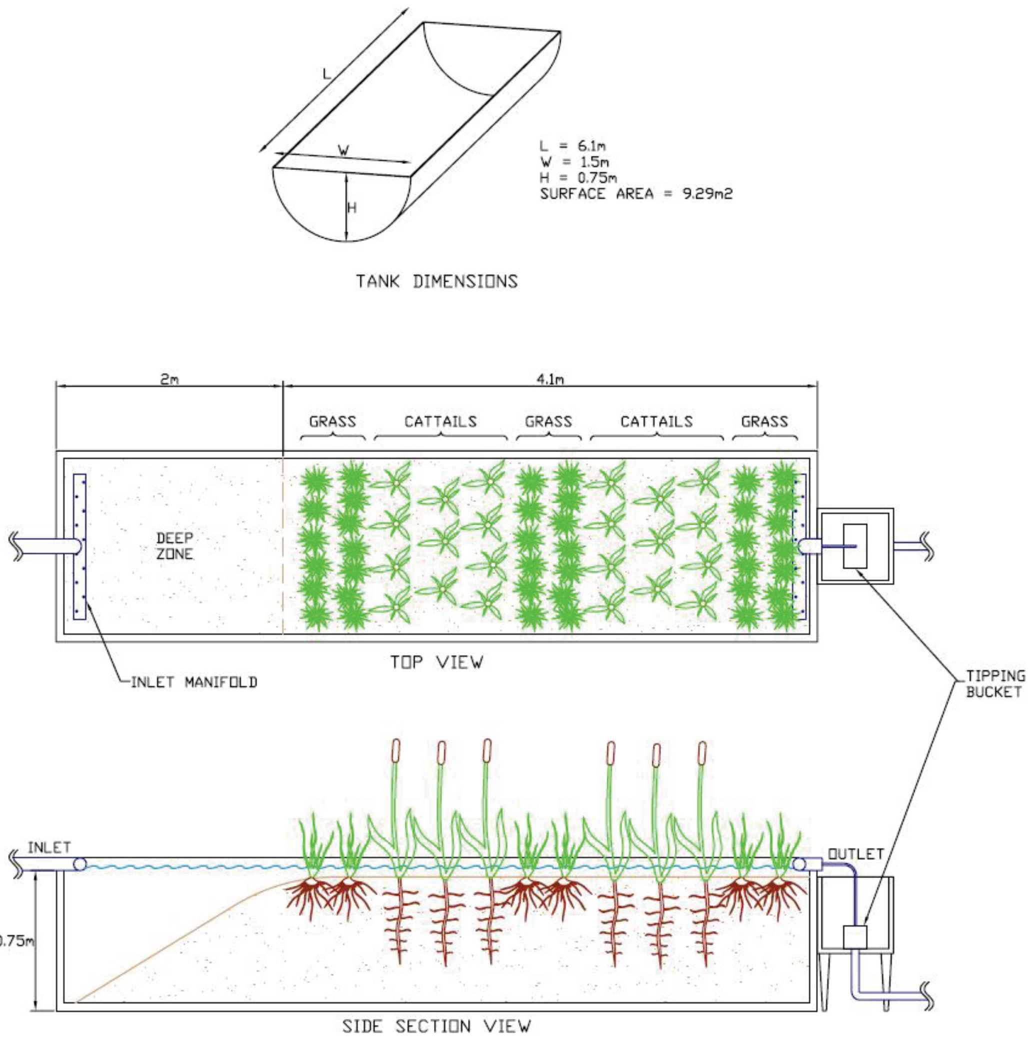

Figure 1.2. Side view and top view of the six soil treatment tanks.

1.4. Objectives

The goal of this work was to provide design criteria for constructed wetlands treating agricultural nonpoint source pollution in Quebec. This study was designed to determine if there was a difference in the ability of two soil types common to Southern Quebec to impact the ability of a surface flow constructed wetland to reduce dissolved phosphorous and nitrogen from a simulated agricultural runoff solution.

The primary objectives were:

1. To discern the dominant phosphorus removal mechanisms occurring within the wetland tanks of each soil type, a sandy clay loam field soil, and a sandy soil,
2. To determine the hydraulic residence time of the wetland tanks and to measure if there was a difference in residence times between soil types,
3. To discern the dominant nitrogen removal mechanism occurring within the wetland tanks of each soil type, and
4. To determine if the conditions necessary to promote denitrification were achieved, and if they differed between the two soil types.

1.5. Thesis Format

Chapter two is a literature review of studies addressing the issue of agricultural nonpoint source nutrient pollution and how constructed wetlands function to remove nutrients from runoff. The objectives listed above were met by carrying out field measurements at the constructed wetland research site from July-October 2006 and June-October 2007. The results of the objectives are presented in two scientific papers and it is the intention of the authors to submit them for publication to peer reviewed scientific journals.

The first two objectives are presented in Chapter three entitled 'Dissolved Phosphorus Reduction from Agricultural Runoff in a Surface-Flow Constructed Wetland'. This paper discusses the phosphorus removal efficiencies by both soil types and how the physico-chemical conditions within the tanks impacted the wetland's ability to adsorb and retain phosphorus. It also discusses the results of a conservative tracer test carried out to determine the mean hydraulic residence time of the treatment tanks.

The last two objectives are presented in Chapter 4 entitled 'Comparison of Two Constructed Wetland Substrates for Reducing Nitrogen Load from Agricultural Runoff'. This paper presents the nitrogen removal capacity of the wetlands with the two different soil types and also explores how the physico-chemical conditions influenced these results. It also assesses if there was a difference in the production of the denitrification by-product nitrous oxide, between the two soil types and the impact on nitrogen removal.

1.6. Scope

The research was carried was out in a controlled, pilot-scale wetland site. The site was exposed to environmental climatic conditions however the simulated agricultural runoff solution was very closely controlled to meet the inflow target concentration of 0.3 mg P L^{-1} and 10 mg N L^{-1}. Runoff nutrient concentration at the field scale varies with precipitation and irrigation events, as well as fertilizer application schedules. The concentrations chosen for this study represent the high end of what is found in field scale runoff therefore the loads are realistic. It is possible that once the system is scaled up, it will require further optimization to deal with variable flow rates and concentrations.

2. Chapter 2- Literature Review

2.1. Nonpoint Source Pollution

There are many sources of pollution that led to both surface and ground water quality deterioration; they are generally classified as either point source or non-point source (NPS). Point source pollution is any defined waste stream, either from an industrial, municipal or agricultural source. NPS pollution is water pollution that does not originate from a defined point, but is generated as a by-product of land use practices such as farming, timber harvesting, construction, mining and urban development.

Pollutants such as sediment, fertilizers and pesticides are transferred from land to surface water and ground water by precipitation, runoff or leaching (Zucker *et al.*, 2008). While there has been progress made in treating and controlling point sources of pollution in recent years, identifying and treating NPS has posed a far greater challenge. The difficulty arises in isolating the contribution of dispersed sources in a scientific manner, particularly in areas of intensive agricultural operations (Berka and Schreier, 2001).

2.2. Global Water Quality and Agriculture

Water quality deterioration is a global issue that affects every single person on earth. According to the International Fund for Agricultural Development's Rural Poverty Portal, 70% of all available freshwater is used for agriculture and 37% of the Earth's land area is used for pasture and crops (IFAD, 2008). Over-pumping of groundwater by the world's farmers exceeds natural replenishment by at least 160 billion cubic meters a year and agricultural land area has increased 12% since the 1960s, equivalent to 1.5 billion hectares (IFAD, 2008). As the global demand for food continues to intensify, so does the necessity for irrigation and chemical inputs, leading to poor drainage, over-pumping of groundwater and over-use of fertilizers and pesticides (IFAD, 2008). The combination of these pressures exacerbates the resulting agricultural NPS pollution. The necessity to produce more and more food is increasing pressure on the world's water resources and it is up to its stewards to discover ways to make food production a sustainable endeavor.

Agricultural NPS pollution is usually in the form of runoff containing excess nutrients such as nitrogen and phosphorus, as well as pesticides. The threat to water resources caused by agriculturally sourced NPS pollution is worldwide, as demonstrated by reports of declining water quality due to nutrient overloading from around the globe (Raisin and Mitchell, 1995; Casey and Klaine, 2001; Kivaisi, 2001; Healy and Cawley, 2002; Kronvang *et al.*, 2005; Michaud *et al.*, 2005; Aye *et al.*, 2006; Litaor *et al.*, 2006; Gentry *et al.*, 2007). NPS phosphorus (P) and nitrogen (N) affect water quality in rivers, lakes, estuaries and coastal ocean zones. In freshwater lakes, excess nutrients, and P in particular, cause eutrophication (Carpenter *et al.*, 1998) In estuarine environments, excess N can be toxic to seagrass which is a vital component to marine ecosystems (Casey and Klaine, 2001).

Eutrophication, the process whereby a body of water becomes rich in dissolved nutrients, results in the overgrowth of algae and weeds. The decomposition of over-abundant plant life leads to a deficiency of dissolved oxygen, effectively rendering the water inhospitable to aquatic life. In the case of freshwater lakes, cyanobacteria outbreaks may occur, preventing any anthropogenic use of the lake such as drinking the water, swimming or fishing (Sharpley, 1995).

2.3. Agricultural NPS Pollution in North America

In North America, agricultural NPS pollution is considered one of the main causes of water quality deterioration and in 1996 the USEPA declared P the primary cause of surface water pollution in the US (USEPA, 1998). In Quebec, nonpoint source P has been deemed the main source of P in Quebec surface water bodies (Ministry of Environment of Quebec, 1999). The Quebec Provincial Government imposed a maximum P concentration in Quebec rivers of 0.03 mg L^{-1}, however levels as high as 0.2 mg L^{-1} have been found in Quebec agricultural watersheds (Adhikari *et al.*, 2007).

The Missisquoi Bay watershed, which is located on the northwest corner of the Canadian section of Lake Champlain, is a particularly overloaded watershed. The water quality standard set by the Missisquoi Bay Phosphorus Reduction Task Force is 0.025 mg L^{-1} (Adhikari *et al.*, 2007). Pike River, which is a major tributary to the Missisquoi Bay, has a mean annual load of 28 tons of P which is 70% higher than what would be required to achieve the water quality standard of 0.025 mg L^{-1}. Approximately 26% of the Missisquoi watershed is agricultural land and yet it is estimated that 79% of this load is coming from agricultural non-point sources (La Flamme *et al.*, 2004; Michaud *et al.*, 2005). Therefore, reducing P in runoff has become a primary objective to combat surface water quality deterioration in Quebec. Excess nitrogen contributes to eutrophication and decline in water quality as well; however P is considered rate-limiting to freshwater algae (Braskerud, 2002b).

2.4. Mechanisms of NPS Pollution

Agricultural intensification has led to the steady increase in P and N application to fields, in both chemical fertilizer and manure form. As a result, the surplus P and N content of the soil amplifies its vulnerability to loss via leaching and erosion (Berka and Schreier, 2001; Kronvang *et al.*, 2005). In areas where intensive livestock farming occurs, excess manure is often spread on fields even when the crops do not require added additional nutrients. Surface soil accumulation of P due to continuous application of manure and/or chemical fertilizer has increased to such a level that P loss management has become a priority (Sharpley, 1995). Surplus fertilizer application for cash crops such as corn and soybeans is common and in British Columbia's Sumas River Watershed, surplus N application (as manure and fertilizer) of 300 kg ha^{-1} have been observed (Berka and Schreier, 2001).

While surface-flow runoff and erosion are known export pathways of P and N, it is important to mention the contribution of tile-drainage. Subsurface drainage, also known as artificial or tile-drainage is necessary in areas where the soil is poorly drained. This is the case in much of southern Quebec where upwards of 700,000 ha is necessarily tile-drained. Studies from central Illinois and the American Cornbelt have quantified nutrient losses from tile drains; for example between 1993 and 1996, P loss to, the upper Embarras River, where 70-85% of the land is tile drained, was estimated at 0.9 kg ha^{-1} yr^{-1} with 46-59% of the dissolved P resulting from tile drainage. N losses averaged 39 kg ha^{-1} yr^{-1} and 68-91% was attributed to tile-drain loss (Kovacic *et al.*, 2000). Work is currently being conducted in the Missisquoi watershed to estimate the relative contributions of surface and subsurface flow.

2.4.1. Mechanisms of Nitrogen Loss in Runoff

Dissolved nitrogen is lost from fields primarily as dissolved nitrate due to its highly soluble nature. It can be leached out through subsurface drains or overland as surface runoff. Although artificial drainage is necessary to lower water tables in poorly drained soils in order to farm them, it also forces NO_3^- laden drainage water more rapidly and directly to receiving water bodies (Kovacic *et al.*, 2000). Nitrogen fertilizer is most often applied as ammonia (NH_4^+); however, it is microbially oxidized to nitrite (NO_2^-) then nitrate (NO_3^-) ions within approximately 2 days. While ammonia is also highly soluble in water, its cationic nature allows it to bind loosely with cation exchange sites within the soil column, thus decreasing its likelihood of being washed away. Nitrate leaching occurs more readily during periods of slow or no crop growth and especially when coupled with high volumes of percolating water (Miller and Gardiner, 1998).

2.4.2. Mechanisms of Phosphorus Loss in Runoff

Phosphorous loss from agricultural fields occurs in dissolved and particulate form. Overland flow is generally the dominant mechanism for P loss from agricultural fields; however, subsurface flow from tile drains has also been found to be an important transport conduit (Gentry *et al.*, 2007). The concentration of P in drainage water is heavily influenced by the soil P status and its capacity to retain phosphates (Aye *et al.*, 2006). The phosphate retention capacity is affected by soil particle size and P buffering capacity of the soil (Sharpley, 1995). Dissolved inorganic phosphorous is also known as soluble reactive phosphorus (SRP), dissolved reactive phosphorus (DRP) and sometimes as orthophosphate (ortho-P). Collectively they refer to bioavailable dissolved P and include inorganic phosphate ions $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} (House *et al.*, 1995). Particulate P on the other hand, is P bound to clay particles that are physically washed off the fields and deposited wherever and whenever the water velocity is slowed enough for the particles to settle out (Braskerud, 2002b).

2.5. Best Management Practices

Mitigation strategies, otherwise known as Best Management Practices (BMPs), to combat nutrient loss from agricultural fields are split into two main groups: (1) soil management and the reduction of nutrient input to agricultural land, and (2) reduction of nutrient loss from high risk areas via filtration structures (Kronvang *et al.*, 2005). In an effort to reduce loss by erosion and leaching, soil nutrient levels can be managed through regular soil testing, type of fertilizer input, timing of the input, and incorporation and tillage practices (Gentry *et al.*, 2007).

In response to the public demand for action at the government level to help regulate water quality issues, the Quebec Ministry of Environment issued a Quebec Water Policy directive in 2002 highlighting five key orientations with the supporting courses of action and associated government commitments (MENV, 2002). In Orientation 4, ‘Continued Clean-up and Improved Management of Water Services: Recovering Lost Uses’, the government of Quebec states that it will introduce a strategy for cleaning up watercourses at the watershed level. This, they proclaim, includes intensifying agricultural clean-up efforts by investing in soil support capacity, establishing wooded riparian corridors and pesticide management.

The Quebec government has also established a moratorium on any new pig farming operations in an effort to directly address the issue of P surpluses in surface water, and restrict the environmental impact of this industry.

Farm scale BMPs aimed at reducing nutrient loads from runoff include riparian buffer strips, sediment control basins at surface inlets, grassed waterways, water table management and constructed wetlands (Michaud *et al.*, 2005; Stämpfli, 2006).

2.5.1. Constructed Wetlands as a Best Management Practice

Constructed wetlands are an interesting BMP for targeting nutrient reduction from NPS agricultural runoff because the concept can be implemented in many different situations and built with materials available locally (Casey and Klaine, 2001; Aye *et* *al.*, 2006). The convergence point of surface drainage ditches or tile-drain outlets are likely positions for constructed wetland construction in order to trap the water and treat it before it escapes to the receiving water bodies. Constructed wetlands have been described as 'environmentally sensitive and cost-effective treatment systems for wastewater renovation' (Hench *et al.*, 2003). They can also can be thought of as 'ecological engineers' (Tanner, 1996) because the concept involves supplying the necessary components and capitalizing on the naturally occurring wetland processes to reduce the targeted pollutants. By understanding the components necessary to optimize these processes, including the hydrology, soil, vegetation and associated microbial populations, it is possible to design and construct efficient, low-cost wastewater treatment systems (Vymazal, 2005).

2.6. Constructed Wetland Design Components

Constructed wetlands contain all the components found in natural wetlands except with the option to control the location of the inflow and the outflow. The flow regime and hydrology, soil substrate, vegetation and microbial communities all make up a wetland ecosystem and it is up to the designer to optimize the combination of all those components in order to maximize nutrient removal.

2.6.1. Constructed Wetland Flow Regimes

Constructed wetlands (CWs) can be classified into two general categories based on flow regime: surface-flow and subsurface-flow (Hammer, 1992). They can then be subdivided based on vegetation into either emergent or submerged plants (Vymazal, 2005). The most common design used for treating agricultural runoff is a surface-flow, emergent vegetation design. This is often referred to in the literature as FWS, or free water surface constructed wetlands. Subsurface-flow with emergent vegetation designs are often seen in studies treating point source agricultural waste streams. The main difference between surface and subsurface-flow designs is the positioning of the outlet pipe. In surface-flow CWs, the inlet and outlet are placed at the same level, whereas in the subsurface-flow designs, the outlet is placed below the level of the inlet, forcing the water to flow through the substrate before it exits (Kadlec and Knight, 1996).

Surface-flow constructed wetlands are usually the design of choice for treating agricultural runoff because of lower installation costs and hydraulic simplicity as compared to subsurface-flow designs (Yang *et al.*, 2001). Surface-flow CWs generally allow for particulate settling to occur without threat to the hydrology of the system. In subsurface-flow CWs, clogging of the substrate can be a problem. In systems where the oxidation-reduction potential is low, clogging may occur from biofilm growth on the substrate particles and it may also occur if the incoming water is high in particulate matter. Where dissolved P is the primary target nutrient for reduction, subsurface-flow designs with high-adsorption capacity substrates are usually studied (Jenssen *et al.*, 2005).

2.6.2. Constructed Wetland Hydrology

Treatment efficiency of constructed wetlands is directly linked to the hydraulic efficiency and therefore the amount of time the polluted water spends in the wetland system (Kadlec, 1994; Werner and Kadlec, 2000; Dierberg *et al.*, 2005). For the sustainable and long term operation of constructed wetlands, it is essential that the hydrologic regime entering the wetland, as well as the within-wetland flow dynamics, be optimized.

2.6.2.1. Hydraulic Efficiency of Constructed Wetlands

One of the major contributors to poor wetland performance (in terms of contaminant removal) is poor system hydrodynamics. Hydraulic efficiency is maximized when full use of the available storage within the wetland is utilized (Persson *et al.*, 1999).

For constructed wetland design, theoretical retention time is based on plug flow assumptions. The theoretical retention time of a constructed wetland system involves a simple calculation of volume divided by flow rate; however, this fails to take into account the hydrological influences in the system which govern water movement patterns and therefore the treatment time (Kadlec and Knight, 1996). Because of uncertainty in exact depth distribution, coupled with variable inflow rates, the volume of a wetland is difficult to quantify; therefore, a tracer study can be extremely useful in experimentally determining the residence time distribution.

From the residence time distribution the mean residence time can then be determined from the centroid of the distribution curve. This is the average amount of time each parcel of water spends in the wetland. Tracer test results are useful in distinguishing the difference between the theoretical and actual retention times, as well as highlighting the possible hydraulic influences such as the active volume of the wetland.

A primary factor influencing the residence time distribution is the water movement patterns within the wetland (Werner and Kadlec, 2000) which are dictated by the soil substrate, vegetation and bottom topography. This phenomenon has been described as 'velocity heterogeneity'. Ideally the spread of the residence time distribution, or velocity heterogeneity, should be reduced to maximize treatment efficiency (Wörman and Kronnäs, 2005). In subsurface-flow designs, the influence of soil substrate on retention time is dictated by the hydraulic conductivity of the soil. The conductivity of the clean substrate can be reduced over time due to blockage of pore space through the accumulation of organic materials such as plant roots. In surface-flow wetlands, the influence of the soil substrate is generally considered indirect as it affects the vegetation and microbial growth, which in turn influence the hydraulic retention time (Kadlec and Knight, 1996).

Preferential flow paths which cause short-circuiting of the water often plague constructed wetlands, negatively impacting the residence time and therefore the treatment efficiency. Preferential flow paths are influenced by stagnant regions, velocity gradients and physical obstructions within the wetland, often resulting in an actual retention time that is less than the theoretical retention time (Shilton and Prasad, 1996; Smith *et al.*, 2005c).

Short-circuiting, also known as channelization, has been shown to be reduced by incorporating transverse deep zones as bottom topography of a constructed wetland is highly influential on the hydraulic residence time.

2.6.2.2. Constructed Wetland Bottom Topography

Deep zones reduce incoming flow rates and aid the distribution of the water which alleviates short-circuiting and maximizes hydraulic residence time (Simi and Mitchell, 1999). Deep zones also direct flow distribution laterally, increase the wetland volume, and promote passive aeration of the water column.

There is evidence that deep zones interspersed with shallow marsh zones has been demonstrated to positively impact mixing. As well, despite the lower volumetric removal rate within deep zones, their presence may decrease the outlet concentration thus improving the wetland performance (Lightbody *et al.*, 2007).

Lightbody *et al.,'s* (2007) study pointed out however, that the location of the deep zone is important. They observed channelization mitigation when a deep zone was placed in the middle of the wetland but no effect from a deep zone placed at the outlet end of the wetland.

Deep zones incorporated in the bottom topography may also increase mixing (Simi and Mitchell, 1999). Kadlec and Knight (1996) explain that the intensity of mixing within the wetland increases with water velocity. It is likely that the degree of mixing is positively associated with increasing the active volume, also referred to as the effective volume ratio. Effective volume ratio is the measured retention time divided by the theoretical retention time. For open water surface flow wetlands, an effective volume ratio, or active zone, of 70% or greater is considered very good. Some researchers argue that any discrepancy between the mean and theoretical hydraulic residence time (ie an effective volume ratio of less than 1) warrants design optimization (Smith *et al*., 2005a).

2.6.2.3. Vegetation Distribution in a Constructed Wetland

In addition to incorporating deep zones within vegetated shallow zones, another proposed design consideration to reduce short-circuiting and dead-zones, is the spatial distribution of vegetation (Jenkins and Greenway, 2005). Wetland cells with greater length to width ratios have been cited to increase hydraulic efficiency (Persson *et al.*, 1999; USEPA, 2000), though Jenkins and Greenway (2005) have suggested that hydraulic efficiency will not be significantly influenced by the length:width ratio in densely vegetated wetlands where channelization is present. They also argue that it is the spatial distribution of vegetation characteristics that are most influential on flow dynamics. A banded pattern across the wetland cell increases hydraulic efficiency drastically they contend, while fringing vegetation lengthwise along the cell promotes channelization, thus greatly reducing hydraulic efficiency.

It has also been suggested that eliminating corners from the traditional rectangular shaped design may help reduce the occurrence of dead-zones within the wetland (Smith *et al.*, 2005a), as well as incorporating an inflow manifold that distributes the incoming water at the inflow (Dierberg *et al.*, 2005; Smith *et al.*, 2005a). The effectiveness of a manifold was demonstrated by a tracer test study conducted on a gravel bed wetland with and without a distribution manifold; the results indicated a 20% increase in residence time when the inflow manifold was used (Shilton and Prasad, 1996).

Shallow areas with emergent vegetation have also been shown to encourage rapid particle settling from incoming water while vegetation cover reduces the risk of sediment resuspension by wind shear (Braskerud, 2002b).

2.6.2.4. Constructed Wetland Flow Models

Developing mathematical models to describe hydraulic regimes and contaminant removal kinetics continues to be a popular research area and advances are being made in understanding the hydraulic influence on contaminant removal mechanisms. Chemical engineering equations for plug-flow reactors (PFR) and continuously stirred tank reactors (CSTR) (Levenspiel, 1999) have been adopted to describe and model fluid dynamics within wetlands (Keefe *et al.*, 2004). CSTR assumes instantaneous dispersion of the fluid within the wetland, and PFR assumes the inflow water moves along the wetland as a ‘plug’ with no longitudinal mixing occurring (Levenspiel, 1999).

Original attempts by the USEPA at modeling fluid behavior in wetlands were based on ideal PFR theory with results considered inaccurate by several groups during the early to mid-1990s (Werner and Kadlec, 2000). More recently, studies aimed at combining PFR and CSTR to describe mixed and unmixed zone interactions are emerging. In reality, water flow within constructed wetlands is 'non-ideal'; somewhere between plug-flow and continuously stirred, resulting in water parcels remaining in the wetland for varying amounts of time.

Tracer tests can be used to physically determine the residence time distribution of the water within the constructed wetlands from which these models are based. From this information researchers are developing models to describe non-ideal flows and coupling them with contaminant decay kinetics to ultimately estimate and predict treatment efficiency (Kadlec and Knight, 1996; Werner and Kadlec, 2000; Carleton, 2002; Keefe *et al.*, 2004). Contaminant decay rates have been shown to be dictated by inflow concentrations and volumetric flow rates (Kadlec and Knight, 1996). Despite the varying wastewater constituents and local environments within which they must be treated, the USEPA (2000) and Canadian Ministry of Environment (2007) have specified a hydraulic residence of time of 5-6 days for free water surface (FWS) constructed wetlands treating municipal wastewater. The NRCS (1991) has suggested 12 days for the treatment of agricultural wastewater. These guidelines however have been developed based on effluent target rates for biological oxygen demand (BOD_5) and total suspended solids (TSS), and are geared towards defined point source waste streams. There are no specifications to date on the necessary hydraulic retention time for constructed wetlands treating diffuse agricultural wastewater.

2.6.3. Effect of Soil Type in a Constructed Wetland

The substrate used to construct a treatment wetland is extremely important as it is the foundation for all the abiotic and biotic components present within the system (Kadlec and Knight, 1996). The physical and chemical structure of the soil influences the internal chemical and biological processes common in wetlands. The ability of the soil to function as a sink for contaminants varies depending on the physico-chemical conditions within the system (Novak *et al.*, 2004).

Phosphorus adsorption capacity of soils is often of interest in the design of CWs due to its potential role as a P sink. The P-binding capacity of a soil usually increases with clay and mineral content; more specifically Fe, Al and Ca and its quantity of exchangeable cations (Vymazal, 2007). However, parameters such as pH, dissolved oxygen and oxidation-reduction potential (ORP) will largely influence the P-exchange processes between the soil and water interface (Lijklema, 1980).

Under oxidized conditions, adsorption and precipitation reactions between soil cations and dissolved P are favored and are the dominant P retention mechanisms. Ca-P compounds are favoured under alkaline conditions and Al-P and Fe-P compound formation is dominant in acidic conditions (Novak *et al.*, 2004). P research into adsorption curves of various soil types has demonstrated that soils eventually reach a saturation point. Exceeding a wetland's P adsorption capacity can result in P release to the receiving water bodies. A larger cation exchange capacity of the soil prolongs the time until saturation is reached. (Del Bubba *et al.*, 2003) suggest that the best way to sustain a soil's long term P removal is to amend it with a high-binding mineral such as calcium to promote precipitation which produces insoluble phosphates.

Studies in the Netherlands and New Zealand have also explored the addition of Fe to riparian soils to precipitate out soluble P in order to prevent it from being leached in the runoff (Kronvang *et al.*, 2005; Aye *et al.*, 2006). The authors of both studies explain that due to the limited capacity of soils to bind P, amendments are necessary to prevent P loss once they are saturated. They also express concern about the possible negative environmental impacts of introducing metals such as Fe and suggest further impact studies on grazing animals, crops and receiving waterways.

Under low oxygen conditions, when ORP is low and the system is considered anaerobic, the soil properties conducive to P binding become severely hindered. In contrast, N removal is favored under anaerobic conditions due to the activation of denitrifiying bacteria (Watts and Seitzinger, 2000). In flooded soils, dissolved inorganic phosphorus solubility is related to the oxidative status of iron (Fe) (Szogi *et al.*, 2004b). When Ferric-iron (Fe^{3+}) is reduced to soluble Ferrous-iron (Fe^{2+}), it releases any bound anion, including phosphate (Vohla *et al.*, 2006). This decreases the soil's capacity to store P, or potentially acting as a source of P even if the soil is not saturated. The reduction of Fe^{3+} to Fe^{2+} is a significant loss of P binding capacity because Fe is one of the most abundant metals in soils (Miller and Gardiner, 1998). Vohla *et al.,* (2006) found a significant negative correlation between oxidation-reduction potential (ORP) and outlet dissolved P and Fe^{2+} concentration in their sandy soil constructed wetland. They have suggested aeration would increase the ORP in order for Fe^{3+} to remain in the soil column and bind incoming dissolved P.

2.6.4. Constructed Wetland Vegetation

The role of vegetation in constructed wetlands has been much discussed in the literature in recent years. In general, studies comparing non-vegetated versus vegetated wetland microcosms have reported better nutrient removal in the vegetated treatment (Tanner, 1996; Yang *et al.*, 2001; Hench *et al.*, 2003; Huett *et al.*, 2005; Lee and Scholz, 2007). Macrophytes, or emergent vegetation, are integral components in both surface and subsurface flow constructed wetlands. There appears to be unanimous agreement in the literature that their primary function is not direct nutrient uptake, but more importantly to create and support habitat for microbial populations responsible for N removal by nitrification and denitrification, through oxygen transport to the root zone and carbon generation.

Macrophytes perhaps further enhance denitrification through plant transpiration whereby NO_3 is pulled into anaerobic sites via the resulting mass flux (Martin *et al.*, 2003). Macrophytes also impact the hydraulic regime of the wetland by acting as physical structures to reduce the turbulence and velocity of incoming water (Brix, 1997; Jenkins and Greenway, 2005). Another important removal mechanism is nutrient sequestration through organic matter accretion (Reddy and Patrick, 1984; Kadlec and Knight, 1996; Tanner, 1996; Sartoris *et al.*, 2000; Thullen *et al.*, 2005). Under anaerobic conditions, decomposition and mineralization of plant litter is attenuated (Healy and Cawley, 2002) thus sequestering nutrients. Plant nutrient sequestration is a complex process because there are several factors which influence the process and must therefore be considered: (1) the age and geographical location of the constructed wetland, (2) the species, (3) the soil type, and (4) the nutrient loading rate.

2.6.4.1. Constructed Wetland Maturation and Climate

The age of the constructed wetland is a key consideration because nutrient sequestration is more importantly relative to biomass production than it is to biomass concentration (Silvan *et al.*, 2004). Thullen et al (2005) also point out that the effect of newly planted species is higher nutrient uptake than would be expected from mature plants (Thullen *et al.*, 2005).

Rapidly colonizing emergent vegetation in a newly constructed wetland will contribute a greater relative nutrient uptake compared to a constructed wetland already colonized with mature vegetation. Vegetation productivity also increases with mean annual temperature and therefore greater nutrient retention rates can be expected in warmer climatic regions (Toet *et al.*, 2005).

Some examples of nutrient uptake by plants in warmer climates come from Kadlec and Knight's (1996) text book 'Treatment Wetlands', a staple for constructed wetland designers. The book gives primary production estimates for cattail nutrient uptake of 60-260 g N m^{-2} $year^{-1}$ and 7.5-40 g P m^{-2} $year^{-1}$, based on studies conducted in Florida. A study out of North Carolina evaluated two constructed wetland cells receiving agricultural wastewater which contained three species of rushes, cattails and bur reed. They observed an annual N storage in plant biomass of 38.7 g m^{-2} and 43.7 g m^{-2} per year respectively (Szogi *et al.*, 2003). Another study of common reed nutrient retention in a New South Wales, Australia wetland found an average retention of 67.23 g N m^{-2} (Hocking, 1989).

In comparison, values reported out of more northern climates are much lower and are often reported per growing season, rather than per year, due to the defined seasonally driven cycles of growing and dying. Several studies on northern climate CWs have reported nutrient removal via biomass incorporation of between 1.5 and 9% for both N and P in mature (>5 year) constructed wetlands (Edwards *et al.*, 2006; Gottschall *et al.*, 2007; Kroger *et al.*, 2007). A study in the Czech Republic on a 5 year old constructed wetland planted with reed canary grass, observed removal rates of 11.3 g N m^{-2} and 1.2 g P m^{-2} corresponding to 9.2% and 3.1% of the incoming N and P respectively (Edwards *et al.*, 2006). A cattail dominated constructed wetland built in 1995 in Ontario, Canada, reported in 2007 plant retention of approximately

7.9 g N m^{-2} in one of the vegetated cell components of the system, accounting for 9% of the total N removal (Gottschall *et al.*, 2007). A New York study on the N and P retention of five wetland species growing in an agricultural wetland buffer found reed canary grass and soft rush have N retention rates of 10.7 g N m^{-2} and 11.8 g N m^{-2} respectively, and P retention of 1.9 g P m^{-2} and 1.3 g P m^{-2} respectively(Kao *et al.*, 2003). A Finnish study on a reclaimed wetland buffer reported retention rates by *E. vaginatum* biomass of 12.67 g m^{-1} N and 1.31 g m^{-1} P, after introducing excess NO_3 and PO_4 for 150 days (Silvan *et al.*, 2004).

It is evident that retention rates between species and geographic regions differ, therefore it is important for the designer of a constructed wetland to make decisions on vegetation based on studies pertaining to their climate and available species. It is also important to understand that mature vegetation that is no longer rapidly colonizing a wetland will ultimately take up less nutrients than a newly planted one. An immature wetland, however, needs time to grow in order to have a positive effect on retention time, and build up an organic carbon substratum for promoting denitrification (Raisin and Mitchell, 1995).

2.6.4.2. Plant Species in a Constructed Wetland

Common species used in colder climates include cattails (*Typha latifolia* L. and *Typha angustifolia* L.), reed canary grass (*Phalaris arundinaceae* L.), common reed (*Phragmites australis* L.), club-rush (*Schoenoplectus lacustris* L.) and soft-rush (*Juncus effuses* L.) (Kadlec and Knight, 1996; Kao *et al.*, 2003; Maddison *et al.*, 2005). Some researchers argue that nutrient uptake by wetland vegetation is not considered a permanent removal mechanism because upon senescence, nutrients are released back into the water. Nevertheless, plant communities have been shown to be integral components for nutrient storage in agricultural constructed wetlands (Kroger *et al.*, 2007) due to their ability to sequester nutrients during the growing season when receiving water bodies are most susceptible to eutrophication (Kao *et al.*, 2003; Gottschall *et al.*, 2007).

The rate of nutrient uptake as well as the rate of decomposition between wetland species has been shown to differ (Kao *et al.*, 2003). Emergent vegetation creates a large fraction of the organic matter produced in wetlands (Alvarez and Becares, 2006) where nutrients can be sequestered (Kadlec and Knight, 1996). Thus, in addition to uptake rates, decomposition rates are important to consider when designing a wetland.

2.6.4.3. Plant Decomposition Rate in a Constructed Wetland

Alvarez and Becares (2006) divide macrophyte decomposition into three phases: (1) a period of swift initial loss as a result of leaching, (2) a longer period of microbial decomposition and colonization (3) and finally mechanical and invertebrate mediated disintegration. The phase length is dependent on environmental factors as well as the detrital quality as a carbon source (Hume *et al.*, 2002; Edwards *et al.*, 2006).

Alvarez and Becares' (2006) comparative study on cattail decay rates with other common wetland vegetation, found that cattails are one of the physically toughest and most resistant macrophytes to decomposition. They conclude that the detritus will remain longer in the system and could destructively block the substrate or deepen the sediment layer. In contrast, not all researchers consider slow decomposition a negative trait. In newly built constructed wetlands carbon can be rate-limiting to denitrifying bacteria. Slowly decomposing species provide a carbon source for microbes the following spring, before species with more rapid life cycles begin growing.

Gottschall *et al.,* (2007) surmise that cattail roots and rhizomes, which store a large component of nutrients during the non-growing season and have a turnover rate of up to 2 years, play an important role in diverting nutrient loads to vulnerable watersheds during the growing season. Kao *et al.,* (2003) studied the N and P accumulation in 5 wetland species and subsequently measured their respective decomposition rates in terms of percentage N and P retained. Soft rush had the highest accumulation of nutrients during the growing season and the highest percentage remaining in the litter the following spring. While reed canary grass had an uptake rate similar to the soft rush, it had the lowest percentage of remaining nutrients the following spring.

The researchers also looked at the percentage nutrients remaining after 150 days of decomposition to demonstrate the benefits of vegetation retention at prolonging nutrient release until the growing season is over and receiving water bodies are less susceptible to eutrophication. In fact, after 150 days, soft rush still contained 9.3 g N m^{-2} and 1.3 g P m^{-2} while reed canary grass only contained 3.3 g N m^{-2} and 0.2 g P m^{-2}. This study highlights the variability between species in their ability to retain nutrients and lends to the argument of harvesting vegetation for permanent nutrient removal. Kroger *et al.*, (2007) studied decomposition rates of plants exposed to agricultural runoff and suggested that at the onset of senescence, the subsequent nutrient translocation from shoots to roots, and the resulting above ground nutrient reduction, may buffer the effects of leaching in the initial phase of decomposition. Their study also showed that retention rates during senescence were lower for P than for N (Kroger *et al.*, 2007).

2.6.4.4. Harvesting Plants in a Constructed Wetland

Harvesting of wetland vegetation as a permanent nutrient removal mechanism is perhaps one of the most controversial issues in the literature. Some researchers claim that biomass removal is ineffective when less than 10% of the nutrients are stored, even in low-loaded systems (Kadlec, 2005; Vymazal, 2007), while others recommend harvesting from wetlands treating diluted wastewater to avoid over-accumulation of organic matter (Alvarez and Becares, 2006). In order to benefit from biomass harvesting in terms of nutrient removal, it is imperative to understand the nature of the species' growth and storage patterns in order to determine which are the best ones for harvesting and at what time of year (Tanner, 1996; Ying *et al.*, 2007).

A study on the effects cattail transpiration and harvesting on nitrate concentration in microcosms suggested that harvesting cattail biomass resulted in increased growth as compared to the unharvested treatment, while transpiration rates were lowest in the harvested treatments (Martin *et al.*, 2003). The results of the study suggest that transpiration rates contributed more to nitrate reductions than did plant uptake due to increased growth. They also found that the overall primary removal mechanism for N was denitrification. While it appears that plants with greater transpiration rates may be more suitable for treating nitrate, the authors acknowledge that the amount of the biomass harvested, and at the time of year when the greatest amount of nutrients is in the above ground shoots, warrants further investigation. A potential advantage to harvesting would be that the plants are kept in immature phases of growth when productivity is higher (Martin *et al.*, 2003; Edwards *et al.*, 2006; Vymazal, 2007). Harvesting of biomass for permanent nutrient removal is a potential constructed wetland management strategy but it is necessary to consider species and biomass partitioning between roots and shoots in order to determine which time of year would yield optimal results (Toet *et al.*, 2005). It is also important to consider the carbon status of the system as well as the amount harvested in order to still promote transpiration for nitrate movement towards the root zone via mass flux (Martin *et al.*, 2003).

2.6.4.5. Constructed Wetland Substrate

The soil substrate greatly influences vegetation growth, and in turn how the vegetation will indirectly support further nutrient removal. The soil substrate itself is a source of nutrients for plants; depending on the wastewater supplied to the wetland, it is possible for one or more necessary nutrients to be lacking. This often occurs with micronutrients and therefore it is up to the soil substrate to provide them. Vegetation type positively affects overall N and P removal not only through uptake, but also through the quality of available carbon incorporated into the soil substrate for nitrification and denitrification (Hume *et al.*, 2002). Vegetation type also influences pH and oxidation status within the system, which impacts adsorption and precipitation of P by the soil (Akratos and Tsihrintzis, 2007). These processes are dependent on the soil substrate and how well the plants are able to grow and establish rooting. The treatment factors of substrate, vegetation and growth period, individually and in combination, all significantly affect nutrient removal (Yang *et al.*, 2001).

A comparison of N and P removal by constructed wetland microcosms filled with a gravel substrate and a mineral soil substrate, with a vegetated and unvegetated treatment of each, found that the unvegetated soil substrate removed the most soluble reactive phosphorus (SRP) due to precipitation reactions between the Ca and Al. The authors postulated that the effect of plant litter in the vegetated soil treatment released some of the SRP back into the water. They go on to recommend however, that plant assimilation may become the primary removal mechanism once the soil has reached saturation and harvesting may be helpful once this occurs. In contrast, inorganic nitrogen was removed more efficiently in the vegetated soil treatment, most likely due to the presence of denitrifying bacteria (Yang *et al.*, 2001).

2.6.5. Microbial Actions in a Constructed Wetland

Microbial actions within a constructed wetland are arguably the most important component for nitrogen treatment. Denitrification is considered the main permanent removal mechanism for N in wetlands (Bachand and Horne, 2000) and there does not appear to be any statements in the literature to the contrary. An interesting addition to the N cycle has been identified in the last decade by a group in the Netherlands. The discovery is termed ANNAMOX,. a pathway whereby bacteria capable of anaerobic, autotrophic oxidation of ammonium, using nitrite as an electron acceptor, form gaseous molecular nitrogen (Anyusheva and Kalyuzhnyi, 2007). ANNAMOX research thus far has indicated these organisms are particularly important for N processing in the ocean (Francis *et al.*, 2007) and their role in constructed wetlands treating agricultural wastewater is emerging.

Denitrification is an important component of the nitrogen cycle that returns N present in plants, soil and water back to the atmosphere (Firth and Edwards, 2000; Watts and Seitzinger, 2000). Research is generally focused on promoting denitrification and decreasing the N_2O:N_2 ratio of gases produced, in order to reduce greenhouse gases (Freeman *et al.*, 1997; Chang *et al.*, 1998; Chen *et al.*, 1999). Nitrous oxide and nitric oxide are intermediary products of the denitrification reaction pathway and have been linked to global warming and ozone layer damage (Firth and Edwards, 2000).

Denitrification is the biological reduction of nitrite (NO_2) and nitrate (NO_3) to N_2 gas. The conditions of the bacterial cultures influence the rate at which denitrification occurs and the resulting N_2O:N_2 ratio (Thomas *et al.*, 1994). Factors affecting the responsible bacteria include O_2, NO_2+NO_3 concentration, pH and availability of carbon (Smith and Tiedje, 1979).

The effect of O_2 is not the same on every species of denitrifying bacteria. Some can carry out denitrification in the presence of O_2 while others cannot; in the presence of oxygen it is called aerobic denitrification as opposed to anaerobic denitrification. Oxygen controls denitrification through gene expression and inhibition of enzymes responsible for it (Thomas *et al.*, 1994). Generally, if the oxygen status in a wetland is low, with corresponding reduced oxidation-reduction potential, NO_3 is the main electron acceptor for cellular respiration thus promoting denitrification (Reddy and Patrick, 1984).

In constructed wetlands, the availability of carbon has been shown to directly impact the ratio of N_2O:N_2 produced, higher available C has been correlated with more complete denitrification (Hunt *et al.*, 2003). In other words, available C:N affects denitrification and 4:1 is considered optimum (Caskey and Tiedje, 1979; Thomas *et al.*, 1994).

A study on the denitrification enzyme activity (DEA) on the litter of three different wetland plant species showed a marked difference, suggesting differences in the quality of organic material between plants for supporting denitrifying bacteria. The authors concluded that because the yield of plant detritus varies significantly between species, the seasonal variation in denitrification capacity is likely to vary between species (Bastviken *et al.*, 2005). This supports the contention that species diversity within wetlands may have a positive effect on supporting denitrification functions (Gilbert, 2004).

2.7. Comparison of Constructed Wetlands Treating Agricultural NPS

Using constructed wetlands as a best management practice for mitigating NPS agricultural pollution in colder climates has been gaining attention in recent years. Many of the design parameters have been adopted from CWs treating point source waste streams such as from dairy and swine barns. Table 2.1 summarizes removal rates and efficiencies from several CWs from different geographic regions treating agriculturally generated NPS.

Table 2.1. Total N and P annual removal by several constructed wetlands receiving agricultural runoff. Size, retention and percent removal are also listed. Ranges are shown when more than one wetland or year was shown in study.

Wetland[a]	Size	Retention time	Total N removed		Total P removed		Reference
	ha	d	g m^{-2} yr^{1}	%	g m^{-2} yr^{1}	%	
Kent Island, Maryland (1)	1.3	12-19	1.7	14	0.76	21	(Jordan *et al.*, 2003)
Indian Lake, Ohio (1)	1.2	ND[b]	39	40	6.2	56	(Fink and Mitsch, 2004)
Palm Beach, Florida (1)	147	4.5	ND	ND	ND	64	(Dierberg *et al.*, 2005)
Embarrass River, Illinois (3)	0.3-0.8	22-38	33	27-52	0.1	(-54)-80	(Kovacic *et al.*, 2000)
S.E. Norway (4)	0.035-0.09	0.4-1	50-285	6-15	26-71	21-44	(Braskerud, 2002b; Braskerud, 2002a)

[a] number in parentheses indicates number of constructed wetlands in study
[b] No data

Comparing constructed treatment wetlands can be difficult and at times misleading. They are custom built to deal with specific target wastewater at specific locations and differ not only in physical shape and dimension, but in vegetation cover, hydraulic retention time and pollutant loading rates. For example, constructed wetlands receiving secondary municipal waste effluent at regulated flow rates are much easier to measure and assess than CWs receiving agricultural runoff.

Agricultural runoff characteristics vary based on rainfall and irrigation events and therefore vary month to month, year to year and watershed to watershed. Hence, it is important to consider removal efficiencies along with total loads when comparing wetlands because small loads may enter and be removed by wetlands at certain times of the year resulting in high removal efficiencies but contributing very little to overall nutrient removal (Kovacic *et al.*, 2000).

Treatment efficiencies vary considerably as seen in Table 1. For CWs treating agricultural runoff, it has been suggested that reasonable long-term retention rates for P be 1-5 g P m^{-2} per year, based on studies performed in northeastern Illinois (Mitsch *et al.*, 1995). Others broaden the range to 0.5-10 g P m^{-2} per year (Kadlec and Knight, 1996). As of yet there are no guidelines for acceptable N removal rates from NPS pollution. The CWs shown in Table 1 all demonstrate higher removal efficiencies for P than N however this trend is highly dependent on the conditions within the wetland system.

Fink and Mitsch (2004) explain that because the mechanisms by which P and N are retained within the wetland differ, the wetland design should depend on which nutrient is more important to attenuate. P removal via chemical reactions with the soil favor oxygenated conditions, while N removal via denitrification favors anaerobic conditions. When the retention of both N and P are equally important then the design must take this into account based on what species of N and P is in the influent.

Braskerud (2002b) suggests that P retention was successful in their small CWs because 51-88% of the incoming P was in particulate form. This meant that physical particle settling was the primary P removal mechanism as 45% of the particulate P was retained while only 5% of the dissolved P was retained. Had a larger fraction of the P been in dissolved form, it is likely that the overall P retention would not have been so high.

Healy and Cawley (2002) point out that when a wetland is well suited for N retention, it is of little use for P reduction. While CWs have been proven useful treating point source waste streams from agricultural as well as municipal and industrial sources, their applicability for treating NPS in colder climates has been questioned (Newman *et al.*, 2000). Research is however proving their usefulness as a BMP, as demonstrated by the Norwegian government's commitment to contributing 70% of the cost of building a wetland to farmers to mitigate P pollution (Braskerud, 2002b).

So far, it appears that constructed wetlands aimed at treating NPS pollution, particularly for N and P retention, are retaining one more successfully than the other due to the lack of ideal conditions for both. As research continues into improving CW systems for nutrient mitigation from agricultural NPS, we can expect to see designs including wetland cells connected in series to attempt to provide conditions conducive to both N and P removal.

2.8. Summary

As the pressure on the world water supply increases with increasing demand for food production, so does the issue of water quality deterioration. In Quebec, Canada, agricultural intensification has lead to increasing amounts of agricultural non point source pollution in the form of nutrient laden runoff. Nitrogen and phosphorus coming from agricultural land is of particular concern because of its negative effects on receiving freshwater bodies. Eutrophication of freshwater is of particular concern because it renders the the water body useless for drinking, swimming or fishing.

Best management practices for the mitigation of agricultural runoff are being implemented, and constructed wetlands are gaining attention as a BMP. While constructed wetlands have been proven to successfully treat point source waste streams, they are emerging as a low-cost tool for treating nonpoint source waste. Previously, the role of constructed wetlands in treating NPS pollution in colder climates was questioned; however, studies out of the northern US and Scandinavia are demonstrating that they are a viable option. Because the success of a wetland system is based on adapting the design to the climatic conditions, research into understanding CW removal mechanisms for N and P, and the factors which influence those mechanisms, is currently taking place in an effort to optimize their design.

2.9. References

Adhikari, B. K., Madramootoo, C., Stämpfli, N. and Chikhaou, M. (2007). Phosphorus load assessment from Pike River watershed and need of TMDL program to attain water quality standard for Missisquoi Bay. 2007 ASABE Annual International Meeting. Minneapolis, Minnesota.

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.

Alvarez, J. A. and Becares, E. (2006). "Seasonal decomposition of Typha latifolia in a free-water surface constructed wetland." Ecological Engineering **28**(2): 99-105.

Anyusheva, M. G. and Kalyuzhnyi, S. V. (2007). "Anaerobic oxidation of ammonium: microbiological, biochemical and biotechnological aspects." Uspekhi Sovremennoi Biologii. Izdatel'stvo Nauka, Moscow, Russia **127**(1): 34-43.

APHA, AWWA and WPCF (1992). Standard methods for the examination of water and wastewater / prepared and published jointly by American Public Health

Association, American Water Works Association, Water Pollution Control Federation. Washington, DC, USA, American Public Health Association.
Aye, T. M., Nguyen, M. L., Bolan, N. S. and Hedley, M. J. (2006). "Phosphorus in soils of riparian and non-riparian wetland and buffer strips in the Waikato area, New Zealand." New Zealand Journal of Agricultural Research **49**: 349-358.
Bachand, P. A. and Horne, A. J. (2000). "Denitrification in constructed free-water surface wetlands: II Effects of vegetation and temperature." Ecological Engineering **14**: 17-32.
Bastviken, S. K., Eriksson, P. G., Premrov, A. and Tonderski, K. (2005). "Potential denitrification in wetland sediments with different plant species detritus." Ecological Engineering **25**(2): 183-190.
Berka, C., H. and Schreier (2001). "Linking water quality with agricultural intensification in a rural watershed." Water Air and Soil Pollution **127**: 389-401.
Berka, C., Schreier, H. and Hall, K. (2001). "Linking water quality with agricultural intensification in a rural watershed." Water Air and Soil Pollution **127**: 389-401.
Bostic, E. M. and White, J. R. (2006). "Soil Phosphorus and Vegetation Influence on Wetland Phosphorus Release after Simulated Drought." Soil Sci Soc Am J **71**: 233-238.
Braskerud, B. C. (2002a). "Factors affecting nitrogen retention in small constructed wetlands treating agricultural non-point source pollution." Ecological Engineering **18**(3): 351-370.
Braskerud, B. C. (2002b). "Factors affecting phosphorus retention in small constructed wetlands treating agricultural non-point source pollution." Ecological Engineering **19**: 41-61.
Brix, H. (1997). "Do macrophytes play a role in constructed treatment wetlands?" Water Sci. Technol. **35**(5): 11-17.
Carleton, J. N. (2002). "Damkohler number distributions and constituent removal in treatment wetlands." Ecological Engineering **19**(4): 233-248.
Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N. and Smith, V. H. (1998). "Nonpoint Pollution of Surface Waters With Phosphorus and Nitrogen." Ecological Applications **8**(3): 559-568.
Casey, R. E. and Klaine, S. J. (2001). "Nutrient Attenuation by a Riparian Wetland during Natural and Artificial Runoff Events." J. Environ. Qual. **30**: 1720–1731.
Caskey, W. H. and Tiedje, J. M. (1979). "Nitrate-Stimulated Mineralization of Ammonium in Anaerobic Soils." Oecologia **4l**: 339-341.
Chang, C., Janzen, H. H., Cho, C. M. and Nakonechny, E. M. (1998). "Nitrous Oxide Emission through Plants." Soil Sci Soc Am J **62**: 35-38.
Chen, X., Boeckx, P., Shen, S. and Van Cleemput, O. (1999). "Emission of N_2O from rye grass (*Lolium perenne* L.)." Biol Fertil Soils **28**: 393-396.
Del Bubba, M., Arias, C. A. and Brix, H. (2003). "Phosphorus Adsorption Maximum of Sands for use as Media in the Subsurface Flow Constructed Reed Beds as Measured by the Langmuir Isotherm." Water Research **37**: 3390-3400.
Dierberg, F. E., Juston, J. J., DeBusk, T. A., Pietro, K. and Gu, B. H. (2005). "Relationship between hydraulic efficiency and phosphorus removal in a submerged aquatic vegetation-dominated treatment wetland." Ecological Engineering **25**(1): 9-23.

Eastman, M. (2008). Field-scale nutrient transport monitoring and modeling of subsurface and naturally drained agricultural lands. Bioresource Engineering. Ste-Anne-de-Bellevue, QC, McGill University, Macdonald Campus. **M.Sc.Thesis**

Ebina, J., Tsutsui, T. and Shirai, T. (1983). "Simultaneous Determination of Total Nitrogen and Total Phosphorous in Water Using Peroxodisulfate Oxidation." Water Research **17**(12): 1721-1726.

Edwards, K. R., Cizkova, H., Zemanova, K. and Santruckova, H. (2006). "Plant growth and microbial processes in a constructed wetland planted with Phalaris arundinacea." Ecological Engineering **27**(2): 153-165.

Fink, D. F. and Mitsch, W. J. (2004). "Seasonal and storm event nutrient removal by a created wetland in an agricultural watershed." Ecological Engineering **23**: 313-325.

Firth, J. R. and Edwards, C. (2000). "Denitrifaction by indigenous microbial populations of river water measured using membrane inlet mass spectrometry." Journal of Applied Microbiology **89**: 123-129.

Francis, C. A., Beman, J. M. and Kuypers, M. M. M. (2007). "New processes and players in the nitrogen cycle: the microbial ecology of anaerobic and archaeal ammonia oxidation." ISME J **1**(1): 19-27.

Freeman, C., Lock, M. A., Hughes, S. and Reynolds, B. (1997). "Nitrous Oxide Emissions and the Use of Wetlands for Water Quality Amelioration." Environ. Sci. Technol. **31**: 2438-2440.

Gentry, L. E., David, M. B., Royer, T. V., Mitchell, C. A. and Starks, K. M. (2007). "Phosphorus Transport Pathways to Streams in Tile-Drained Agricultural Watersheds." J Environ Qual **36**: 408-415.

Gilbert, J. (2004). Examining the Link Between Macrophyte Diversity, Bacterial Diversity, and Denitrification Function in Wetlands. College of Food, Agriculture, & Environmental Science. Columbus, Ohio, Ohio State University. **Ph.D.Thesis**

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.

Hafner, S. D. and Jewell, W. J. (2006). "Predicting nitrogen and phosphorus removal in wetlands due to detritus accumulation: A simple mechanistic model." Ecological Engineering **27**(1): 13-21.

Hammer, D. A. (1992). "Designing constructed wetlands systems to treat agricultural nonpoint source pollution." Ecological Engineering **1**(1-2): 49-82.

Healy, M. and Cawley, A. M. (2002). "Nutrient Processing Capacity of a Constructed Wetland in Western Ireland." J Environ Qual **31**: 1739-1747.

Hench, K. R., Bissonnette, G. K., Sexstone, A. J., Coleman, J. G., Garbutt, K. and Skousen, J. G. (2003). "Fate of Physical, Chemical, and Microbial contaminants in Domestic Wastewater Following Treatment by Small Constructed Wetlands." Water Research **37**(921-927).

Hocking, P. J. (1989). "Seasonal dynamics of production, and nutrient accumulation and cycling by *Phragmites asutralis* (Cav.) Trin. *ex* Studel in a nutrient-enriched swamp in Inland Australia. I. Whole Plants." Marine and Freshwater Research **40**(5): 421-444.

House, W. A., Denison, F. H. and Armitage, P. D. (1995). "Comparison of the uptake of inorganic phosphorus to a suspended stream bed-sediment." Water Research **29**(3): 767-779.
Huett, D. O., Morris, S. G., Smith, G. and Hunt, N. (2005). "Nitrogen and Phosphorus Removal from Plant Nursery Runoff in Vegetated and Unvegetated Subsurface Flow Wetlands." Water Research **39**: 3259-3272.
Hume, N. P., Fleming, M. S. and Horne, A. J. (2002). "Denitrification Potential and Carbon Quality of Four Aquatic Plants in Wetland Microcosms." Soil Sci. Soc. Am. J. **66**: 1706-1712.
Hunt, P. G., Matheny, T. A. and Szogi, A. A. (2003). "Denitrification in Constructed Wetlands Used for Treatment of Swine Wastewater." J Environ Qual **32**: 727-735.
IFAD (2008). "Water to combat rural poverty, Rural Poverty Portal, International Fund for Agricultural Development." from http://www.ruralpovertyportal.org/.
Jenkins, G. A. and Greenway, M. (2005). "The hydraulic efficiency of fringing versus banded vegetation in constructed wetlands." Ecological Engineering **25**(1): 61-72.
Jenssen, P. D., MÃ¦hlum, T., Krogstad, T. and VrÃ¥le, L. (2005). "High Performance Constructed Wetlands for Cold Climates." Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering **40**(6/7): 1343-1353.
Jordan, T. E., Whigham, D. F., Hofmockel, K. H. and Pittek, M. A. (2003). "Nutrient and Sediment Removal by a Restored Wetland Receiving Agricultural Runoff." J Environ Qual **32**: 1534-1547.
Kadlec, R. H. (1994). "Detention and mixing in free water wetlands." Ecological Engineering **3**(4): 345-380.
Kadlec, R. H. (2005). "Phosphorus Removal in Emergent Free Surface Wetlands." Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering **40**(6/7): 1293-1306.
Kadlec, R. H. (2008). "The effects of wetland vegetation and morphology on nitrogen processing." Ecological Engineering **In Press, Corrected Proof**.
Kadlec, R. H. and Knight, R. L. (1996). Treatment Wetlands. Boca Raton, Florida, Lewis Publishers.
Kao, J. T., Titus, J. E. and Zhu, W.-X. (2003). "Differential Nitrogen and Phosphorus Retention by Five Wetland Plant Species." Wetlands **23**(4): 979-987.
Keefe, S. H., Barber, L. B., Runkel, R. L., Ryan, J. N., McKnight, D. M. and Wass, R. D. (2004). "Conservative and reactive solute transport in constructed wetlands." Water Resources Research **40**(American Geophysical Union): W01201, doi:10.1029/2003WR002130.
Kellogg, R. L. and Maizel, M. S. (1994). "The Potential for Leaching of Agrichemicals used in Crop Production: A National Perspective." Journal of Soil and Water Conservation **May-June**: 294-298.
Kivaisi, A. K. (2001). "The potential for constructed wetlands for wastewater treatment and reuse in developing countries: a review." Ecological Engineering **16**: 545-560.
Kovacic, D. A., David, M. B., Gentry, L. E., Starks, K. M. and Cooke, R. A. (2000). "Effectiveness of Constructed Wetlands in Reducing Nitrogen and Phosphorus Export from Agricultural Tile Drainage." J Environ Qual **29**: 1262-1274.

Kroger, R., Holland, M. M., Moore, M. T. and Cooper, C. M. (2007). "Plant senescence: A mechanism for nutrient release in temperate agricultural wetlands." Environmental Pollution **146**: 114-119.

Kronvang, B., Bechmann, M., Lundekvam, H., Behrendt, H., Rubaek, G. H., Schoumans, O. F., Syversen, N., Andersen, H. E. and Hoffmann, C. C. (2005). "Phosphorus Losses from Agricultural Areas in River Basins: Effects and Uncertainties of Targeted Mitigation Measures." J Environ Qual **34**(6): 2129-2144.

La Flamme, C., Enright, P. and Madramootoo, C. (2004). Sediment and Nutrient Removal Efficiencies in a Constructed Wetland in Southern Quebec. ASAE/CSAE Annual International Meeting. Ottawa, Ontario, Canada.

Lee, B.-H. and Scholz, M. (2007). "What is the role of Phragmites australis in experimental constructed wetland filters treating urban runoff?" Ecological Engineering **29**(1): 87-95.

Levenspiel, O. (1999). Chemical Reaction Engineering. Hoboken, NJ, USA, John Wiley & Sons.

Lightbody, A. F., Nepf, H. M. and Bays, J. S. (2007). "Mixing in deep zones within constructed treatment wetlands." Ecological Engineering **29**(2): 209-220.

Lijklema, L. (1980). "Interaction of orthophosphate with Iron(III) and Aluminum Hydroxides." Environmental Science and Technology **14**(5): 537-541.

Litaor, M. I., Eshel, G., Reichmann, O. and Shenker, M. (2006). "Hydrological Control of Phosphorus Mobility in Altered Wetland Soils." Soil Sci Soc Am J **70**(6): 1975-1982.

Maddison, M., Soosaar, K., Lohmus, K. and Mander, U. (2005). "Cattail Population in Wastewater Treatment Wetlands in Estonia: Biomass Production, Retention of Nutrients, and Heavy Metals in Phytomass." Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering **40**(6/7): 1157-1166.

Martin, J. F., Hofherr, E. and Quigley, M. F. (2003). "EFFECTS OF TYPHA LATIFOLIA TRANSPIRATION AND HARVESTING ON NITRATE CONCENTRATIONS IN SURFACE WATER OF WETLAND MICROCOSMS." Wetlands **23**(4): 835-844.

MENV (2002). Water. Our Life. Our Future. Quebec Water Policy, Ministere de l'Evironnement. Quebec, QC.

Michaud, A. R., Lauzier, R. and Laverdière, M. R. (2005). "Mobilite du phosphore et intervention agroenvironnementale en bassin versant agricole: Etude de cas du ruisseau au Castor, tributaire de la riviere Aux Brochets, Quebec." Agrosolutions **16**(1): 47-60.

Miller, R. W. and Gardiner, D. T. (1998). Soils in Our Environment. Upper Saddle River, New Jersey, USA, Prentice-Hall Inc.

Mitsch, W. J., Cronk, J. K., Wu, X., Nairn, R. W. and Hey, D. L. (1995). "Phosphorus retention in Constructed Freshwater Riparian Marshes." Ecological Applications **5**: 830-845.

Newman, J. M., Clausen, J. C. and Neafsey, J. A. (2000). "Seasonal performance of a wetland constructed to process dairy milkhouse wastewater in Connecticut." Ecological Engineering **14**(1-2): 181-198.

Novak, J. M., Stone, K. C., Szogi, A. A., Watts, D. W. and Johnson, M. H. (2004). "Dissolved Phosphorus Retention and Release from a Coastal Plain In-Stream Wetland." J Environ Qual **33**(1): 394-401.
Patrick, W. H., Gambrell, R. P. and Faulkner, S. P. (1996). Redox measurements in soil. Methods of Soil Analysis, Part 3, 677 South Segoe Rd, Madison, Wisconsin, 53711, USA: SSSA**:** 1255-1273.
Persson, J., Somes, N. L. G. and Wong, T. H. F. (1999). "Hydraulics Efficiency of Constructed Wetlands and Ponds." Water Sci. Technol. **40**(3): 291-300.
Raisin, G. W. and Mitchell, D. S. (1995). "The Use of Wetlands for the Control of Non-Point Source Pollution." Water Sci. Technol. **32**(3): 177-186.
Reddy, K. R. and Patrick, W. H. (1984). "Nitrogen transformations and loss in flooded soils and sediments." CRC Crit. Rev. Environ. Control **12**: 273-309.
Sakadevan, K. and Bavor, H. J. (1998). "Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems." Water Research **32**(2): 393-399.
Sartoris, J. J., Thullen J.S., Barber, L. B. and Salas, D. E. (2000). "Investigation of nitrogen transformations in a southern California constructed wastewater treatment wetland." Ecological Engineering **14**: 49-65.
Schoumans, O. F. and Chardon, W. J. (2003). "Risk assessment methodologies for predicting phosphorus losses." Journal of Plant Nutrition and Soil Science **166**(4): 403-408.
Sharpley, A. N. (1995). "Soil phosphorus dynamics: agronomic and environmental impacts." Ecological Engineering **5**(2-3): 261-279.
Shilton, A. N. and Prasad, J. N. (1996). "Tracer Studies of a Gravel Bed Wetland." Water Sci. Technol. **34**(3-4): 421-425.
Silvan, N., Vasander, H. and Laine, J. (2004). "Vegetation is the main factor in nutrient retention in a constructed wetland buffer." Plant & Soil **258**(1/2): 179-187.
Simi, A. and Mitchell, C. A. (1999). "Design and Hydraulic Performance of a constructed wetland treating oil refinery wastewater." Water Science and Technology **40**(3): 301.
Smith, E., Gordon, R., Madani, A. and Stratton, G. (2005a). "Cold climate hydrological flow characteristics of constructed wetlands." Canadian Biosystems Engineering: **47** 1.1-1.7.
Smith, M. S. and Tiedje, J. M. (1979). "The Effect of Roots on Soil Denitrification." Soil Sci Soc Am J **43**: 951-955.
Stämpfli, N. (2006). Tools for Phosphorus Management, Soil and Water Quality Management Course BREE 625. McGill University, Ste-Anne-de-Bellevue, QC.
Szogi, A. A., Hunt, P. G. and Humenik, F. J. (2003). "Nitrogen Distribution in Soils of Constructed Wetlands Treating Lagoon Wastewater." Soil Sci Soc Am J **67**: 1943-1951.
Szogi, A. A., Hunt, P. G., Sadler, E. J. and Evans, D. E. (2004a). "Characterization of Oxiation-Reduction Processes in Constructed Wetlands for Swine Wastewater Treatment." Applied Engineering in Agriculture **20**(2): 189-200.
Szogi, A. A., Hunt, P. G., Sadler, E. J. and Evans, D. E. (2004b). "Characterization of Oxidation-Reduction Processes in Constructed Wetlands for Swine Wastewater Treatment." Applied Engineering in Agriculture **20**(2): 189-200.

Tanner, C. C. (1996). "Plants for constructed wetland treatment systems -- A comparison of the growth and nutrient uptake of eight emergent species." Ecological Engineering **7**(1): 59-83.
Tanner, C. C., Sukias, J. P. S. and Upsdell, M. P. (1998). "Organic matter accumulation during maturation of gravel-bed constructed wetlands treating farm dairy wastewaters." Water Research **32**(10): 3046-3054.
Thomas, K. L., Lloyd, D. and Boddy, L. (1994). "Effects of oxygen, pH and nitrate concentration on denitrification by *Pseudomnas* species." Federation of European Microbiological Societies, Microbiology Letters **118**: 181-186.
Thullen, J. S., Sartoris, J. J. and Nelson, S. M. (2005). "Managing vegetation in surface-flow wastewater-treatment wetlands for optimal treatment performance." Ecological Engineering **25**(5): 583-593.
Toet, S., Bouwman, M., Cevaal, A. and Verhoeven, J. T. A. (2005). "Nutrient Removal Through Autumn Harvest of Phragmites australis and Thypha latifolia Shoots in Relation to Nutrient Loading in a Wetland System Used for Polishing Sewage Treatment Plant Effluent." Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering **40**(6/7): 1133-1156.
UCLA: Academic Technology Services, S. C. G. (2007). "Introduction to SAS." Retrieved November 24, 2007, from http://www.ats.ucla.edu/stat/sas/notes2/
USEPA (1998). National water quality inventory: 1996 Report to Congress. EPA 841-R-97-008. Office of water, U.S. Environmental Protection Agency. Washington, D.C.
USEPA (2000). Constructed Wetlands Treatment of Municipal Wastewaters. Cincinatti, Ohio, United Stated Environmental Protection Agency**:** 1-165.
Vohla, C., Alas, R., Nurk, K., Baatz, S. and Mander, U. (2006). "Dynamics of phosphorus, nitrogen and carbon removal in a horizontal subsurface flow constructed wetland." Science of The Total Environment **In Press, Corrected Proof**: 105.
Vymazal, J. (2005). "Constructed wetlands for wastewater treatment." Ecological Engineering **25**(5): 475-477.
Vymazal, J. (2006). "Removal of nutrients in various types of constructed wetlands." Science of The Total Environment **doi:10.1016/j.scitotenv.2006.09.014**: 105.
Vymazal, J. (2007). "Removal of nutrients in various types of constructed wetlands." Science of The Total Environment **380**(1-3): 48-65.
Watts, S. H. and Seitzinger, S. P. (2000). "Denitrification rates in organic and mineral soils from riparian sites: a comparison of N_2 flux and acetylene inhibition method." Soil Biology and Biochemistry **32**: 1383-1392.
Werner, T. M. and Kadlec, R. H. (2000). "Wetland residence time distribution modeling." Ecological Engineering **15**(1-2): 77-90.
Wörman, A. and Kronnäs, V. (2005). "Effect of pond shape and vegetation heterogeneity on flow and treatment performance of constructed wetlands." Journal of Hydrology **301**(1-4): 123-138.
Yang, L., Chang, H.-T. and Huang, M.-N. L. (2001). "Nutrient Removal in Gravel- and Soil-based Wetland Microcosms With and Without Vegetation." Ecological Engineering **18**: 91-105.

Ying, G., ShiPeng, L., Yin, X.-N., Lei, Y.-C., Shan, X.-Q. and Jie, C. (2007). Sustainable Frowth and Nutrient Uptake of Plants in a Subtropical Constructed Wetland in Southern China. Fresenius Environmental Bulletin, **16** (9a): 1023-1029.

Zucker, L. A., Brown, L. C. and Volgstadt, C. E. (2008) "Nonpoint Source Assessment: User's Guide to Ohio's Surface Waters." Bulletin 873-98, Ohio State University **Volume**, DOI:

Preface to Chapter 3

Agricultural runoff containing phosphorus is a threat to freshwater quality in Quebec. Constructed wetland design must be adapted to the local environment and the contents of the agricultural runoff. The following chapter addresses the role of substrate in a constructed wetland built to treat agricultural runoff containing levels of P typical in Quebec. The two soil substrates tested are common in Quebec and the study addresses how the P retention within the wetland was impacted by them. We were interested in discerning if one soil substrate would remove more than the other, and why this occurred.

3. Chapter 3- Phosphorus Reduction from Agricultural Runoff in a Pilot-Scale Surface-Flow Constructed Wetland

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3.1. Abstract

Excess P in surface waters in Quebec is the primary cause of water quality deterioration and the majority of it is coming from agricultural land. This study was aimed at studying two substrates, a sandy clay loam and a sand soil, used in a surface-flow constructed wetland (CW) to compare how they influenced P retention within the CW. A secondary aim was to determine the hydraulic residence time of the wetland tanks and to measure any difference in times between soil types. Field measurements were taken at the pilot-scale surface-flow constructed wetland site between July 5 and October 1, 2007. It consisted of three replicate tanks containing the sandy clay loam and three containing the sand soil. The surface area of each tank was 9.29 m^2 and was cylindrical in shape with a radius of 0.75 m. The inlet end was characterized by a deep zone which sloped upwards to a shallow zone which occupied 66% of the surface area and was planted with reed canary grass (*Phalaris arundinacea* L.) and cattails (*Typha latifolia* L.). The tanks were flooded continuously for the duration of the study with artificial agricultural runoff solution containing 0.3 mg L^{-1} dissolved reactive P and 10 mg L^{-1} nitrate-N. The six treatment tanks received 19.6 to 33.4 g of P over the study period and the rate of retention was 0.9 to 1.6 g m^2. This corresponded to an average removal efficiency of 41%; there was no significant difference in the P retention by the tanks containing the different soil types. The sandy clay loam tanks were more reduced and had greater vegetation growth than the sand tanks. This likely led to the reduction of Fe^{3+} in the sandy clay loam soil and subsequent release of bound P which was then taken up by the colonizing vegetation. The higher nutrients inherent in the sandy clay loam as compared to the sand would have supported the greater vegetation growth thus allowing for a greater vegetation uptake of P. The net overall results show no difference in P retention between the two soil types. A conservative tracer test using

bromide revealed a mean hydraulic retention time of approximately 2.2 days for all tanks; however, the active volume of the sand tanks was greater. This investigation suggests that a sandy soil may be less prone to reducing conditions in a surface-flow CW and therefore maintain its role as a sink for P adsorption and precipitation for longer than the sandy clay loam. Further studies should investigate passive aeration and increasing the hydraulic retention time to increase the retention of P.

3.2. Introduction and Background

Nutrient overloading of freshwater bodies in North America has had a significant impact on their degradation. Diffuse, or non-point source (NPS) pollution has been deemed the primary source of these excess nutrients, more specifically phosphorus and nitrogen, and agriculture is the number one contributor to NPS pollution (Kellogg and Maizel, 1994). As large-scale farming operations continue to intensify production, soil P levels are increasing beyond their absorption capacity and the excess is being lost in surface runoff and subsurface drainage water. Phosphorus is targeted for reduction because it is often rate limiting to the growth of freshwater algae (Braskerud, 2002b). The high soil P is the result of both manure spreading and mineral P fertilizer application; in the case of livestock operations, they often produce more manure than there is land available for spreading, leading to over application. In the case of crop producers, over-application of mineral fertilizer is common as maximum crop yield is the goal (Berka *et al.*, 2001).

Generally, constructed wetlands (CWs) treating direct on-farm waste such as manure pile runoff or milk house wash for example, are dealing with much more concentrated waste streams. In contrast, agricultural runoff is characterized by large volumes of water with lower concentrations coming from agricultural land, either from the surface or subsurface drains. In Quebec, the increasing number of blue-green algae outbreaks in lakes and streams has been attributed to excess P in the watersheds with upwards of 70% estimated to be coming from agricultural non-point sources. In most natural ecological systems, phosphorus is the growth-limiting nutrient as nitrogen is naturally more abundant. The Quebec Ministry of Agriculture, Fisheries and Food, Quebec Farmers Association and Lake Champlain Coalition, a joint committee between the province of Quebec and states of Vermont and New York, are developing measures to control and monitor the amount of P entering the watersheds. Controlling the source of the nutrients is the most cost-effective long term management option (Berka *et al.*, 2001) and therefore best management practices at the farm scale to reduce and ideally prevent nutrient loss from the farm are being studied and implemented (Hammer, 1992). Constructed wetlands are an interesting best management tool as the concept can be implemented in almost any situation and built with locally available materials (Casey and Klaine, 2001; Aye *et al.*, 2006). For example a constructed wetland built on municipal land at the conjunction of drainage ditches from several farms could be implemented with the goal being to trap the runoff water and reduce the nutrient load before it reaches the tributaries. In designing a best management tool, it is important to understand not only the nutrient removal mechanisms which occur naturally in a wetland, but how these mechanisms are affected by the available structural components and the local environment. This study explored how P removal was impacted by two different soil substrates in order to help optimize the design of the constructed wetland within the local framework of the target runoff.

The goal of this research was to test if the soil substrate had an impact on a surface flow constructed wetland's ability to reduce dissolved phosphorus from agricultural runoff. This was achieved by studying six open ditch-style tanks at a pilot-scale constructed wetland site. It was expected that the soil substrate would impact the amount of dissolved phosphorus removed through differing adsorption capacities and differing plant yields. The more specific aim was to determine if there was a difference between two soil types common to Southern Quebec; a sandy clay loam field soil and a sandy soil, in their ability to reduce dissolved phosphorous from a simulated agricultural runoff solution. The simulated agricultural runoff solution contained 0.3 mg P L^{-1} as orthophosphate and 10 mg N L^{-1} as nitrate. The results of the nitrate removal by both soil types are presented in Chapter 4. The P concentration of 0.3 mg L^{-1} was chosen because it is 10 times greater than the threshold level of 0.03 mg TP L^{-1} permitted to enter surface waters as determined by the Quebec Ministry of Environment (2001). Levels found in non point source agricultural runoff in Southern Quebec have been found above 0.3 mg L^{-1} (Eastman, 2008). A secondary goal was to determine experimentally what the mean hydraulic retention time was for the constructed wetland treatment mesocosms with the different soil types and how this impacted P removal efficiencies. It was expected that the field soil would outperform the sandy soil in P removal for three reasons; it would 1) allow for greater P binding directly to the soil particles because of a larger pool of Al^{3+} and Fe^{3+}, 2) it would have a longer hydraulic residence time due to the higher clay content and 3) due to its higher nutrient content, it would promote and sustain and larger vegetation cover thus increasing the amount of P uptake by plants. In order to compare these two soil types, we monitored water-dissolved P-concentrations at the inflow and outflow as well as dissolved oxygen, oxidation-reduction potential, pH and temperature inside the mesocosms. Soil P levels and vegetation density were also determined.

3.3. Methodology

3.3.1. Site description

Field measurements were made at a pilot-scale constructed wetland research site located 3km north of McGill University's Macdonald Campus in Ste-Anne-de-Bellevue, Quebec, Canada. The site became operational in the summer of 2006. It consisted of six mesocosms which were above-ground, black, open high density polyethylene (HDPE) half-cylinder shaped tanks; three of the six open ditch-style tanks were filled with a sandy soil and the other three with a sandy clay loam field soil. Each tank measured 6.1 m in length, 1.5 m in diameter and 0.75 m radius and had a surface area of 9.29 m^2. The volume was approximately 4.17m^3 with 65% occupied by soil. Table 3.1 summarizes some of the soil properties of the two soil types.

Table 3.1. Summary of the soil characteristics where OM = organic matter, Al and Fe determined by Mehlich III extraction. (± standard deviation)

Soil type	Sand[a]	Silt[a]	Clay[a]	OM %	Al (mg kg^{-1})	Fe (mg kg^{-1})
Sand	96	3	1	0.8	232.7 (4.6)	108.9 (4.5)
Sandy Clay Loam (Field soil)	60	19	21	3.2	591.8 (9.9)	626.1 (6.3)

[a]Size group of soil particles: Sand 2mm-53µm, Silt 53-2µm, Clay < 2µm

At the inlet end of the tanks there was a deep zone from which the soil sloped upwards to the shallow zone. The shallow zone occupied approximately 66% of the surface area and was vegetated with alternating sections of reed canary grass (*Phalaris arundinaceae* L.) and cattails (*Typha latifolia* L.); there were three bands of reed canary grass at the front, middle and end of the shallow zone which were separated by patches of cattails. The water flowed from the deep zone, through the shallow vegetated section to the outlet (Figure 3.1). The inlet manifold was a 1-m piece of perforated 10.16-cm sewer pipe that formed a T with the inlet pipe. The outlet manifold was similar to the inlet and funneled the water out through a 2.54-cm diameter section of Taigon ® tubing into a tipping bucket. The tipping bucket was connected to a datalogger recording the volume of flow exiting each tank. The incorporation of a deep zone was important to reduce incoming flow rates and aid the distribution of the water in order to alleviate short-circuiting and maximize hydraulic residence time (Simi and Mitchell, 1999) The inlet T-shaped manifold was installed to further distribute the incoming water and improve the hydraulic retention time. It was demonstrated through the results of tracer test on a gravel bed wetland with and without a distribution manifold, that the hydraulic residence was increased with a distribution manifold (Shilton and Prasad, 1996).

There were three mixing tanks located above the distribution tanks where the artificial runoff solution was mixed. The target concentration of the runoff solution was 10 mg L^{-1} nitrate-N and 0.3 mg L^{-1} dissolved reactive phosphorous as orthophosphate. This solution was gravity fed via 5.08-cm drainage pipe to the two distribution tanks which were connected to each other by two 10.16-cm drainage pipes. The distribution tanks were connected to the vegetated treatment tanks via 10.16-cm white PVC sewer pipe. The target inflow rate to each treatment tank was 1L min^{-1} because it was estimated that this would result in a minimum hydraulic retention time of 1 day, based on theoretical calculations of the empty tanks.

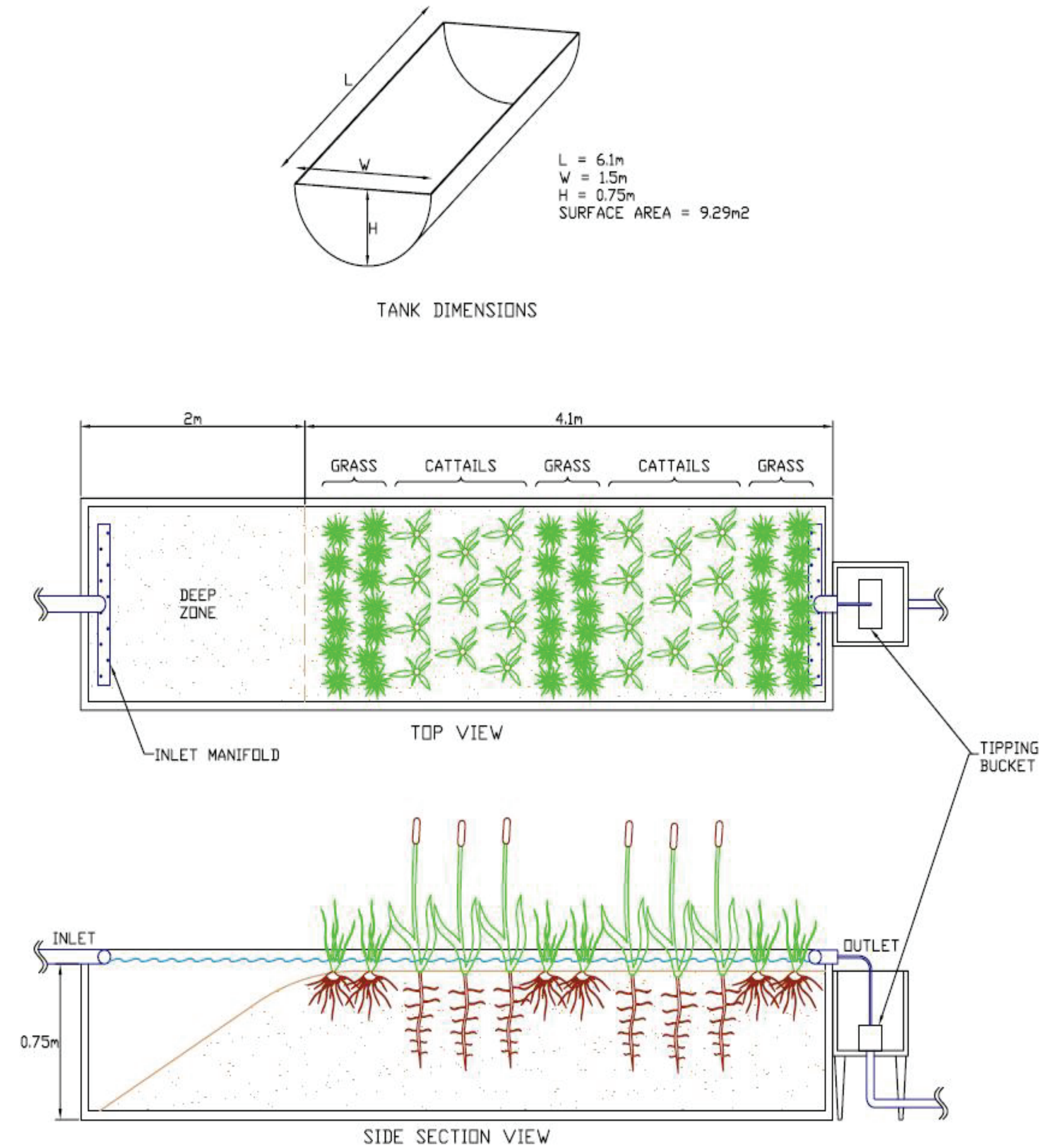

Figure3.1. Side and top view of the six soil treatment tanks.

3.3.2. Sample collection and analysis for P

The study began July 5, 2007 by running municipal water through the treatment tanks. Water samples and water column information such as dissolved oxygen (DO), oxidation-reduction potential (ORP), temperature and pH was collected to determine initial conditions. Starting July 10, 2007 the municipal water supply was stopped and the system started receiving the artificial runoff solution continuously until October 1, 2007. Outlet water samples from each wetland treatment tank were collected by a custom-built Avensys autosampler every 42 hours in 1-L Nalgene HDPE bottles. Upon collection, a composite of the four samples collected every 42 hours from the same tank was mixed by adding 30 mL of each into the sample bottle. Therefore, a more representative sample was obtained because it was composed of a mixture of the four individual samples collected during that week. Grab samples from the mixing and distribution tanks were collected as well. Water samples were collected weekly and immediately filtered through 0.45-micron nylon membranes into acid-washed 120-mL Nalgene HDPE bottles. Non-filtered samples were also collected in acid-washed bottles and then transported in an ice-filled cooler back to the laboratory 4º C fridge for analysis. Dissolved oxygen (DO), pH, oxidation-reduction potential (ORP) and temperature data was also collected weekly in the deep zone and shallow zone of vegetated tanks, as well as from the surface water of the distribution and mixing tanks. These data were collected using a Horiba portable pH meter (Model Series D-52, Horiba International Corporation, Kyoto, Japan) with corresponding DO probe, ORP probe, and a pH/temperature probe. All probes were calibrated and stored according to Horiba's specifications (Horiba D series operation manual, 2001).

Filtered water samples were analyzed for dissolved reactive phosphorous (DRP) as *ortho*-phosphate and total dissolved phosphorous (TDP), and unfiltered water samples were analyzed for total phosphorous (TP). All analyses were carried out on a Lachat Flow Injection Analysis System (Model QuikChem® 8500, Lachat Instruments, Loveland, Colorado) with detection range of 0.01 to 2.00 mg P/L. To measure TDP and TP, 5-mL aliquots of the filtered and unfiltered samples were digested with a peroxodisulfate oxidation method (Ebina *et al.*, 1983) and then analyzed for *ortho*-phosphate using the Lachat autoanalyzer. It was found that there was no particulate P entering or exiting the wetland tanks due to the lack of difference between TDP and TP so only TDP results are reported in this paper. Dissolved organic P was calculated as the difference between total dissolved P and ortho-phosphate (Kovacic *et al.*, 2000), referred to as dissolved reactive phosphorus (DRP).

Soil samples were collected in November 2006 and November 2007. In November 2006, nine samples were collected from each tank at the front, middle and back of the shallow zone at depths 0-10.16 cm, 20-30 cm and 50 cm. In November

2007, five samples were collected from each tank, three from the three depths in the middle section and 0-10.16 cm from the front and back section. Samples were air dried at room temperature and then Mehlich III extraction was performed to quantify extractable P, aluminum and iron. P was analyzed on a Lachat flow-injection autoanalyzer, and Al and Fe were analyzed on an ICP flame. Organic matter was determined by 'loss on ignition'.

3.3.3. Tracer study

A bromide tracer study was conducted on the six vegetated tanks to determine the mean retention time of each. Bromide was chosen because of its inert properties and high recovery rate, as demonstrated in other wetland tracer studies (Smith *et al.*, 2005b; Tanner *et al.*, 1998), and loss due to uptake by vegetation was not a threat as the growing season was over. The study was conducted from October 15 to October 22, 2008. The mass of bromide added was 1000 times the detection limit of 0.1 mg L^{-1}, multiplied by the tank volume, and was therefore 417 g for the vegetated tanks. The bromide (as ACG grade potassium bromide) was dissolved in four litres of distilled water and was added to the inflow of each tank at 9am on October 15. Outflow water samples were collected every 3 hours from the tanks until 9am on October 22. Outflow flow data was collected continuously by dataloggers connected to tipping buckets. An error occurred with the dataloggers and flow data was lost for the first three days of the tracer test. Flow data was obtained for the period of October 18 to 22, 2007 and interpolated back to estimate flows for the 15th, 16th and 17th. Samples were analyzed in the lab for bromide concentration using the Standard Methods Bromide Colorimetric Method (APHA *et al.*, 1992).

3.3.4. Statistical analyses

A statistical model using repeated measures over time was employed to determine if the outlet concentration for DRP and TDP was different between the two soil treatments over the three-month study. Outlet concentrations of P from the three replicates for each of the sandy soil and field soil tanks were compared using the mixed procedure of the Statistical Analysis Software (SAS®) package. For all tests a p-level of 0.05 was used. Equation 1 was the model used and it employed both fixed and random variables; the effect of soil, time (ie week), and soil*time were fixed and the effect of the tank (nested within soil) and the residual error were random.

$$Y_{ijk} = \mu + soil_i + week_j + soil*week_{ij} + tank_{ik} + e_{ijk} \qquad (1)$$

Where:
$i = 1,2,3$; $j = 1, 2,3,4$ $k = 1, 2, 3$;
Y_{ijk} is the observation of i^{th} soil in j^{th} week in k^{th} tank
μ is the model constant
e_{ijk} is the error associated with the i^{th} soil, j^{th} week in the k^{th} tank

Four covariance structures were tested to model the e_{ijk} for both the DRP and TDP data sets: Unstructured, Variance Components, Compound Symmetry and Autoregression 1. Autoregression 1 gave the lowest Bayesian Information Criterion (BIC) value for both data sets with significantly better fit statistics than the three other covariance structures. Table 3.2 summarizes the covariance parameter estimates for the error associated with the tank, the residual error of the model and the correlation (R) value of the covariance structure.

Table 3.2. Summary of covariance parameter estimates from the model using covariance structure Autoregression 1 (AR(1)).

Data Set	Random effect (σ^2_{tank})	AR(1) (R)	Residual (σ^2_e)
DRP	0.01096	0.3447	0.08835
TDP	0.001041	0.1250	0.03334

For both data sets, the Bayesian Information Criterion value was not smaller upon running the model without the random statement (tank); therefore, there was no improvement to the goodness of fit of the model with the random statement; ie there is no effect of the tank. Table 3.3 summarizes the tests of the fixed effects; for DRP the effect of soil was shown to be reasonably significant at p=0.088 and the effect of soil on TDP was significant at p=0.007. For both data sets there was an effect of time but no effect of the soil-by-week interaction. This suggests that soil type and time do not combine to influence the overall average DRP or TDP (UCLA: Academic Technology Services, 2007). The effect of time reflects the fluctuations in the outlet concentration over the course of the study. The differences of the least square means between the two soil types for both DRP and TDP are not significant, p=0.9995 and 0.9994, respectively. Overall, these results suggest that the outlet concentration of TDP is significantly different from the inlet, the DRP concentration is reasonably significantly different from the inlet, and there is no difference between the outlet DRP and TDP values of the two soil types.

Table 3.3. Values of probability for F-tests for fixed effects

Data Set	Soil	Week	Soil*Week
DRP	0.0836	0.0065	0.1681
TDP	0.00700	<.0001	0.4441

3.4. Results and Discussion

3.4.1. Tracer study results

The mean residence time was calculated using chemical reactor residence time distribution theory (Levenspiel, 1999). The experimental tanks did not experience steady-state flows so the bromide concentration found in each water sample taken every three hours, was multiplied by the flow during those three hours.

(1) $C_T = C_o\,(g\ L^{-1}) \times Q\ (L\ 3hrs^{-1})$

Where:

C_T = total grams bromide per 3hr time unit
C_o = sample bromide concentration
Q = inflow rate ($L\ 3hrs^{-1}$)

With concentration converted into bromide mass per unit time, it was possible to integrate the area under the curve to find the total amount of grams recovered.

(2) $A = \int C_T\,dt = \sum C_{Ti}\,\Delta t_i$

Where:

A = area under curve
i = 1,2,3,4…60
Δt_i = i^{th} 3hr time unit
C_{Ti} = is the grams of bromide from the i^{th} 3hr time unit

The mean residence time (RT) was then calculated by:

$$(3) \qquad RT = \frac{\int t C_T \, dt}{\int C_T \, dt} = \frac{\sum t_i C_{Ti} \, \Delta t_i}{\sum C_{Ti} \, \Delta t_i}$$

Where:

t = unit time (3 hrs)

The active volume of a wetland is considered to be the volume responsible for mixing of the system calculated by (Smith *et al.*, 2005; Simi and Mitchell, 1999):

$$(4) \qquad V_a = \frac{Q_a \times RT}{V_T} \times 100$$

Where:

V_a = active volume of the wetland (%)
Q_a = inflow rate (m^3 day^{-1})
V_T = total volume of the wetland ($4.17 m^3$)

Table 3.4 summarizes the results from the bromide tracer test study. Unfortunately the datalogger recording the flow from replicate 1 of the field soil treatment failed and so it was impossible to calculate its retention time. However the retention times for the other replicates were quite close to each other.

Table 3.4. Bromide mass recovery, retention and active volume of each wetland treatment tank.

Treatment Tank	**Mass recovery of bromide (%)**	**Retention Time (days)**	**Active Volume (%)**
Sand 1	115.86	**1.30**	74.92
Sand 2	62.67	**2.22**	71.54
Sand 3	61.92	**2.38**	56.55
Field 1	No data	**No data**	No data
Field 2	84.25	**2.12**	47.04
Field 3	72.45	**2.26**	29.36

The calculated retention time for field soil replicates 2 and 3 and sand soil replicates 2 and 3 was very similar at approximately 2.2 days. The active volume however, was seen to be greater in the sand soil tanks than in the field soil tanks. It is possible that this is due to the increased vegetation density observed in the field soil tanks; Dierburg *et al*., (2005) have reported that in practice, wetland vegetation can result in a decrease in the effective volume ratio. Effective volume ratio, or active volume, is the measured retention time divided by the theoretical retention time. The concept of the active volume is also known as the mixing efficiency within the wetland and is characterized by the combined effect of slow and fast flow paths (Kadlec, 2008). Despite the possible effect of the greater vegetation density lowering the active volume of the field soil tanks, the actual retention time was not different from the sand treatment tanks.

The sand soil tank 1 had a much shorter retention time of only 1.3 days. This was a direct result of a much faster inflow rate due to an inconsistency in the inflow weir. It is likely that this increased inflow volume also led to the bromide recovery of 115% which isn't theoretically possible as the background levels of bromide were undetectable. Samples were collected every 3 hours and the concentration was integrated with the total outflow during the 3 hour period. When the outflow concentration was at its peak and a sample was taken, it is possible that the particular concentration captured was higher than the average for that 3 hour period, thus artificially inflating the mass recovered for that period. The mass recoveries obtained for the remaining four soil treatment tanks (61-84%) was consistent with what others have recovered in bromide tracer studies in constructed wetlands; Smith *et al*., (2005) recovered 72-81% of the bromide from the tracer tests performed in winter and spring on two constructed wetlands with retention times of 14 to 19 days. Tanner *et al*., (1998) reported bromide recoveries of 82-94% for three CW cells with retention times of 1 and 2 days.

For all three treatment tanks, it was observed that the active volume decreased with an increase in retention time. It is likely that the degree of mixing is positively associated with increasing the active volume and the intensity of mixing within the wetland increases with water velocity (Kadlec and Knight, 1996). A Norwegian study of six surface flow constructed wetlands treating agricultural runoff heavy with particulate P, found a positive effect of increased hydraulic load on the phosphorus settling velocity, despite the decrease in residence time (Braskerud, 2002). Because the P was in dissolved form in this study, it is possible that the degree of mixing and therefore active volume was not as important as retention time. It is interesting to note that despite the differences in active volume in the soil treatment tanks, the mean retention time was similar in four out of the five tanks tested. The outlier (sand tank 1) had a greater inflow rate than the other four tanks due to a faulty weir, which explains the reduced retention time. This suggests that the treatment occurring is almost equivalent in the two soil types irrespective of active volume.

3.4.2. Phosphorous removal

The outflow concentrations of DRP and TDP in all three treatments varied with inflow concentration. The outflow concentrations were significantly lower than the inlet concentrations ($p=0.08$ and $p=0.007$ respectively) however there was no difference between the outlet concentrations from the two soil treatments themselves ($p=0.9995$ and $P=0.9994$ respectively). As seen in Figure 3.2, the outlet concentration curve of TDP of the two soil types followed the inlet concentration curve and interestingly, the sand soil and field soil follow a similar trend over the three month course of the study. The average inlet TDP concentration over the course of the study was 0.306 mg L^{-1} and the average outlet TDP concentration from the field soil treatment was 0.161 mg L^{-1} and for the sandy soil treatment was 0.159 mg mg L^{-1} with no significant difference between the two (Figure 3.3). This corresponds to an average decrease in concentration of 52%. The corresponding values for DRP were consistently lower than TDP; however, the associated standard error was much greater than that observed for TDP.

In order to determine the total percent reduction for each tank the average weekly inlet and outlet concentrations for each tank were multiplied by the total number of litres that flowed out during the corresponding week. In the two soil treatments, despite the load variability (due to inconsistent flow rates between the replicates), the percentage of the total grams of P that were retained by the wetland was similar between the treatment replicates (Table 3.5).

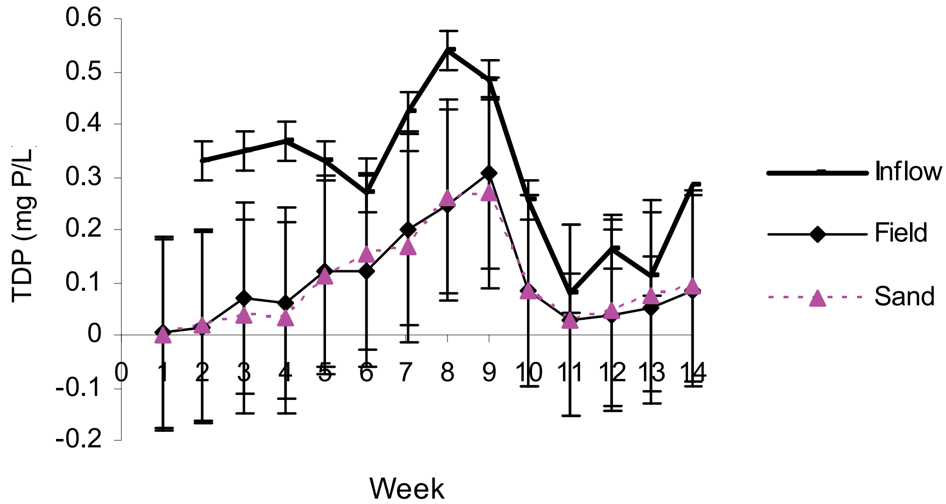

Figure 3.2. The least square means of the weekly concentration of TDP from July 10 to October 1, 2007. (± std error).

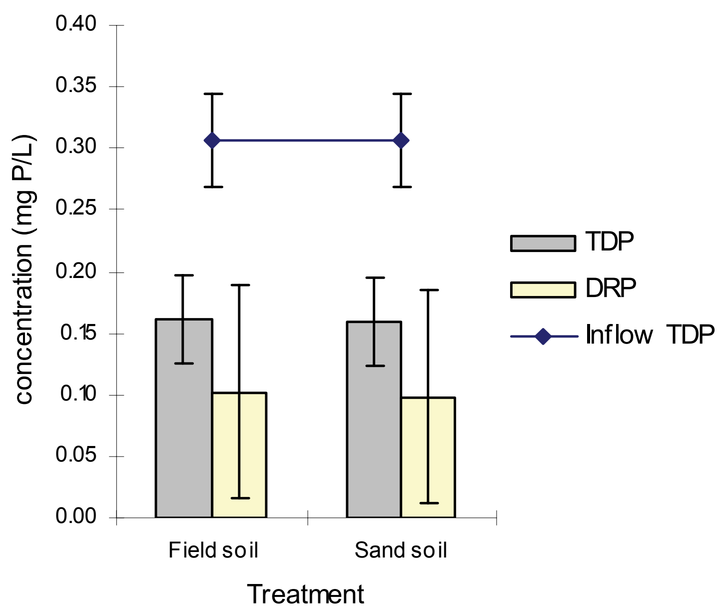

Figure 3.3. Average outlet concentration of DRP and TDP from July 10 to October 1, 2007. (± std error).

Table 3.5. The total number of grams of TDP that entered each soil treatment tank and the total number of grams that came out (± std deviation).

Soil type	Replicate	Grams loaded	Grams retained	% retained	Rate of retention ($g\ m^2\ summer^{-1}$)
Sand	1	33.4	14.9	44.7	1.6
	2	26.5	10.8	40.8	1.2
	3	19.6	7.9	40.2	0.9
average		**26.5 (±6.9)**		**41.9 (±2.4)**	
Field	1	28.9	9.8	33.9	1.1
	2	33.7	14.7	43.5	1.6
	3	26.5	11.7	44.3	1.3
average		**29 (±3.6)**		**40.5 (±5.8)**	

There was a difference in load of 13.8 g between sand tank replicates 1 and 3, yet the percentage of the load retained differed by less than 4%. Because this study took place over 87 days beginning July 5 and ending October 1, 2007, it is an inaccurate estimate of the yearly average because it would likely be inflated; a two-year study on a CW of the Walbridge River in Southern Quebec demonstrated an increased efficiency of P removal during spring and summer (La Flamme *et al.*, 2004).

TDP includes inorganic and organic forms of dissolved phosphorus and in this study, despite the lack of difference between the two soil types in TDP removal efficiencies, there was a larger standard error associated with the DRP than the TDP, making it difficult to detect a difference between them. It does however indicate that there was an organic fraction of the TDP in the outlet which would have resulted from the release of immobilized P from the dead and decaying vegetation back into the water column. Based on total loads, inlet TDP was 75% DRP and 25% dissolved organic phosphorus (DOP) and sand soil outlet was 60% DRP and 40% DOP, with field soil outlet 65% DRP and 35% DOP (Figure 3.4). These data suggest that the DOP fraction was unaffected by the wetland tanks and the DRP fraction was reduced. This observation is congruent with other CW studies where the outlet DOP was either similar to or greater than the outlet DOP (Kovacic *et al.*, 2000; Fink and Mitsch, 2004).

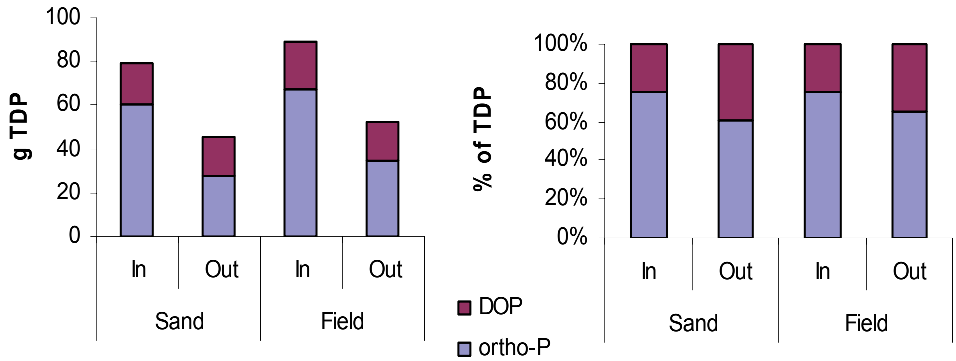

Figure 3.4. Phosphorus species composition of total dissolved phosphorus relative to g of TDP in and out from each soil type (left). P species composition of 100% TDP that went in and came out of the two soil types (right).

The physicochemical properties of the wetland system dictate which P removal mechanisms will dominate, should P removal occur (Kadlec, 2005). Wetland nutrient cycling is dependent on the process dynamics present within the system such as oxidation-reduction potential (ORP), dissolved oxygen (DO), pH and temperature (Sharpley, 1995; House *et al.*, 1995). In general, the main P-cycling pathways within a wetland can be grouped as sorption-desorption, precipitation-dissolution and immobilization-mineralization (Schoumans and Chardon, 2003). P entering a wetland in either organic or inorganic form is subject to interconversion between the two. Inorganic P in the form of dissolved PO_4^{3-} ions can complex with ligands, either organic or inorganic, and these complexes can become bound within the soil structure through the processes of adsorption and precipitation. Under aerobic conditions, P readily forms insoluble complexes with hydrous oxides of aluminum and iron and calcium (Sakadevan and Bavor, 1998; Kadlec, 1994). Dissolved inorganic P ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) is also readily taken up by plants and microbes (immobilized) and converted into organic P forms. The litter from living organisms can re-release organic P into the system; it can either be converted back into inorganic dissolved P (mineralized), remain immobilized through incorporation into the sediments or exit the wetland as dissolved organic P. In this CW it is likely that a combination of P dynamics was occurring however there was no net effect on the dissolved organic P fraction exiting the tanks.

3.4.2.1. Reducing conditions and wetland chemistry

Figure 3.5 shows the oxidation-reduction potential in the water column over the three-month study period. During the first two weeks in August, the ORP dropped sharply in both soil treatments from almost +250 mV to below +100 mV in the sand tanks, and below +50 mV in the field soil tanks. During the first week in September, the ORP dropped into the negative range; 0 to -70 mV in the sand tanks and to -150 mV in the field soil tanks. The dissolved oxygen (Figure 3.6) in the water of both tanks dropped concurrently with the ORP during the first week in August from around 6 mg L^{-1} to just below 2 mg L^{-1}, and remained there until the study was finished on October 1.

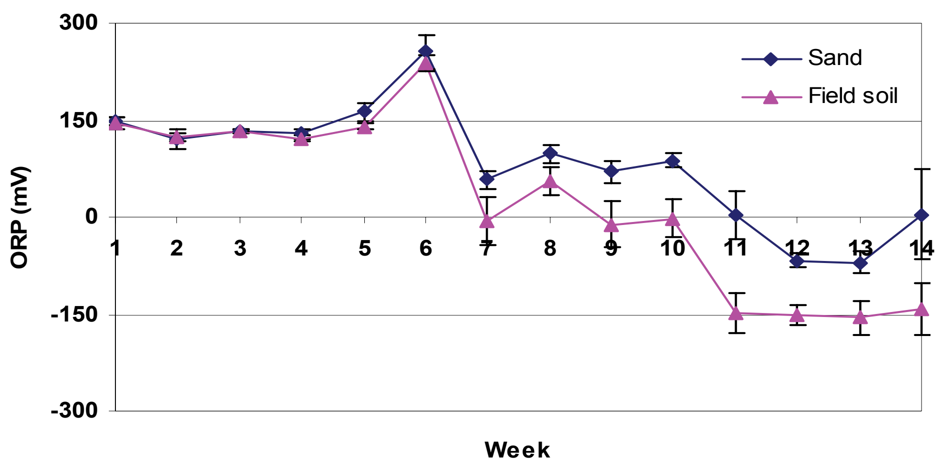

Figure 3.5. Weekly oxidation-reduction potential measurements taken from the water column in the treatment tanks from July 10 to October 1, 2007 (± std error).

After the first month of operation, the conditions in all six treatment tanks had become anaerobic, as indicated by the low ORP and low DO. This shift was in response to the tanks reaching equilibrium under saturated conditions; the tanks were filled with municipal water at the end of June and until then had been empty of water since the previous summer explaining why aerobic conditions dominated throughout July. They were flushed with municipal water for a week before the agricultural runoff solution was introduced on July 5, 2007.

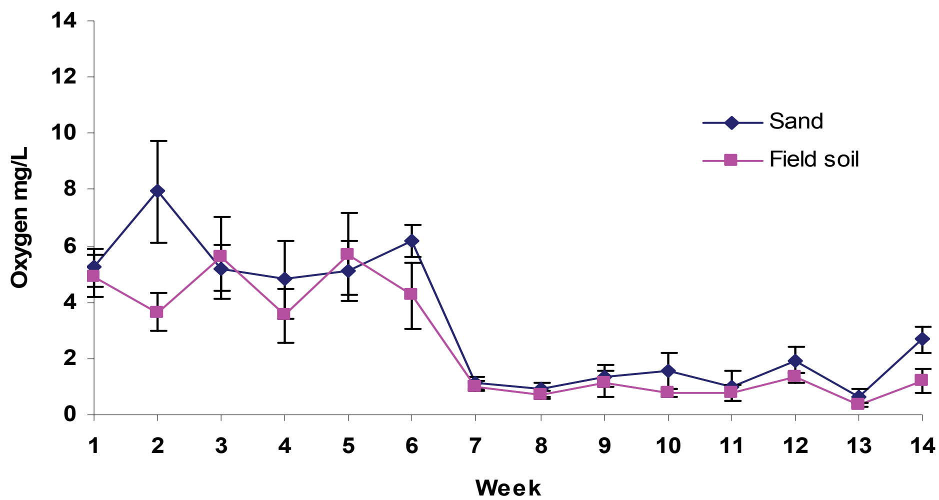

Figure 3.6. Weekly dissolved oxygen concentration in the water column in the treatment tanks from July 10 to October 1, 2007 (± std error).

The introduction of nitrate coupled with the very low flow rates, and the decomposition of plant detritus and organic matter would have driven the shift towards anaerobic conditions. As oxygen was consumed by cellular respiration during the decomposition process, the microorganisms would have switched from O_2 to NO_3^- as the metabolic electron acceptor. As conditions became more reduced, nitrate reduction would have been followed by the reduction of manganese oxide, iron oxide, sulfate and then finally carbon dioxide (Patrick *et al.*, 1996; Szogi *et al.*, 2004a). In these experimental tanks, the rate of oxygen consumption was greater than the amount entering in the inflow and the amount being diffused into the soil via the plant roots. This resulted in the reduced conditions observed at the beginning of August. While increasing retention time has been shown to improve P retention, in this case it may not have improved the removal efficiency because of the reduced conditions and low dissolved oxygen. These parameters are fundamentally dictated by inflow rates and physical CW design and affect the level of treatment the polluted water will receive. The design of these tanks coupled with the low inflow rate would have provided opportunity for dissolved organic carbon (DOC) to build up in the water column, thus promoting oxygen consumption through bacterial respiration and driving the ORP levels down, inhibiting the soil column to act as a P sink.

3.4.2.2. Role of soil column in a constructed wetland

The ability of soil to bind and retain P through adsorption and precipitation is greatly influenced by its Al and Fe concentration as well as the quantity of other exchangeable cations (CEC). However, under reducing conditions, these soil properties become ineffectual in P retention. The ORP conditions control the phosphate exchange processes between the water and soil interface (Lijklema, 1980). During the month of August, the ORP in the tanks of both soil types was in the range of -100 to +100 mV where, according to Patrick *et al*., (1996), the system can be considered anaerobic and reduced. It is in this range that Ferric-iron (Fe^{3+}) is reduced to soluble Ferrous-iron (Fe^{2+}), releasing any bound anion, including phosphate. The conditions in the field soil tanks reached highly reduced anaerobic status when the ORP level dropped to below -100mV at the beginning of September 2007. The reduced conditions observed in the tanks of the two soil treatments were low enough to transform the soils into a net source of P rather than a sink.

It then becomes interesting to investigate soil P levels; Figure 8 shows the amount of P contained in the field soil and sand soil. The samples were taken in November 2006 and November 2007, after the tanks were drained for the winter. (During the summer of 2006 the tanks were flooded continuously for a period of six weeks with the same agricultural runoff solution). The P concentration was tested in each sample and the results for the two soil types are pooled in Figure 3.7. It was assumed that the soil properties were constant between the November 2006 sampling and the beginning of the 2007 study, as the tanks were drained at the end of October 2006 and not filled again until the beginning of the 2007 study. The average soil P concentration for the sand soil was 12.8 mg kg^{-1} in 2006 and 2007, suggesting no net retention of P over the three month study.

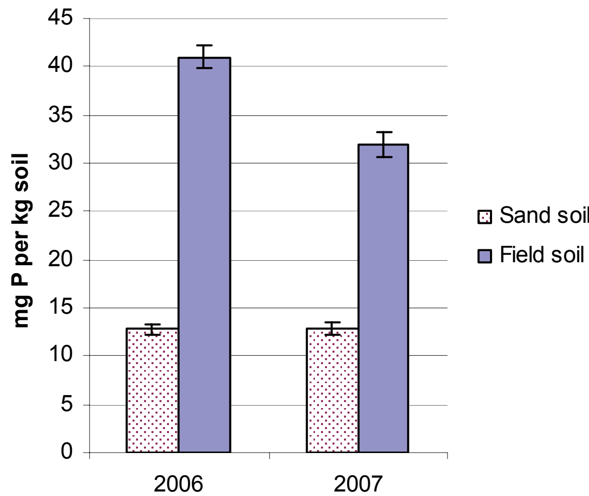

Figure 3.7. Mehlich 3 extracted P from sand soil and field soil tanks in November of 2006 and 2007(± std error).

The P concentration in the field soil dropped 24.3% over the course of the study. It measured 41 mg kg^{-1} in November 2006 and to 31 mg kg^{-1} in November 2007. This observation supports the probability that the status of the reducing conditions was not only preventing P from binding onto soil particles, but also releasing the stored P present in the soil. It is possible that because of the coarser texture of the sand as compared to the field soil, there was enough oxygen diffusion into the soil pore water from plant roots to create aerobic microsites (Edwards *et al.*, 2006) for exchange reactions to occur between soil particles and P; the overall effect of these sites being no net loss of soil P due to desorption. The observed ORP levels in the sand soil tanks did not reach as low as the levels seen in the field soil which can be interpreted as there being more oxygen available in the sand than in the field soil, allowing the sand soil tanks to reach equilibrium with the inflow dissolved phosphorus. This occurred despite the sand soil containing less Fe and Al than the field soil. The pH was taken weekly in the water column of the treatment tanks and it was found to hover at neutral in both soil treatments ranging between 7.23 and 7.83. It has been demonstrated that P removal efficiency of CWs improves as hydraulic retention time is increased (Akratos and Tsihrintzis, 2007); however, in anaerobic conditions such as observed in this study, increasing the hydraulic residence time has limited benefits without oxidizing the system.

There is a discrepancy in the P cycling between the two soil types. Despite their overall same P retention, as seen in the lack of difference between mean outlet concentration and percent removal calculated from loading rates, it is necessary to discuss the loss of soil P in the field soil. It has been shown that loss of P from soil to the overlying water increases with higher soil P concentration (Bostic and White, 2006) and that a low average oxidation-reduction potential can increase the outflow iron (Fe) and P concentrations. Vohla, *et al*., (2006) found a negative correlation (R=-0.59) between ORP and DRP and TP as well as a lower soil P concentration in areas of their constructed wetland that were anaerobic. The dissolved oxygen and ORP in the tanks in this study did not differ significantly between the inflow (deep zone) and outflow (shallow zone) thus suggesting that the entire tanks were anaerobic and subject to loss of P from the soil.

It was observed that 24% of the extractable P in the field soil was lost during the 3- month study; however, this was not translated into an increase in outlet P concentration with respect to the sand soil. The P released from the soil was likely taken up by the vegetation, as discussed in section 3.4.2.3. As Fe^{3+} is reduced to Fe^{2+} and phosphate ions are released, they become available for plant uptake. The role a constructed wetland soil plays in P storage is much debated; Sakadevan and Bavor (1998) state that even though vegetative components (living and dead) play an important role in short term P storage, it is the soil column that is most effective in long term P storage. Kadlec (2005) and Vymazal (2006) argue that the sequestration of organic P in the accretion of residuals from the biogeochemical cycle (life and death of flora and fauna) and particulate settling to form new sediments and soil is the long term storage for P in a free water surface constructed wetland where emergent vegetation is present. Hafner and Jewell (2006) have even developed a simple mechanistic model to predict with P and N removal by constructed wetlands based on detritus accumulation with reasonable success.

Our findings suggest compliance with soil accretion as the dominant storage mechanism due the anaerobic nature of the in situ conditions in the tanks of both soil types. No net increase in soil P within the sand tanks and a net loss of soil P within the field soil tanks suggest that the soil column was not serving as a storage mechanism. This is congruent with Kadlec's (1996) statement that in surface-flow constructed wetlands, after the soil medium has become saturated [with water] and is considered hydric, its primary role is no longer to filter P out of the water, but to sustain the vegetation and microbes which cycle P through their life and death.

3.4.2.3. Role of vegetation

The vegetation density was greater in the field soil tanks than in the sand soil tanks as seen in the photo in Figure 3.8. The tank on the left is a field soil replicate and the tank on the right is a sand soil replicate. In the field soil tanks, the cattails spread to the deep zones whereas they did not in the sand tanks. Also in the field soil tanks, the reed canary grass spread into the cattail areas filling in the spaces between them, and this was seen to a much lesser extent in the sand tanks. At the end of August 2007, the percent cover of the soil surface by the plants was estimated by dividing each tank into three quadrats and counting the reed canary grass tufts and cattail plants. It was found that the field soil tanks had an average of 100 cattail shoots and the sand tanks had an average of 48 cattail shoots. Each tank was planted with 28-32 cattail transplants from a nearby pond at the beginning of July. It was also estimated that the field soil tanks had 67% of the surface area covered by reed canary grass and 40% cover in the sand soil tanks.

Figure 3.8. Photograph taken August 20, 2007 of a field soil tank replicate (left) and sand soil replicate.

In this research site, it is likely that the additional P released from the field soil was incorporated into plant biomass as nutrient accumulation in plants depends on the rate of biomass production (Maddison *et al.*, 2005); 50% greater cattail production in the field soil tanks and almost 30% more reed canary grass than in the sand tanks was observed. Silvan *et al.,* (2004) also observed after the first year of a CW study, that vigorously colonizing vegetation was a significant factor in P retention with an estimated 25% removal efficiency reported. To begin with, the field soil was richer than the sand soil and it was likely this higher background nutrient (both micro and macro) content supported the greater biomass production. It should also be emphasized that this was only the second growing season these tanks had experienced so the vegetative component was still in the establishment stage (Gottschall *et al.*, 2007). It is generally accepted that the primary role of vegetation in wetlands is to physically slow incoming water, promote bacterial processes and facilitate chemical processes; however, Brix (1997) suggests vegetation has a significant impact on nutrient reduction from wastewater when the loading levels are low. It is difficult to establish generalized criteria to CWs treating agricultural runoff as the concentration and volume of water being treated fluctuate throughout the year. While there doesn't appear to be a consensus in the literature about what constitutes high and low loading rates, the loading rates used in this study were 3.6 g m^{-2} per 87 days, approximately equivalent to 0.4 kg ha^{-1} d^{-1}, and could be considered a lower load. Because the vegetation in the CW is still in the process of establishing itself, it is probable that the nutrient uptake increased with increased biomass production in the field soil tanks and that it was this sink that offset the excess DRP released from the soil column through plant assimilation.

Gottschall *et al.,* (2007) studied nutrient removal and plant storage in a well-established CW in eastern Ontario to demonstrate this idea. Their CW consisted of five sections in series, the 2^{nd} and 4^{th} being surface-flow wetland cells, planted in 1995 with *Typha latifolia L.* L. and *Typha angustifolia* L. They found that in the 2^{nd} cell, there was a higher amount of nutrients stored but there was no net change in storage over the course of the growing season. The 4^{th} cell was less highly-loaded than the 2nd cell and exhibited a net increase in storage over the growing season. It is interesting to note however that the net increase in storage in the second cell of this mature wetland accounted for less than 5% of the overall TP removal. While it is probable that the field soil tanks in this study had a larger amount of P incorporated into vegetation biomass during the 2007 growing season, it can be expected that as the wetland matures, the importance of plant assimilation as a P sink will decline year to year, despite being subjected to lower loads (Edwards *et al.*, 2006).

3.5. Conclusions

Two soil types common in Quebec, Canada, a sand soil and a sandy clay loam field soil, were used as substrates in surface-flow constructed wetland tanks to assess their impact on P removal from an artificial agricultural runoff solution. A conservative tracer test was also performed to determine if there was a difference in mean hydraulic residence time between the two soil types. The following conclusions were drawn from this study:

(1) The net removal efficiency between the sand soil and field soil surface-flow constructed wetland tanks in this study did not differ; both removed approximately 40% of the incoming TDP. There was no change in the soil P concentration of the sand soil and a 24% reduction in the field soil over the course of the study. This reduced soil P concentration in the sandy clay loam soil tanks, coupled with 50% more cattails and 30% more reed canary grass, suggests that plant assimilation compensated for the P released from the soil column due to the highly-reduced conditions. Low ORP in both soil types would have prevented or reversed precipitation-adsorption reactions and therefore residual organic matter accretion from the biogeochemical cycle was likely the dominant P sink for the 40% TDP that was successfully removed.

(2) Once the vegetation has fully colonized the tanks after several years of operation, its role as a nutrient sink may diminish. The field soil may act as a potential source of P due to its tendency to become more reduced than the sand tanks.

(3) The hydraulic retention time was approximately 2.2 days for the tanks in this study. While increasing retention time has been shown to improve P retention, in this case it may not have improved the removal efficiency because of the reduced conditions. A difference between the field soil and sand soil's ability to remove P may emerge as the CW ages, as the field soil had a larger pool of Melich III extractable iron than did the sand. However the active volume of the wetland should be taken into consideration as the sand tanks had active volumes ranging from 56 to 74% whereas the field soil tanks were between 29 and 47%. This may indicate that there is more contact between the sand soil and polluted water than there is between the field soil and polluted water which would theoretically lead to the binding of more P.

(4) Acknowledging the fact that these surface flow CW tanks are still in the process of establishment and maturation, the authors of this study would recommend a sand soil for use as a CW wetland substrate in southern Quebec as there is less P to lose from the soil if ORP is low enough to reduce iron and there is more water movement within the soil column.

3.6. Recommendations for future work

(1) With an overall P removal of approximately 40%, the design of the vegetated tanks used in this research project could be improved to in an effort to increase the removal efficiency. A mixing device placed in the deep zone to aerate the water column could help increase the oxidation-reduction potential to a level where Fe^{3+} is no longer being reduced, allowing it to react with dissolved P thus immobilizing it. In addition to improving the ORP conditions, increasing the hydraulic retention would allow more treatment within the CW.

(2) One of the limitations to this study was that it didn't address how this CW design would impact particulate P as is often present in runoff events such as the spring snow melt. Further study of the capacity of this design to reduce particulate P

from agricultural runoff would be interesting as the deep zone combined with a slow inflow rate in theory should allow for particulate settling.

(3) Future work at this sight should include further testing for iron as well as plant tissue analysis. Outlet water sample analysis for soluble Fe^{2+} concentration as well as soil sample analysis for Fe concentration would confirm that the P loss from the soil was indeed coupled with the reduction of insoluble Fe^{3+} to soluble Fe^{2+}. Plant analysis for P would complete the P mass balance and confirm that the P released from the soil was indeed taken up by the vegetation.

(4) The tracer study conducted to determine the hydraulic residence of the tanks should be repeated three times. The results would be more robust and suitable for statistical scrutiny with a triplicate data set.

3.7. 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.

APHA, AWWA and WPCF (1992). Standard methods for the examination of water and wastewater / prepared and published jointly by American Public Health Association, American Water Works Association, Water Pollution Control Federation. Washington, DC, USA, American Public Health Association.

Aye, T. M., Nguyen, M. L., Bolan, N. S. and Hedley, M. J. (2006). "Phosphorus in soils of riparian and non-riparian wetland and buffer strips in the Waikato area, New Zealand." New Zealand Journal of Agricultural Research **49**: 349-358.

Berka, C., Schreier, H. and Hall, K. (2001). "Linking water quality with agricultural intensification in a rural watershed." Water Air and Soil Pollution **127**: 389-401.

Bostic, E. M. and White, J. R. (2006). "Soil Phosphorus and Vegetation Influence on Wetland Phosphorus Release after Simulated Drought." Soil Sci Soc Am J **71**: 233-238.

Braskerud, B. C. (2002). "Factors affecting phosphorus retention in small constructed wetlands treating agricultural non-point source pollution." Ecological Engineering **19**: 41-61.

Brix, H. (1997). "Do macrophytes play a role in constructed treatment wetlands?" Water Sci. Technol. **35**(5): 11-17.

Casey, R. E. and Klaine, S. J. (2001). "Nutrient Attenuation by a Riparian Wetland during Natural and Artificial Runoff Events." J. Environ. Qual. **30**: 1720–1731.

Dierberg, F. E., Juston, J. J., DeBusk, T. A., Pietro, K. and Gu, B. H. (2005). "Relationship between hydraulic efficiency and phosphorus removal in a submerged aquatic vegetation-dominated treatment wetland." Ecological Engineering **25**(1): 9-23.
Eastman, M. (2008). Field-scale nutrient transport monitoring and modeling of subsurface and naturally drained agricultural lands. Bioresource Engineering. Ste-Anne-de-Bellevue, QC, McGill University, Macdonald Campus. **M.Sc.Thesis**
Ebina, J., Tsutsui, T. and Shirai, T. (1983). "Simultaneous Determination of Total Nitrogen and Total Phosphorous in Water Using Peroxodisulfate Oxidation." Water Research **17**(12): 1721-1726.
Edwards, K. R., Cizkova, H., Zemanova, K. and Santruckova, H. (2006). "Plant growth and microbial processes in a constructed wetland planted with Phalaris arundinacea." Ecological Engineering **27**(2): 153-165.
Fink, D. F. and Mitsch, W. J. (2004). "Seasonal and storm event nutrient removal by a created wetland in an agricultural watershed." Ecological Engineering **23**: 313-325.
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.
Hafner, S. D. and Jewell, W. J. (2006). "Predicting nitrogen and phosphorus removal in wetlands due to detritus accumulation: A simple mechanistic model." Ecological Engineering **27**(1): 13-21.
Hammer, D. A. (1992). "Designing constructed wetlands systems to treat agricultural nonpoint source pollution." Ecological Engineering **1**(1-2): 49-82.
House, W. A., Denison, F. H. and Armitage, P. D. (1995). "Comparison of the uptake of inorganic phosphorus to a suspended stream bed-sediment." Water Research **29**(3): 767-779.
Kadlec, R. H. (2005). "Phosphorus Removal in Emergent Free Surface Wetlands." Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering **40**(6/7): 1293-1306.
Kadlec, R. H. (2008). "The effects of wetland vegetation and morphology on nitrogen processing." Ecological Engineering **In Press, Corrected Proof**.
Kadlec, R. H. and Knight, R. L. (1996). Treatment Wetlands. Boca Raton, Florida, Lewis Publishers.
Kellogg, R. L. and Maizel, M. S. (1994). "The Potential for Leaching of Agrichemicals used in Crop Production: A National Perspective." Journal of Soil and Water Conservation **May-June**: 294-298.
Kovacic, D. A., David, M. B., Gentry, L. E., Starks, K. M. and Cooke, R. A. (2000). "Effectiveness of Constructed Wetlands in Reducing Nitrogen and Phosphorus Export from Agricultural Tile Drainage." J Environ Qual **29**: 1262-1274.
La Flamme, C., Enright, P. and Madramootoo, C. (2004). Sediment and Nutrient Removal Efficiencies in a Constructed Wetland in Southern Quebec. ASAE/CSAE Annual International Meeting. Ottawa, Ontario, Canada.
Levenspiel, O. (1999). Chemical Reaction Engineering. Hoboken, NJ, USA, John Wiley & Sons.

Lijklema, L. (1980). "Interaction of orthophosphate with Iron(III) and Aluminum Hydroxides." Environmental Science and Technology **14**(5): 537-541.
Maddison, M., Soosaar, K., Lohmus, K. and Mander, U. (2005). "Cattail Population in Wastewater Treatment Wetlands in Estonia: Biomass Production, Retention of Nutrients, and Heavy Metals in Phytomass." Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering **40**(6/7): 1157-1166.
Patrick, W. H., Gambrell, R. P. and Faulkner, S. P. (1996). Redox measurements in soil. Methods of Soil Analysis, Part 3, 677 South Segoe Rd, Madison, Wisconsin, 53711, USA: SSSA**:** 1255-1273.
Sakadevan, K. and Bavor, H. J. (1998). "Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems." Water Research **32**(2): 393-399.
Schoumans, O. F. and Chardon, W. J. (2003). "Risk assessment methodologies for predicting phosphorus losses." Journal of Plant Nutrition and Soil Science **166**(4): 403-408.
Sharpley, A. N. (1995). "Soil phosphorus dynamics: agronomic and environmental impacts." Ecological Engineering **5**(2-3): 261-279.
Shilton, A. N. and Prasad, J. N. (1996). "Tracer Studies of a Gravel Bed Wetland." Water Sci. Technol. **34**(3-4): 421-425.
Silvan, N., Vasander, H. and Laine, J. (2004). "Vegetation is the main factor in nutrient retention in a constructed wetland buffer." Plant & Soil **258**(1/2): 179-187.
Simi, A. and Mitchell, C. A. (1999). "Design and Hydraulic Performance of a constructed wetland treating oil refinery wastewater." Water Science and Technology **40**(3): 301.
Smith, E., Gordon, R., Madani, A. and Stratton, G. (2005). "Cold climate hydrological flow characteristics of constructed wetlands." Canadian Biosystems Engineering: **47**: 1.1-1.7.
Szogi, A. A., Hunt, P. G., Sadler, E. J. and Evans, D. E. (2004). "Characterization of Oxiation-Reduction Processes in Constructed Wetlands for Swine Wastewater Treatment." Applied Engineering in Agriculture **20**(2): 189-200.
Tanner, C. C., Sukias, J. P. S. and Upsdell, M. P. (1998). "Organic matter accumulation during maturation of gravel-bed constructed wetlands treating farm dairy wastewaters." Water Research **32**(10): 3046-3054.
UCLA: Academic Technology Services, S. C. G. (2007). "Introduction to SAS." Retrieved November 24, 2007, from http://www.ats.ucla.edu/stat/sas/notes2/
Vohla, C., Alas, R., Nurk, K., Baatz, S. and Mander, U. (2006). "Dynamics of phosphorus, nitrogen and carbon removal in a horizontal subsurface flow constructed wetland." Science of The Total Environment **In Press, Corrected Proof**: 105.
Vymazal, J. (2006). "Removal of nutrients in various types of constructed wetlands." Science of The Total Environment **doi:10.1016/j.scitotenv.2006.09.014**: 105.
Werner, T. M. and R. H. Kadlec (2000). "Wetland residence time distribution modeling." Ecological Engineering **15**(1-2): 77-90.

Preface to Chapter 4

Agricultural runoff containing phosphorus is indeed a threat to freshwater quality in Quebec. Phosphorus in runoff is almost always accompanied by high concentrations of nitrogen. Nitrogen is also a threat to water quality as it also promotes eutrophication. The previous chapter dealt with assessment of two wetland substrates in their ability to influence phosphorus retention in a surface-flow constructed wetland. The following chapter explores how these same two substrates affects the ability of the constructed wetland to reduce nitrogen from the same runoff solution.

4. Chapter 4- Comparison of Two Constructed Wetland Substrates for Reducing Nitrogen Load from Agricultural Runoff.

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4.1.Abstract

Agricultural nonpoint source nitrogen is a threat to surface waters in Quebec due its ability to promote eutrophication; a major threat to water quality. Constructed wetlands are gaining interest for their role in treating nonpoint source nutrient pollution. This study was aimed at studying two substrates, a sandy clay loam field soil and a sand soil, used in a surface-flow constructed wetland (CW), to compare how they influenced N retention. A secondary aim was to assess the production of nitrous oxide and determine if there was any difference between the two soil types. Field measurements were taken at a pilot-scale surface-flow constructed wetland site between July 5 and October 1, 2007. The site consisted of three replicate tanks containing the sandy clay loam and three containing the sand soil. The surface area of each tank was 9.29 m^2 and was cylindrical in shape with a radius of 0.75 m. The inlet end was characterized by a deep zone which sloped upwards to a shallow zone which occupied 66% of the surface area and was planted with reed canary grass (*Phalaris arundinacea* L.) and cattails (*Typha latifolia* L.). The mean residence time was 2.2 days. The tanks were flooded continuously for the duration of the study with artificial agricultural runoff solution containing 10 mg L^{-1} nitrate-N and 0.3 mg L^{-1} dissolved reactive P. The six treatment tanks received 689 to 1100 g of N over the study period and the average rate of retention by sand tanks was 40 g m^2 (±20) and 69 g m^2 (±12) by the field soil tanks. This corresponded to average removal efficiencies of 41% and 63% respectively, with the difference being reasonably significant (p=0.09). Nitrous oxide emissions from the tanks were also measured and no difference was found between the two soil types (p=0.466). The more severely reduced conditions in the field soil tanks, coupled with higher available carbon present in the organic matter, likely promoted a higher rate of complete denitrification (lower N_2O:N_2). The field soil also supported greater biomass production compared to the sand soil, which

would have resulted in a larger uptake of N. This investigation suggests that the sandy clay loam field soil has the capacity to retain more N than the sand soil due to a greater nutrient assimilation, organic matter accretion rate and available carbon for supporting denitrifying microbial populations.

4.2.Introduction and background

Agricultural non-point source pollution (NPS) has been deemed the primary source of nitrogen and phosphorus overloading of freshwater bodies in North America (Kellogg and Maizel, 1994). As industrial farms continue to intensify production, so does the use of nitrogen as a fertilizer. The excess N applied to fields come from both manure spreading and mineral N fertilizer application. In the case of livestock producers, they often have more manure available for spreading over a limited amount of land, leading to over-application. In the case of crop producers, over-application of mineral fertilizer is common as maximum crop yield is the goal (Berka *et al.*, 2001). Excess nitrate (NO_3) in surface and shallow ground water can contribute to eutrophication in receiving freshwater and estuarine systems (Casey and Klaine, 2001). It is therefore important to remove or reduce nitrogen from agricultural drainage water before it enters the receiving water bodies. Implementing on-farm best management practices (BMPs), in addition to manure management plans, are necessary for mitigating nutrient loss from agricultural land. BMPs such as riparian buffer strips along fields, catch basins along stream channels and constructed wetlands in runoff ditches, are examples of structures useful for reducing nutrient loads from runoff (Michaud *et al.*, 2005).

Constructed wetlands (CWs) have proven effective in treating point source waste streams high in nitrogen such as manure pile runoff or milk house wash for example (Kadlec and Knight, 1996). This success has lead to the increasing interest in using CWs to treat non point source pollution such as agricultural runoff (Raisin and Mitchell, 1995), which is characterized by large volumes of water with lower concentrations (Kovacic *et al.*, 2000). The maximum allowable level for drinking water is 10 mg L^{-1} nitrate-N; however, it is known to be an environmental threat to receiving water bodies at concentrations far below this. Depending on the individual water chemistries of the receiving water, eutrophication has been documented to occur at concentrations of total N as low as of 0.4 N L^{-1} (Casey and Klaine, 2001). The most cost-effective long term management option is controlling the source of the nutrients (Berka *et al.*, 2001) by managing their application to agricultural land. In addition, on-farm surface-flow constructed wetlands are an interesting best management tool as the concept can be implemented with low initial investment capital and minimal maintenance. For the design of a CW however, it is important to understand the factors influencing the natural processes which occur within it and therefore its potential treatment efficiency.

Denitrification is a central component of the N cycle that returns inorganic N present in plants and soils, of both aquatic and terrestrial ecosystems, to the atmosphere (Firth and Edwards, 2000; Watts and Seitzinger, 2000). CWs designed to remove N from inflowing water aim to capitalize on this microbially mediated process for permanent removal (Bachand and Horne, 2000). Microbial populations responsible for denitrification can vary depending on their living conditions; the substrate and supply of nutrients within the CW will ultimately dictate which microbial communities will flourish. Nitrous oxide emission is an indicator of microbial denitrification activity (Chang *et al.*, 1998; Firth and Edwards, 2000) because the intermediary of the reduction of NO_2+NO_3 to N_2 is nitrous oxide (N_2O). Influential environmental factors in a constructed wetland's capacity to support denitrification include oxidation-reduction potential (ORP), dissolved oxygen (DO), temperature, pH and bioavailable carbon (Kadlec and Knight, 1996).

The goal of this research was to test if the soil substrate had an impact on a surface-flow constructed wetland's ability to reduce dissolved nitrogen from agricultural runoff. The more specific aim was to determine if there was a difference between two soil types common to Southern Quebec, Canada; a sandy clay loam field soil and a sandy soil, in their ability to reduce dissolved nitrogen from a simulated agricultural runoff solution. It was expected that denitrification would be the dominant N removal mechanism and that the field soil would support a greater amount of denitrifying activity due to its greater carbon content. The simulated agricultural runoff solution contained 10 mg N L^{-1} as nitrate and 0.3 mg P L^{-1} as dissolved inorganic phosphorus, levels which are commonly found in nonpoint source agricultural runoff in Southern Quebec (Eastman, 2008). In order to compare these two soil types, dissolved N concentrations at the inflow and outflow as well as dissolved oxygen, oxidation reduction potential, pH and temperature were monitored within a pilot-scale constructed site. This study was also interested to see if indeed N_2O was being produced and how it changed in the different substrates over the course of the study.

4.3.Methodology

4.3.1. Experimental Site

The pilot-scale constructed wetland research site is located 3km north of McGill University's Macdonald Campus in Ste-Anne-de-Bellevue, Quebec, Canada. Details of this site may be found in Chapter 3. Briefly, it consisted of six above-ground, black open, high density polyethylene (HDPE) half-cylinder shaped tanks; three of the six open tanks were filled with a sandy soil and the other three with a sandy clay loam field soil. Each tank had a volume of approximately 4.17m^3 with 65% occupied by soil and surface area of 9.29m^2. Table 4.1 summarizes some of the soil properties of the two soil types.

Table 4.1. Summary of the soil characteristics where OM = organic matter (± standard deviation).

Soil type	Sand[a]	Silt[a]	Clay[a]	pH	%OM 2006	%OM 2007
Sand	96	3	1	6.2 (0.5)	0.2 (0.1)	0.8 (0.8)
Sandy Clay Loam (Field soil)	60	19	21	7.4 (0.3)	2.6 (0.2)	3.2 (0.7)

[a]Size group of soil particles: Sand 2mm-53µm, Silt 53-2µm, Clay < 2µm

At the inlet end of the tanks, there was a deep zone from which the soil sloped upwards to the shallow zone. The shallow zone occupied approximately 66% of the surface area and was vegetated with alternating sections of reed canary grass (*Phalaris arundinaceae* L.) and cattails (*Typha latifolia* L.). The water flowed from the deep zone, through the shallow vegetated section to the outlet.

There were three mixing tanks located above the distribution tanks where the artificial runoff solution was mixed. The target concentration of the runoff solution was 10 mg L^{-1} nitrate-N and 0.3 mg L^{-1} dissolved reactive phosphorous as orthophosphate. The corresponding N loading rate was approximately 100 g m^{-2} per 87 days, equivalent to 11.5 kg ha^{-1} d^{-1}. The mean hydraulic residence time for the treatments tanks was 2.2 days with the exception of 1.3 days for the first replicate of the sand soil tanks.

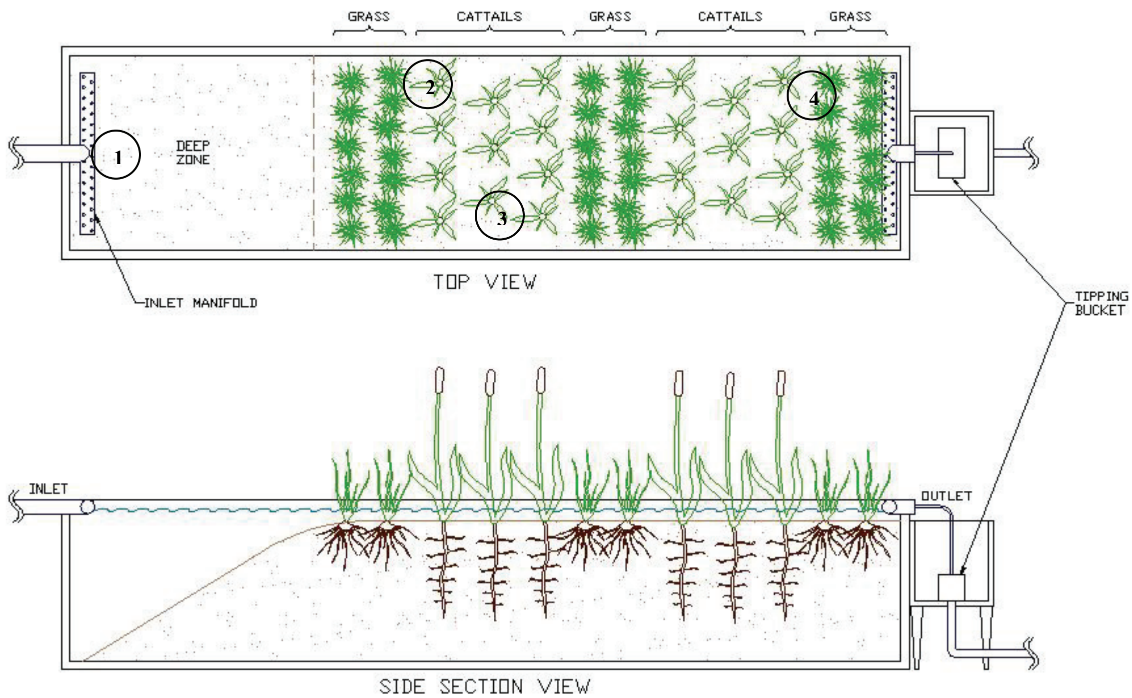

Figure 4.1. Side and top view of the six soil treatment tanks. Numbered circles represent location of gas sampling chambers.

4.3.2. Water sample collection and analysis

The study began July 5, 2007 by running municipal water through the treatment tanks. Water samples and water column information such as dissolved oxygen (DO), oxidation-reduction potential (ORP), temperature and pH was collected to determine initial conditions. Starting July 10, 2007, the municipal water supply was stopped and the system started receiving the artificial runoff solution continuously until October 1, 2007. Outlet water samples from each wetland treatment tank were collected by a custom-built Avensys autosampler every 42 hours in 1-L Nalgene HDPE bottles. Upon collection, a composite of the four samples collected every 42 hours from the same tank, was made by adding 30 mL of each into a 120-mL HDPE sample bottle. Therefore, a more representative sample was obtained because it was composed of a mixture of the four individual samples collected during that week. Grab samples from the mixing and distribution tanks were collected as well. Water samples were collected weekly and immediately filtered through 0.45 micron nylon membranes into acid-washed 120-mL Nalgene HDPE bottles. Non-filtered samples were also collected in acid-washed bottles and then transported in an ice-filled cooler back to the laboratory and stored in fridge at 4 ºC. Dissolved oxygen (DO), pH, oxidation-reduction potential (ORP) and temperature data was collected weekly in the deep zone and shallow zone of vegetated tanks, as well as from the surface water of the distribution and mixing tanks. These data were collected using a Horiba portable pH meter (Model Series D-52, Horiba International Corporation, Kyoto, Japan) with corresponding DO probe, ORP probe, and a pH/temperature probe. All probes were calibrated and stored according to Horiba's specifications (Horiba D series operation manual, 2001).

Filtered water samples were analyzed for nitrate and nitrite-nitrogen (NO_3-N + NO_2-N), ammonia (NH_4) and total dissolved nitrogen (TDN), and unfiltered water samples were analyzed for total nitrogen (TN). All analyses were carried out on a Lachat Flow Injection Analysis System (Model QuikChem® 8500, Lachat Instruments, Loveland, Colorado). Dissolved nitrated was reduced to nitrite via a cadmium column, and then reacted with sulfanilamide with detection range of 0.2 to 20 mg N/L (Egan, 2003). NH_4 analysis was carried out by heating the sample with salicylate and hypochlorite under alkaline conditions with detection range of 10 to 500 μg N/L (Bogren, 2003). To measure TDN and TN, 5mL aliquots of the filtered and unfiltered samples were digested with a peroxodisulfate oxidation method (Ebina *et al.*, 1983) and then analyzed for NO_3-N using the Lachat autoanalyzer. There was no difference between TDN and TN so it was concluded that no particulate N was entering or exiting the wetland tanks. TDN results will therefore be reported in this chapter. NO_2-N accounted for less than 0.1% of NO_3-N + NO_2-N so for this paper, values are reported as NO_3-N. Filtered water samples were also analyzed for dissolved organic carbon (DOC) with a Shimadzu TOC Analyzer (Model VCPN, Shimadzu Scientific Instruments, Columbia, MD) using a combustion catalytic oxidation method (APHA *et al.*, 1992).

4.3.3. Gas sample collection for nitrous oxide

Gas samples were collected from 4 regions of each of the six treatment tanks biweekly between July 30th and September 28th, 2007. Cylinders measuring 1.95 m high by 0.265 m in diameter, capped with removable air-tight lids that were fitted with a battery operated 10-cm computer fan, were used to collect gas samples from the treatment tanks. The 106-L chambers were placed over 4 regions of the tank for 30 minutes before being sampled and then moved to the next tank. The chambers were mixed continuously during the sampling time by the fans. A sample of ambient air was taken at time 0 for each tank. Every sampling date, the chambers were fitted on to collars fixed in the soil to ensure that sampling occurred in the same place each time.

Three chambers were placed in the shallow zone and one in the deep zone. The chamber placed in the deep zone was 75 cm longer than the other three so that the headspace was equal to those in the shallow zone. In the shallow zone, one chamber was placed over a patch with no plants, one over a cattail, and one over a tuft of reed canary grass. Each chamber was fitted with a 30-cm piece of Taigon® tubing protruding from the wall and fixed at the end with a three-way stopcock. The two opposite ends of the stopcock fit into the tubing and a 60-mL syringe respectively. The adjacent stopcock spout had a silicone septum glued to it. Each time a sample was withdrawn, the valve was turned to block the septum-covered spout and the syringe was pumped 10 times to ensure a mixed sample. When the syringe was filled, the valve was turned to block the chamber and another 60-mL syringe fitted with a 26 gauge needle was inserted into the septum and a sample was withdrawn from the first syringe. Samples were collected by inserting a syringe into the sampling tube through a septa glued to the open end of a three way stopcock. The syringe was pumped ten times before withdrawing a sample and injecting it into an evacuated 12-mL soda glass Labco Exetainer® containing 0.5g magnesium perchlorate as a dessicant. The Exetainers® were transported back to the lab in a protective cardboard box and the contents were analyzed within two days. The gas samples were analyzed for N_2O on a Gas Chromatograph (GC) equipped with electron capture detector-ECD (Model 5890 Series, Hewlett-Packard, Hewlett-Packard Company, Avondale, PA). The method of rapid analysis of N_2O, developed by (Mosier and Mack, 1980), was used in this experiment.

4.3.4. Data Analysis

A statistical model using repeated measures over time was employed to determine if the outlet concentrations of NO_3-N, NH_3-N, dissolved organic N, TDN and DOC were different between the sand soil and field soil treatments over the three-month study. Outlet concentrations from the three replicates for each of the sandy soil tanks and field soil tanks were compared using the mixed procedure of the Statistical Analysis Software (SAS®) package. For all tests we assumed a strong significance at ά =0.05 and reasonable significance at ά =0.1. Equation 1 was the model used and it employed fixed and random variables; the effect of soil, time (ie week), and soil*time interaction were fixed and the effect of the tank (nested within soil) and the residual error were random. The soil term included the inlet as well as outlet concentration.

$$Y_{ijk} = \mu + soil_i + week_j + soil*week_{ij} + tank_{ik} + e_{ijk} \qquad (1)$$

Where:
i = 1,2,3; j = 1, 2,3,4 k = 1, 2, 3;
$Yijk$ is the observation of i^{th} soil in j^{th} week in k^{th} tank
μ is the model constant
e_{ijk} is the error associated with the i^{th} soil, j^{th} week in the k^{th} tank

Four covariance structures were tested to model the e_{ijk} for both all the nitrogen species and DOC data sets: Unstructured, Variance Components, Compound Symmetry and Autoregression 1. Autoregression 1 gave the lowest Bayesian Information Criterion (BIC) value for all data sets with significantly better fit statistics than the three other covariance structures. It should be noted that the DOC model was not run with the inlet concentration (due to less frequent sampling) therefore the comparison was lonely between the two soil types. Despite there no difference between soil ($p=0.1981$), they were different from the influent the first week in September as determined by a t-test.

Table 4.2. Values of probability for F-tests for fixed effects.

Data Set	Soil	Week	Soil*Week
TDN	<.0001*	<.0001*	0.0003*
NO_3-N	<.0001*	<.0001*	0.0002*
NH_4-N	0.0255*	<.0001*	0.0012*
DON	0.5041	<.0001*	0.4328
DOC	0.1981	<.0001*	0.0364*

(* indicates strong siginificance)

Nitrous oxide results were analyzed using a randomized complete block design analysis of variance to determine if there was a difference between the collar positions (including ambient air) on each sampling date and to determine if there was an overall difference in N_2O emissions between the sand soil, field soil and ambient on each sampling date. Statistical analysis was carried out using the model in equation 2 in the GLM procedure of the Statistical Analysis Software (SAS®) package.

$$Y_{ij} = \mu + soil_i + position_j + soil*position_{ij} + e_{ij} \qquad (2)$$

Where:
$i = 1,2,3$; $j = 1, 2,3,4$ $k = 1, 2, 3$;
Yij is the observation of i^{th} soil in j^{th} position
μ is the model constant
e_{ij} is the error associated with the i^{th} soil, j^{th} position

On all five sampling dates, there was no significance between two of the parameters; soil by position interaction (differences of least square means adjusted with Scheffe) or differences between emissions from the two soil types (differences of least square means adjusted with Scheffe). However, on all five sampling dates there was a difference between the soil treatments and ambient concentration.

4.3.5. Results and Discussion

The outlet TDN and NO_3-N concentrations of the two soil types followed a similar trend over the three month course of the study (Figures 4.2 and 4.3). The outlet concentration began to decrease between August 6th and 13th (weeks 6 and 7). The September 10th sampling day (week 11) indicates a large pulse release of TDN and NO_3-N from the sand tanks and corresponding smaller one from the field soil tanks. It can be speculated that a drop in temperature which occurred during this week caused a die-off of some of the denitrifying bacteria, inhibiting treatment of the inflow water for that particular week before the population readjusted itself. The daytime water temperature inside the tanks experienced a drop from 22.4 C to 16.6 C, which was the largest change observed over the course of the study (Figures 4.2, 4.3).

Many studies have demonstrated that microbially mediated processes, including both nitrification and denitrification, are temperature dependent (Rousseau *et al.*, 2001; Kuschk *et al.*, 2003; Mander *et al.*, 2003). Kuschk *et al.,*'s (2003) four year study of N removal in a subsurface flow CW demonstrated that removal rates oscillated year round. They found denitrification was restricted during spring and autumn as a result of annual temperature changes and probably limited by carbon source. Carbon-limitation is not suspected to be the cause of the outlet spike in N concentration due to abrupt nature and increasing dissolved organic carbon (DOC) observed in the same sample. It is suspected that the sudden decrease in temperature in the same week is responsible for the lack of treatment that occurred. The spike in outlet concentration was greater in the sand soil than the field soil likely due to the sparser vegetation cover, corresponding to a lower density microbial population. The inlet TDN and NO_3 concentrations show fluctuations, most likely due to the timing of the addition of the KNO_3 to the mixing tank.

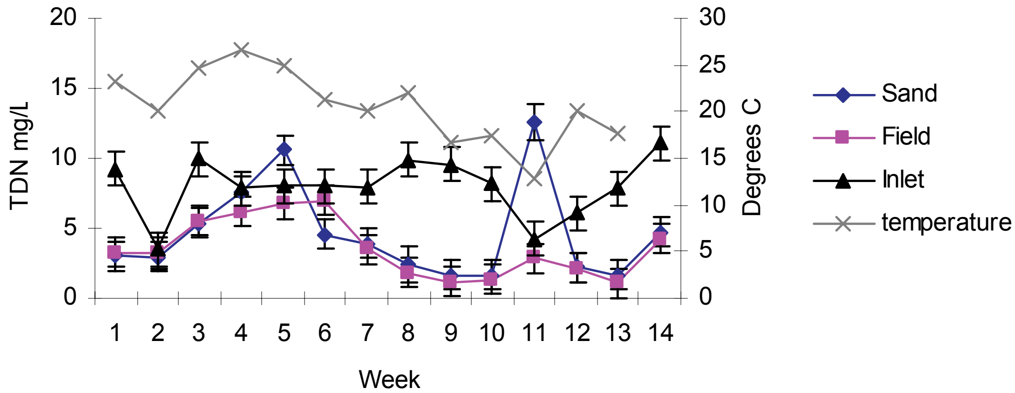

Figure 4.2. The Inlet and outlet concentration of TDN, and the mean water temperature within the tanks, plotted over the 14 week study period from July 10 to October 1, 2007 (± std error).

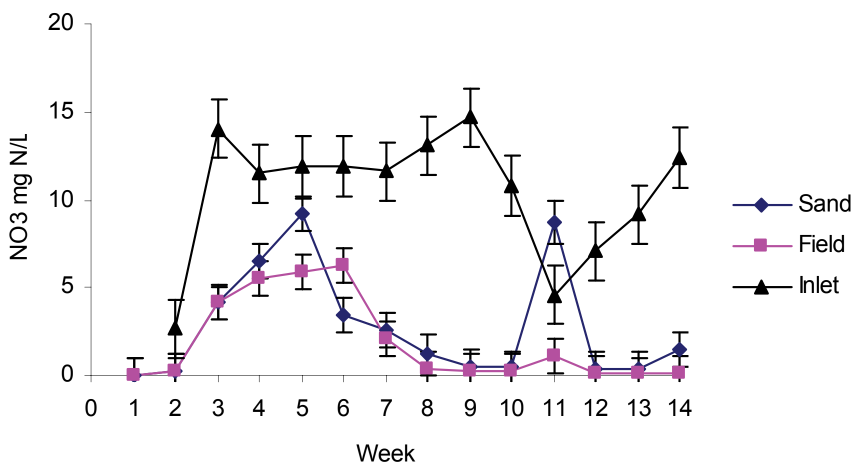

Figure 4.3. Inlet and outlet concentrations of NO_3-N plotted over the 14 week study period from July 10 to October 1, 2007 (± std error).

When comparing outlet concentration, the difference between the TDN average outlet concentration of the sand tanks and field soil tanks was reasonably significant ($p=0.097$). The average inlet TDN concentration (calculated from the weekly samplings of the mixing tank and two distribution tanks) was 11 +/- 1.5 mg N/L with outlet TDN concentration from the sand soil tanks at 4.7 mg N/L and from the field soil tanks at 3.6 mg N/L (Figure 4.4). A similar trend was observed with the outlet NO_3-N concentration; for the sand soil it was 2.8 mg N/L and 1.9 mg N/L for the field soil. However, the difference between the least square means for NO_3-N concentration between the two soil types was not significantly different ($p=0.122$).

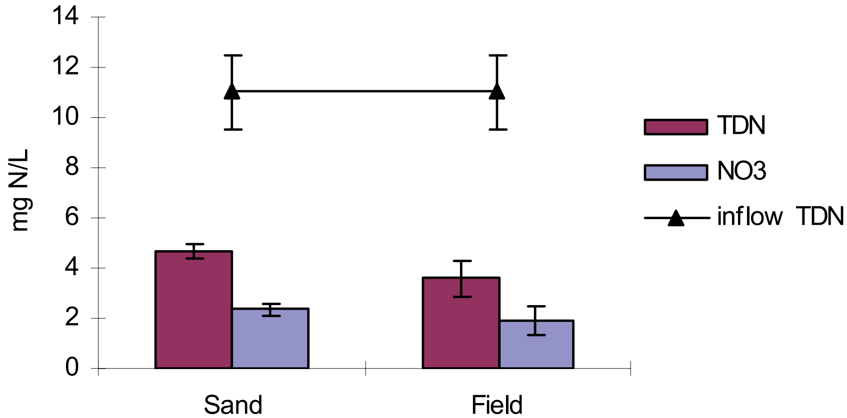

Figure 4.4. Least square mean and associated error of the outlet concentration of TDN and NO_3-N from the sand tanks and field soil tanks over the 14 week study. The line represents the average inflow TDN concentration (± std error).

Ammonia concentration in the inlet and outlets was monitored to determine if ammonification was occurring within the treatment tanks or within the distribution tanks. Even though NH_4 was not added to the simulated agricultural runoff, small amounts were produced. Despite the minimal overall contribution of NH_4 to the inorganic dissolved nitrogen fraction, it's interesting to compare the fate of ammonia in both soil types.

The inflow NH_4 concentration ranged from below detection limit (10 µg N L^{-1}) to 38.2 µg N L^{-1}, except on September 10th (week 11) and October 1st (week 14) when values of 149 and 381 µg N L^{-1} respectively, were observed (Figure 4.5).

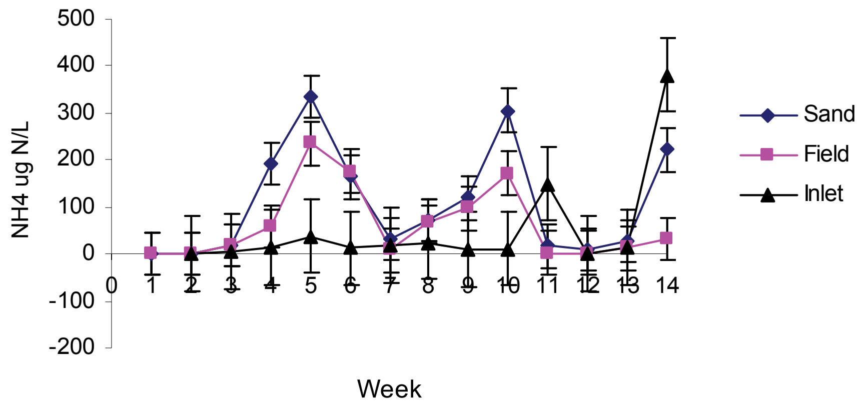

Figure 4.5. Inlet and outlet concentrations of NH_4-N plotted over the 14 week study period from July 10 to October 1, 2007 (± std error).

The outflow concentration trend was again similar between the two soil types with peaks on July 30th and September 3rd (weeks 5 and 10) and sand displayed the greatest outflow concentration. In fact there was no difference between the average inflow NH_4 concentration which was 116 and sand soil outflow concentration of 107 μg N L^{-1} (p=0.727).

However the average field soil tank outlet NH_4 concentration was 63 μg N L^{-1} which was significantly lower than the inlet and sand soil outlet concentrations (p=0.054). This would suggest that ammonification took place to a small degree in the reservoir tanks and was unaffected by the sand soil tanks, and reduced by the field soil tanks.

Ammonification describes the biological conversion of organic nitrogen to ammonia which is the first step of organic N mineralization (Reddy and Patrick, 1984). NH_4 is a reduced form of nitrogen and needs to be oxidized to NO_2 and NO3 in order to be further converted to N_2 gas through denitrification (Kadlec and Knight, 1996). Once organic N has been converted into NH_4, which is present in water as NH_4^+, it can then undergo volatilization to NH_3 gas or be assimilated microbially or through plant uptake or be oxidized to nitrate. The conditions under which each step occurs is heavily influenced by the medley of environmental factors that make up a wetland ecosystem. The rate of ammonification is much slower under anaerobic than aerobic conditions; however, ammonia nitrogen is more likely to accumulate in anaerobic environments due to decreased nitrification rates caused by low oxidation-reduction potential and low dissolved oxygen concentrations (Reddy and Patrick, 1984). It is possible that the field soil with its higher density of plant roots experienced a more consistent aerobic layer at the water/soil interface to support a microorganism population capable of oxidizing NH_4^+ to NO_3^- (Wu, 1999). It is also possible that NH_4^+ ions were adsorbed as exchangeable ions on clay particles present in the soil or incorporated into the physical clay lattice structure (Vymazal, 2006).

In order to determine the total percent reduction for each tank, the average weekly inlet and outlet concentrations for each tank were integrated with the corresponding weekly flow. In the two soil treatments, there was variability in the input load (due to inconsistent flow rates between the replicates), however it does not correlate with the output load. The sand soil tanks removed a combined total of 40% of the inflow TDN and the field soil tanks removed a combined total of 63% of inflow TDN.

The inflow TDN was composed, on average, of 1% NH_4, 11% Org N and 88% NO_3. Despite the fact that only NO_3-N was added to the simulated runoff solution, some of the N was transformed into organic and ammonia fractions. This was likely due to algae and microbial contamination within the holding tanks and was combated by covering them with dual-sided black and white tarps. This same phenomenon was observed in another experiment where they were using simulated nursery runoff and were only able to maintain a NO_3-N fraction of 80% (Huett *et al.*, 2005). The breakdown of the outlet TDN components for the two soil treatments was slightly different; the outlet from sand it was 2% $NH_{4,}$ 27% Org N and 71% $NO_{3,}$ and from the field soil tanks it was 2% $NH_{4,}$ 36% Org N and 62% NO_3. Figure 4.6 demonstrates the overall composition of the dissolved nitrogen entering and exiting the wetland tanks as well as the overall percentage of each contributing species of nitrogen. Nitrate experienced the largest relative reduction in both soil types; it was reduced by 52% by sand soil tanks and 74% from field soil tanks and denitrification was suspected to be the largest sink. NH_4 on the other hand, was increased by 14% in the sand soil tanks and reduced by 28% by the field soil tanks.

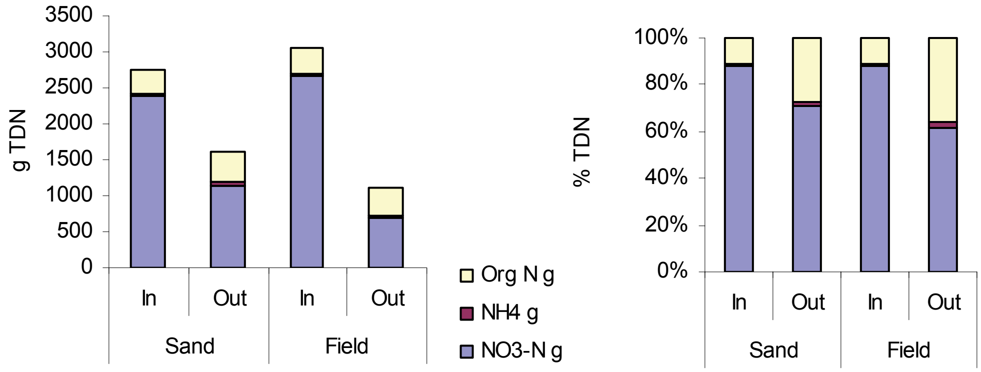

Figure 4.6. Nitrogen species composition of total dissolved nitrogen relative to mass of TDN in and out from each soil type (left). Nitrogen species composition of 100% total dissolved going in and out of the two soil types (right).

The dissolved organic N (DON) load was increased in the sand soil tanks by 42% and 20% by the field soil tanks. Despite greater TDN retention by the field soil, it is interesting to note that a greater percentage of the N exiting the wetland was in the dissolved organic form.

The vegetation density was greatest in the field soil tanks which necessarily corresponded to a larger biomass and therefore, organic N pool so it is possible that more of the NO_3 was being converted into DON. When comparing DON concentration over the course of the study, there was no significant difference between the inlet and outlet concentrations of the two soil types throughout the study ($p=0.504$), as visualized in Figure 4.7.

Despite the fact that there was no difference in outlet DON concentration between the two soil types and it did not significantly change over time, it accounted for a larger fraction of the total TDN output by the field soil tanks. Internal organic matter loading caused by senescing plants is known to increase DON loading (Sartoris *et al.*, 2000; Thullen *et al.*, 2005), and the field soil tanks experienced almost 50% more vegetation cover by the end of the study. This shows that the field soil tanks were more effectively removing the NO_3 than the sand soil tanks, as well as better retaining DON produced by plant and microbial life cycling.

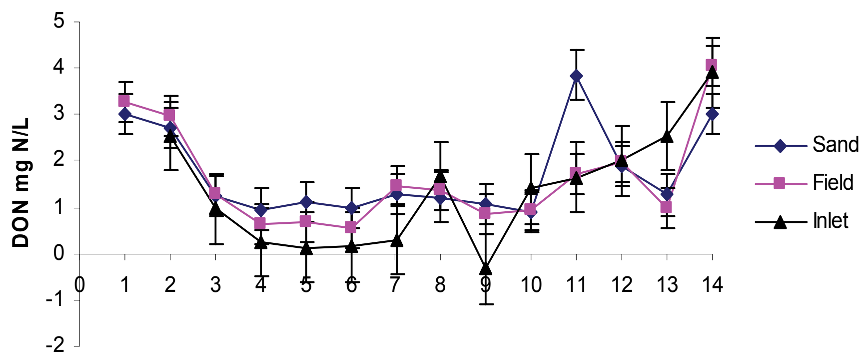

Figure 4.7. Inlet and outlet dissolved organic nitrogen plotted over the 14 week study from July 10 to October 1, 2007 (± std error).

Despite the seemingly large difference in removal efficiency between the sand and field soil tanks (40% and 63% respectively), it is important to note the variation between the three replicates of each treatment. Table 4.3 outlines the total grams of TDN removed by each replicate. The variation between the two soil types makes the difference reasonably statistically different at a 90% confidence level.

Table 4.3. The total number of grams of TDN that entered each soil treatment tank and the total number of grams that came out (± std deviation).

Soil type	Replicate	Grams loaded	Grams retained	% retained	Rate of retention (g m^2 summer $^{-1}$)
Sand	1	1100.5	559.2	50.8	60.2
	2	948.9	178.7	18.8	19.2
	3	689.3	375.9	54.5	40.5
average		**912.9 (±207.9)**		**41 (±19)**	**40 (±20)**
Field	1	935.3	708.0	75.7	76.2
	2	1201.9	710.0	59.0	76.4
	3	910.1	508.3	55.9	54.7
average		**1015.8 (±161.7)**		**63 (±10)**	**69 (±12)**

4.3.6. Denitrification

4.3.6.1. Physicochemical properties

In order to determine if denitrification was indeed occurring in the wetland tanks, several parameters known to influence this process were monitored. Oxidation-reduction potential, dissolved oxygen, temperature and pH measurements were measured weekly from two regions inside the tanks; the deep zone at the inlet end of the tank and the shallow zone at the outlet end. There was no significant difference between the two zones in each tank therefore the results were grouped together for each tank.

Wetland nutrient cycling is dependent on the process dynamics present within the system such as oxidation reduction potential, dissolved oxygen, pH and temperature (Sharpley, 1995) (House *et al.*, 1995). Figure 4.8 shows the oxidation-reduction potential in the water column over the three month study.

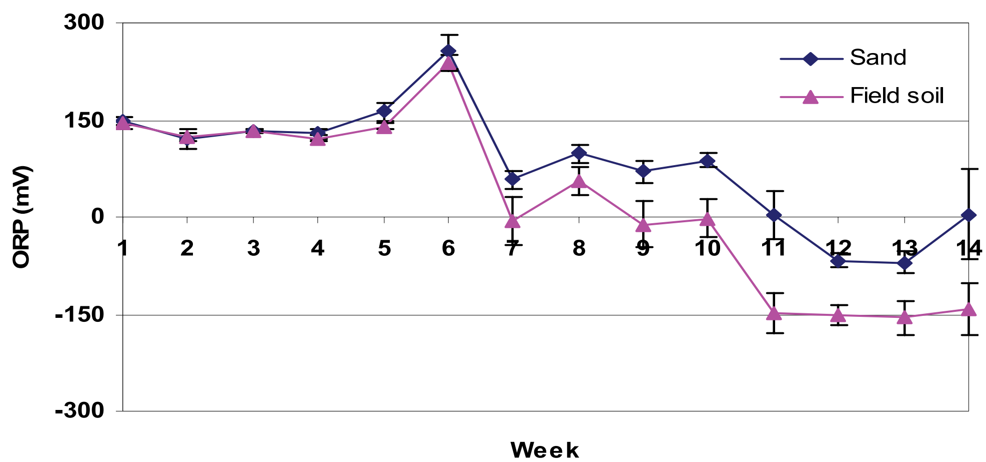

Figure 4.8. Weekly oxidation reduction potential measurements taken from the water column in the treatment tanks from July 10 to October 1, 2007 (± std error).

During the first two weeks in August, the ORP dropped sharply in both soil treatments from almost +250 mV to below +100 mV in the sand tanks, and below +50 mV in the field soil tanks. During the first week in September the ORP dropped into the negative range; 0 to -70 mV in the sand tanks and to -150 mV in the field soil tanks. The dissolved oxygen (Figure 4.9) in the water of both tanks dropped concurrently with the ORP during the first week in August from around 6 mg L^{-1} to just below 2 mg L^{-1} and remained there until the study was finished on October 1rst.

After the first month of operation. the conditions in all six treatment tanks had become anaerobic, as indicated by the low ORP and low DO. This shift was in response to the tanks reaching equilibrium under saturated conditions; the tanks were filled with municipal water at the end of June and until then had been empty of water since the previous summer so aerobic conditions dominated throughout July. They were flushed with municipal water for a week before the agricultural runoff solution was introduced on July 5th, 2007.

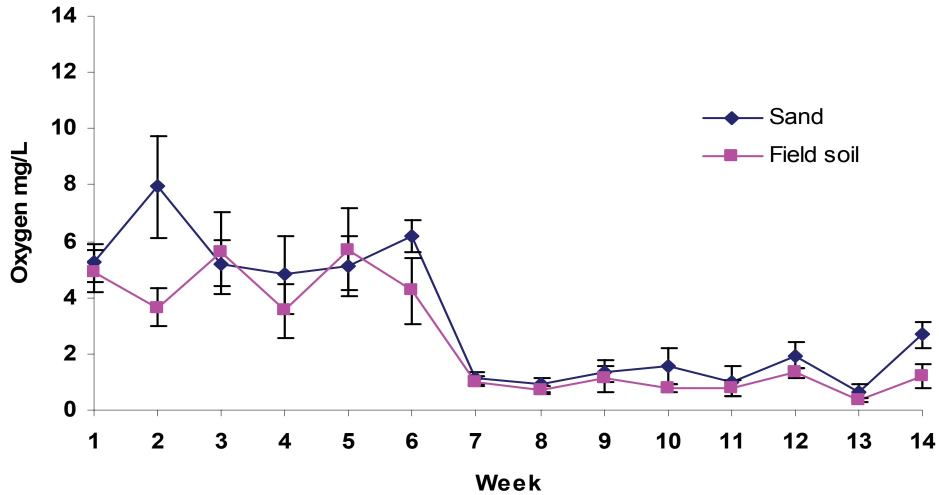

Figure 4.9. Weekly dissolved oxygen concentration in the water column in the treatment tanks from July 10 to October 1, 2007 (± std error).

The introduction of nitrate, coupled with the very low flow rates, and the decomposition of plant detritus and organic matter would have driven the shift towards anaerobic conditions. As oxygen was consumed by cellular respiration during the decomposition process, the microorganisms switch from O_2 to NO_3^- as the metabolic electron acceptor. As conditions become more reduced, nitrate reduction is followed by manganese oxide, iron oxide, sulfate and then finally carbon dioxide is reduced (Patrick *et al.*, 1996; Szogi *et al.*, 2004a). In these experimental tanks, the rate of oxygen consumption was greater than the amount entering in the inflow and the amount being diffused into the soil via the plant roots. This resulted in the reduced conditions observed at the beginning of August. During the month of August, the ORP in the tanks of both soil types was in the range of -100 to +100 mV where according to Patrick *et al.,* (1996), the system is considered anaerobic and reduced. The conditions in the field soil tanks reached highly reduced anaerobic status when the ORP level dropped to below -100mV at the beginning of September, 2007. Miller and Gardiner (1998) explain that when rice paddies are flooded, the degree to which the conditions become reduced is impacted by the organic matter content of the soil. They noted when comparing the flooding of two soils with similar pH, the one with the greatest OM content will experience the most reduced conditions which could explain in our case, why the field soil was more reduced than the sand soil.

4.3.6.2. Dissolved organic carbon

In addition to the soil OM, it is interesting to compare the concentrations of DOC coming out of the two soil types as seen in Figure 4.10. According to the statistical model, there was no effect of soil (p=0.198) on DOC outlet concentration; however, there was an effect of the soil by time interaction (p=0.0364). The concentration from both tanks increased after week 11 (September 10) by more than a factor of 2, and it was at this point that the outlet concentration was greater than the inlet concentration. The inlet agricultural solution was mixed with municipal water which was the exogenous DOC source therefore, the inlet solution was tested for DOC monthly as it was expected to be consistent. The similar DOC concentration between soil types leaching from detritus accumulation within the tanks was similar, despite the field soil tanks having greater vegetation density. However, when total DOC loads were compared between the two soil types, the field soil tanks had a 10% overall greater output than the sand soil tanks. From the perspective of the local environment within the tanks, DOC concentration is important because it shows that the microorganisms were subjected to the same concentration. OM matter accumulation between 2006 and 2007 was 1.2 fold in the field soil tanks and close to 4 fold in the sand soil tanks (Table 4.1) but due to a large error this increase was not significant in the sand soil tanks. This is consistent with a New Zealand study on OM accretion where it was found that in the first two years of operation it increased 1.2-2 fold and decreased in the following years (Tanner *et al.*, 1998).

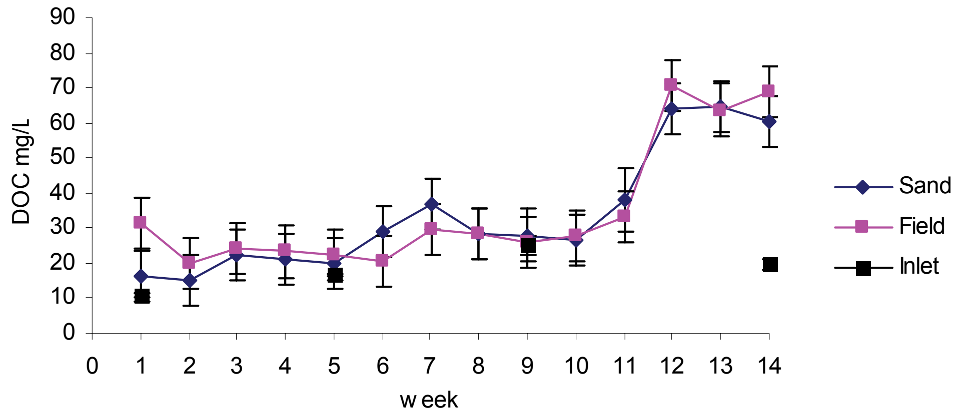

Figure 4.10. Inlet and outlet dissolved organic carbon plotted over the 14 week study from July 10 to October 1, 2007 (± std error).

4.3.6.3. Nitrous oxide emissions

As well as monitoring the parameters in the water column known to influence denitrification, gas sampling was also conducted biweekly to determine if nitrous oxide was being produced in the tanks. Observed nitrous oxide emissions peaked on the August 14th sampling date and declined steadily until the study ended at the end of September, 2007 (Figure 4.11). The emission rate for each soil type was determined by treating the four samples from each tanks as replicates for the individual tank so n=12 for each soil type. There was no statistically significant difference between the emission rate of the two soil types on each given sampling date. The N_2O emission rate from the sand soil was 65 µg m^{-2} hr^{-1} on the first sampling date (July 30th) and then increased to129 µg m^{-2} hr^{-1} on August 14th before starting to decline. This can be explained by the trend in reducing conditions; anaerobic conditions dominated the first month of operation as the soils had been dry previous to flooding. As the system was making the shift from aerobic to anaerobic conditions, denitrication began to occur as seen by the N_2O emission as well as the decreasing outlet concentration of the NO_3 component of the TDN (Freeman *et al.*, 1997). The August 14 sampling date shows the highest emission rates because DO and ORP were continuing to decrease thus increasing the reducing conditions and further promoting denitrification. In the field soil tanks however, the July 30 and August 14 sampling dates were almost the same (97 and 101 µg m^{-2} hr^{-1} respectively) and then started to decrease similarly to the sand soil tanks. This difference in the first two weeks was likely less pronounced than in the sand due to the greater intrinsic available carbon as related to the OM content of the field soil. The overall trend of decreasing nitrous oxide emissions and decreasing outlet TDN concentrations as the summer progressed indicated the denitrification reaction became more efficient, resulting in a lower $N_2O:N_2$ ratio (Thomas *et al.*, 1994; Bastviken *et al.*, 2005) (Smith and Tiedje, 1979). This increased denitrification would have been heavily influenced by the available carbon status within the tanks (Thomas *et al.*, 1994) (Hunt *et al.*, 2003).

The increased OM between 2006 and 2007, and the increased DOC concentration from the outlet of all the tanks was indicative of an increasing carbon pool within the system. This corresponds to the seasonal vegetation growth and inherent litter accumulation within the systems. As nitrous oxide is an intermediary in the overall reduction reaction of NO_3 in solution to N_2 gas that is related to carbon availability, it is possible that accumulation of carbon as plant litter within the tanks aided in reducing incomplete denitrification as the summer progressed, thus supporting low TDN outputs and minimizing N_2O emissions. This is important as nitrous oxide emission is an indicator of microbial denitrification activity but is also a potent greenhouse gas (Chang *et al.*, 1998; Firth and Edwards, 2000). This is consistent with the results of a study on a CW treating swine wastewater in South Carolina where they found that as total soil carbon increased, the amount of incomplete denitrification decreased. Firestone *et al*., (1980) postulated that as conditions become increasingly anoxic, an increase in nitrous oxide production follows. It is then consumed however, as a result of the stimulated nitrogenous oxide reductase enzymes, which reduce nitrous oxide to nitrogen gas.

The results averaged for each soil type are presented in Figure 4.11 the contribution from the individual sampling chambers are presented in Figure 4.12 to visualize the contribution of each to the averages.

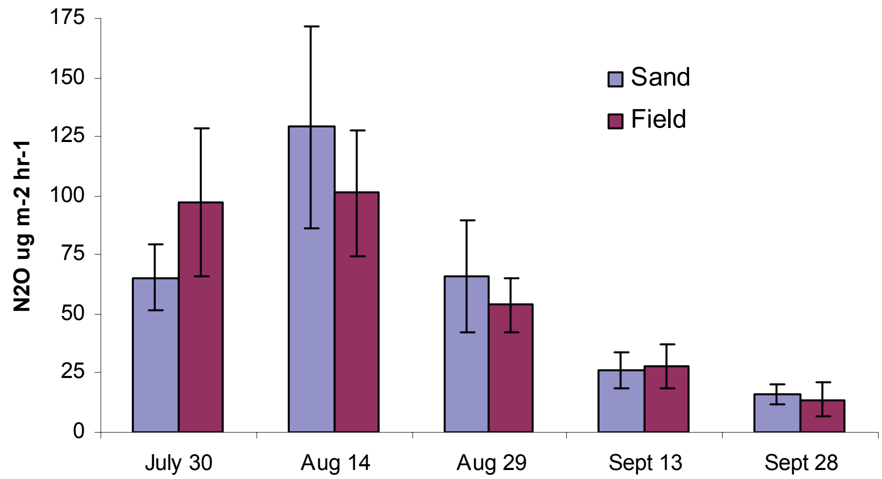

Figure 4.11. Nitrous oxide production from each soil substrate at two week intervals from July 30 to September 28, 2007 (± std error).

In the field soil tanks, sampling position 1 (deep zone) was significantly different from ambient on two of the middle sampling dates (p=0.034 and p=0.049 respectively) and position 2 (bare soil) was significant on the three middle sampling dates (p=0.089, p=0.064, and p=0.043 respectively). Position 3 (cattail) was not significant on any sampling dates and position 4 (reed canary grass) was significant on the first sampling date (p=0.012).

This was almost exactly opposite of the trend seen in the sand soil tanks; positions 1 and 2 were only significant on one sampling day each (p=0.032 and p=0.008 respectively) however positions 3 and 4 were reasonably significant on two and four sampling days respectively (p=<0.1). It is difficult to detect any trends within this information; however, it is interesting that the contributions from each position are not equivalent for each sampling date for either soil types.

It does appear that as the study continued, the microbial population was increasing the active denitrification zone from the inlet end to the outlet end, as seen by the greater relative contribution of positions 3 and 4 on the last two sampling dates. This was perhaps most pronounced in the sand soil tanks as positions 3 and 4 were significant as the sampling dates progressed.

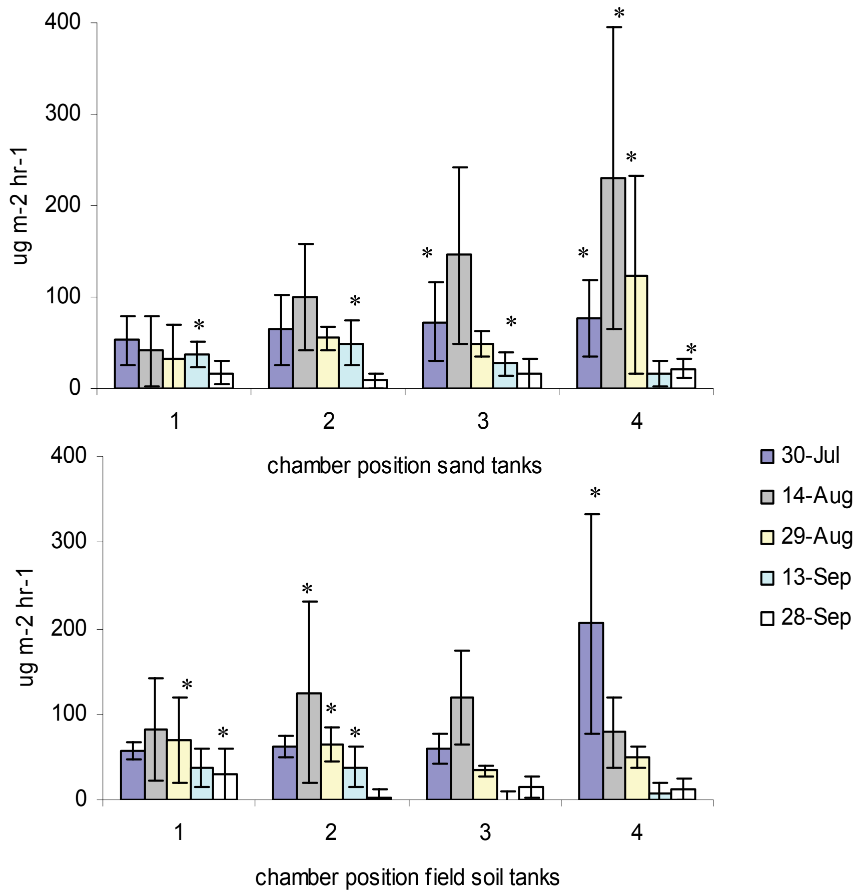

Figure 4.12. Nitrous oxide emission rates in ug m^{-2} hr^{-1} at each chamber position for the five sampling dates. Concentrations (from which the emission rate was calculated) that were significantly different from ambient are marked with an asterisk (± std error).

The pattern in the field soil tanks was not as evident perhaps due to an already present microbial population and available carbon within the OM. Other studies have shown that plants acts as conduits for releasing gases produced in the deeper soil layers and so it was suspected that perhaps there would be a difference between the sampling positions within the wetland tanks (Chang *et al.*, 1998; Chen *et al.*, 1999).

The results from this study suggest spatial heterogeneity in terms of N_2O production, as seen by the varying emission rates from the different sampling positions. The study did not possess the required precision to elucidate a difference between the emission rates from the cattails, reed canary grass, deep zone and shallow zone. It would be interesting to conduct further studies to assess the relative contribution of different wetland plant species to gas release from saturated wetland soils.

4.3.6.4. Role of vegetation

The vegetation density was greater in the field soil tanks than in the sand soil tanks by the end of the study. All tanks were originally planted with the same number of cattails and of reed canary grass tufts; however, the field soil tanks had twice as many cattails and 30% more surface area covered by reed canary grass (data presented in Chapter 3, section 3.4.2.3). While biomass concentrations were not tested due the destructive nature of the tests and small size of the tanks, in this study it is probable that more N was incorporated into plant biomass in the field soil tanks as nutrient accumulation in plants depends on the rate of biomass production (Maddison *et al.*, 2005). Because the vegetation in this CW was still in the process of establishing itself, the nutrient uptake increased with increased biomass production. It is likely this higher biomass production in the field soil tanks, was responsible for a greater proportion of the nutrient removal, than in the sand soil tanks. The field soil was richer than the sand soil and it was likely this higher background nutrient (both micro and macro) content supported the higher biomass production. It should be emphasized that this was only the second growing season these tanks had experienced so the vegetative component was still in the establishment stage when N assimilation is greater than in established CWs (Gottschall *et al.*, 2007).

As well as assimilation and microbial support, vegetation performs the critical role of supplying or increasing the layer of organic matter (OM) (Edwards *et al.*, 2006). High accretion rates of plant detritus in surface flow CWs is an important source of OM which provides a sustainable supply of carbon for microbial denitrification (Tanner *et al.*, 1998). Brix (1997) suggests vegetation has a significant impact on nutrient reduction through organic matter accumulation only when the loading levels are low. While there doesn’t appear to be a consensus in the literature about what constitutes high and low loading rates, field scale nonpoint source waste streams such as agricultural runoff vary in concentration and volume throughout the year, thus varying the loading rates. Many studies report high N uptake by plants in the first 3-5 years of operation while plant cover is being established; however, it’s questionable whether or not plant uptake is a sustainable removal mechanism in the long term. For example a 5-year old CW wetland planted with *Phalaris. Arundinaceae* L. (reed canary grass), demonstrated that N assimilation was significant in the first half of the growing season and the overall N uptake by plants was 9.2% of the incoming N (Edwards *et al.*, 2006). Another study on 10-year old CW, planted with *Typha latifolia* L. and *Typha angustifolia* L (two species of cattail) in eastern Ontario demonstrated this idea; it was found that in the 4th cell in series, which was less highly-loaded than the previous cells in which there was no net plant storage, that over the growing season the plants removed 9% of the total Kjeldahl nitrogen (Gottschall *et al.*, 2007).

An important consideration when assessing the role of plants is that they may act as temporary storage for N (Silvan *et al.*, 2004), for example standing dead cattail shoots as well as roots and rhizomes can have a turnover rate of one or two years (Kadlec and Knight, 1996). While it is not a permanent storage, this is important as it prevents overloading of the receiving water bodies during the growing season, when they are at their most vulnerable (Kao *et al.*, 2004; Gottschall *et al.*, 2007; Kroger *et al.*, 2007). Picek *et al*., (2007) demonstrated that in CWs that are not heavily loaded with wastewater, plants are of primary importance as a source of available carbon for microorganisms as well as providing plant exudate which also affect microbial processes and pore water quality, thus increasing the efficiency of nitrogen removal from the wastewater by supporting denitrifying microorganisms with easily decomposable organic matter.

4.4.Conclusions

Two soil types common to Southern Quebec, Canada, a sand soil and sandy clay loam field soil were assessed in their ability reduce dissolved nitrogen from a simulated agricultural runoff solution containing 10 mg N L^{-1} as nitrate. It was expected that the field soil would outperform the sand soil in N removal because of its greater organic matter content and associated carbon content, as well as its capacity to support a greater vegetation density. Denitrification and biomass sequestration were the hypothesized dominant N sinks in this two-year old constructed wetland. The following conclusions were drawn from this work:

(1) This study demonstrated that field soil was better at promoting denitrification than sand soil that was planted with cattails and reed canary grass and with an average hydraulic retention time of 2.2 days when flooded with simulated agricultural runoff, typical in Quebec.

(2) The field soil tanks outperformed the sandy soil tanks with an overall removal of 63% TDN compared to 41% TDN removal. It was likely due to the richer soil having been able to support a larger vegetation biomass which was in turn responsible for greater nutrient assimilation, OM accretion rate and available carbon, for supporting greater microbial populations.

(3) As demonstrated by the decreasing dissolved N concentrations in the outflow, as well as dissolved oxygen and oxidation-reduction potential within the tanks, the water column conditions were anaerobic after the first month of operation. Denitrification was also apparent through the observation of nitrous oxide emissions coming from both soil types. While there was no significant difference in emission rates between the two soil types, it was likely that more N_2O was being further reduced to N_2 in the field soil tanks, due to the higher carbon availability.

(4) Nitrogen transformations occurred in both soil types; NH_4^+ was produced in the sand soil tanks and the outflow contained 14% more than the inflow. In contrast, the field soil tanks removed 28% of the inflowing NH_4^+, probably due to the higher root-rhizome density and corresponding aerobic microzones where NH_4^+ would have been reduced to NO_3. Dissolved organic nitrogen was also produced in both tanks with 20% more in the outlet from the sand than field soil tanks. This may have been caused by the more severely reduced conditions in the field soil tanks under which OM accumulates more quickly thus sequestering DON.

(5) DOC concentration increased in the outlet from both soil types in September, 2007. As well as being an indication of carbon loading within both systems, it is an indication of potential BOD_5 being produced. It would be pertinent to monitor this in future studies of this site.

4.5. References

APHA, AWWA and WPCF (1992). Standard methods for the examination of water and wastewater Washington, DC, USA,, American Public Health Association, American Water Works Association, Water Pollution Control Federation. American Public Health Association.

Bachand, P. A. and Horne, A. J. (2000). "Denitrification in constructed free-water surface wetlands: II Effects of vegetation and temperature." Ecological Engineering **14**: 17-32.

Bastviken, S. K., Eriksson, P. G., Premrov, A. and Tonderski, K. (2005). "Potential denitrification in wetland sediments with different plant species detritus." Ecological Engineering **25**(2): 183-190.

Berka, C., Schreier, H. and Hall, K. (2001). "Linking water quality with agricultural intensification in a rural watershed." Water Air and Soil Pollution **127**: 389-401.

Bogren, K. (2003). Ammonia in Surface Water and Wastewater. 5600 Lindburgh Drive, Loveland, CO, 80539, USA.

Brix, H. (1997). "Do macrophytes play a role in constructed treatment wetlands?" Water Sci. Technol. **35**(5): 11-17.

Casey, R. E. and Klaine, S. J. (2001). "Nutrient Attenuation by a Riparian Wetland during Natural and Artificial Runoff Events." J. Environ. Qual. **30**: 1720–1731.

Chang, C., Janzen, H. H., Cho, C. M. and Nakonechny, E. M. (1998). "Nitrous Oxide Emission through Plants." Soil Sci Soc Am J **62**: 35-38.

Chen, X., Boeckx, P., Shen, S. and Van Cleemput, O. (1999). "Emission of N_2O from rye grass (*Lolium perenne* L.)." Biol Fertil Soils **28**: 393-396.

Eastman, M. (2008). Field-scale nutrient transport monitoring and modeling of subsurface and naturally drained agricultural lands. Bioresource Engineering. Ste-Anne-de-Bellevue, QC, McGill University, Macdonald Campus. **MSc**.

Ebina, J., Tsutsui, T. and Shirai, T. (1983). "Simultaneous Determination of Total Nitrogen and Total Phosphorous in Water Using Peroxodisulfate Oxidation." Water Research **17**(12): 1721-1726.

Edwards, K. R., Cizkova, H., Zemanova, K. and Santruckova, H. (2006). "Plant growth and microbial processes in a constructed wetland planted with Phalaris arundinacea." Ecological Engineering **27**(2): 153-165.

Egan, L. (2003). Determination of Nitrate/Nitrite in Surface and Wastewaters by Flow Injection Analysis. 5600 Lindburgh Drive, Loveland, CO, 80539, USA.

Firestone, M. K., Firestone, R. B. and Tiedje, J. M. (1980). "Nitrous Oxide from Soil Denitrification: Factors Controlling Its Biological Production." Science **208**(4445): 749-751.

Firth, J. R. and Edwards, C. (2000). "Denitrifaction by indigenous microbial populations of river water measured using membrane inlet mass spectrometry." Journal of Applied Microbiology **89**: 123-129.

Freeman, C., Lock, M. A., Hughes, S. and Reynolds, B. (1997). "Nitrous Oxide Emissions and the Use of Wetlands for Water Quality Amelioration." Environ. Sci. Technol. **31**: 2438-2440.

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.

House, W. A., Denison, F. H. and Armitage, P. D. (1995). "Comparison of the uptake of inorganic phosphorus to a suspended stream bed-sediment." Water Research **29**(3): 767-779.

Huett, D. O., Morris, S. G., Smith, G. and Hunt, N. (2005). "Nitrogen and Phosphorus Removal from Plant Nursery Runoff in Vegetated and Unvegetated Subsurface Flow Wetlands." Water Research **39**: 3259-3272.

Hunt, P. G., Matheny, T. A. and Szogi, A. A. (2003). "Denitrification in Constructed Wetlands Used for Treatment of Swine Wastewater." J Environ Qual **32**: 727-735.

Kadlec, R. H. and Knight, R. L. (1996). Treatment Wetlands. Boca Raton, Florida, Lewis Publishers.

Kao, J. T., Titus, J. E. and Zhu, W.-X. (2004). "Differential Nitrogen and Phosphorus Retention by Five Wetland Plant Species." Wetlands **23**(4): 979-987.

Kellogg, R. L. and Maizel, M. S. (1994). "The Potential for Leaching of Agrichemicals used in Crop Production: A National Perspective." Journal of Soil and Water Conservation **May-June**: 294-298.

Kovacic, D. A., David, M. B., Gentry, L. E., Starks, K. M. and Cooke, R. A. (2000). "Effectiveness of Constructed Wetlands in Reducing Nitrogen and Phosphorus Export from Agricultural Tile Drainage." J Environ Qual **29**: 1262-1274.

Kroger, R., Holland, M. M., Moore, M. T. and Cooper, C. M. (2007). "Plant senescence: A mechanism for nutrient release in temperate agricultural wetlands." Environmental Pollution **146**: 114-119.

Kuschk, P., Wießner, A., Kappelmeyer, U., Weißbrodt, E., Kästner, M. and Stottmeister, U. (2003). "Annual cycle of nitrogen removal by a pilot-scale subsurface horizontal flow in a constructed wetland under moderate climate." Water Research **37**(17): 4236-4242.

Maddison, M., Soosaar, K., Lohmus, K. and Mander, U. (2005). "Cattail Population in Wastewater Treatment Wetlands in Estonia: Biomass Production, Retention of Nutrients, and Heavy Metals in Phytomass." Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering **40**(6/7): 1157-1166.

Mander, U., Kuusemets, V., Lohmus, K., Mauring, T., Teiter, S. and Augustin, J. (2003). "Nitrous oxide, dinitrogen and methane emission in a subsurface flow constructed wetland." Water Sci. Technol. **48**(5): 135-142.

Michaud, A. R., Lauzier, R. and Laverdière, M. R. (2005). "Mobilite du phosphore et intervention agroenvironnementale en bassin versant agricole: Etude de cas du ruisseau au Castor, tributaire de la riviere Aux Brochets, Quebec." Agrosolutions **16**(1): 47-60.

Miller, R. W. and Gardiner, D. T. (1998). Soils in Our Environment. Upper Saddle River, New Jersey, USA, Prentice-Hall Inc.

Mosier, A. R. and Mack, L. (1980). "Gas chromatographic system for precise, rapid analysis of nitrous oxide." Soil Sci Soc Am J **44**: 1121-1123.

Patrick, W. H., Gambrell, R. P. and Faulkner, S. P. (1996). Redox measurements in soil. Methods of Soil Analysis, Part 3, 677 South Segoe Rd, Madison, Wisconsin, 53711, USA: SSSA**:** 1255-1273.

Picek, T., Cízková, H. and Dusek, J. (2007). "Greenhouse gas emissions from a constructed wetland--Plants as important sources of carbon." Ecological Engineering **31**(2): 98-106.
Raisin, G. W. and Mitchell, D. S. (1995). "The Use of Wetlands for the Control of Non-Point Source Pollution." Water Sci. Technol. **32**(3): 177-186.
Reddy, K. R. and Patrick, W. H. (1984). "Nitrogen transformations and loss in flooded soils and sediments." CRC Crit. Rev. Environ. Control **12**: 273-309.
Rousseau, D., Wilde, W. d., Jonkers, C., Geenens, D., Vanrolleghem, P. and Pauw, N. d. (2001). "Short-term behaviour of an experimental constructed wetland at low temperatures." Mededelingen - Faculteit Landbouwkundige en Toegepaste Biologische Wetenschappen **66**(4): 233-237.
Sartoris, J. J., Thullen J.S., Barber, L. B. and Salas, D. E. (2000). "Investigation of nitrogen transformations in a southern California constructed wastewater treatment wetland." Ecological Engineering **14**: 49-65.
Sharpley, A. N. (1995). "Soil phosphorus dynamics: agronomic and environmental impacts." Ecological Engineering **5**(2-3): 261-279.
Silvan, N., Vasander, H. and Laine, J. (2004). "Vegetation is the main factor in nutrient retention in a constructed wetland buffer." Plant & Soil **258**(1/2): 179-187.
Smith, M. S. and Tiedje, J. M. (1979). "The Effect of Roots on Soil Denitrification." Soil Sci Soc Am J **43**: 951-955.
Szogi, A. A., Hunt, P. G., Sadler, E. J. and Evans, D. E. (2004). "Characterization of Oxiation-Reduction Processes in Constructed Wetlands for Swine Wastewater Treatment." Applied Engineering in Agriculture **20**(2): 189-200.
Tanner, C. C., Sukias, J. P. S. and Upsdell, M. P. (1998). "Organic matter accumulation during maturation of gravel-bed constructed wetlands treating farm dairy wastewaters." Water Research **32**(10): 3046-3054.
Thomas, K. L., Lloyd, D. and Boddy, L. (1994). "Effects of oxygen, pH and nitrate concentration on denitrification by *Pseudomnas* species." Federation of European Microbiological Societies, Microbiology Letters **118**: 181-186.
Thullen, J. S., Sartoris, J. J. and Nelson, S. M. (2005). "Managing vegetation in surface-flow wastewater-treatment wetlands for optimal treatment performance." Ecological Engineering **25**(5): 583-593.
Vymazal, J. (2006). "Removal of nutrients in various types of constructed wetlands." Science of The Total Environment **doi:10.1016/j.scitotenv.2006.09.014**: 105.
Watts, S. H. and Seitzinger, S. P. (2000). "Denitrification rates in organic and mineral soils from riparian sites: a comparison of N_2 flux and acetylene inhibition method." Soil Biology and Biochemistry **32**: 1383-1392.
Wu, M.-Y. (1999). Experimental Studies of Wetland Systems, Washington State University. **Ph.D. Thesis**.

5. Chapter 5- General Summary and Conclusions

5.1. General Summary

Intensification of agricultural practices in Quebec has lead to an increase in water quality deterioration in its freshwater lakes and rivers. Agricultural runoff has been recognized as the primary pathway for the transport of phosphorus and nitrogen to fresh water bodies. Constructed wetlands as a filtration structure to reduce the P and N load in runoff is a potential best management strategy; however, design criteria have not been optimized for the treatment of nonpoint source waste streams in colder climates. The goal of this research was to study the impact on nutrient reduction by a constructed wetland using two soil types common in Quebec.

This research project endeavored to compare two different substrates in surface-flow constructed wetlands with emergent vegetation. The capacity of a sandy soil and a sandy clay loam soil to influence the removal mechanisms for P and N was studied between July, 2006 and October, 2007.

A simulated agricultural solution was passed through three sandy soil and three sandy clay loam soil-filled wetland tanks from July 10 to October 1, 2007, and inlet and outlet water samples were collected weekly. They were analyzed for total N, nitrate and ammonia, organic N, total P, dissolved P, and organic P. Flow data was collected in order to calculate total loads. The physico-chemical conditions of oxidation-reduction potential, dissolved oxygen, pH and temperature, were monitored weekly within the experimental tanks and gas samples were collected and analyzed for nitrous oxide. Soil samples were analyzed annually and the vegetation percent ground cover was estimated annually. In October 2007, a conservative tracer test was conducted to elucidate the mean hydraulic retention time of the wetland tanks.

Chapter three addresses the difference in P load removal efficiency between the two soil types as well as the mean hydraulic retention time determined from the tracer study. Chapter four addresses the results of the removal of N by the two soil types, as well as the nitrous oxide production observed in each one.

5.2. Conclusions

The following conclusions were drawn from this study:

(1) The net removal efficiency between the sand soil and field soil surface-flow constructed wetland tanks in this study did not differ; both removed approximately 40% of the incoming TDP. There was no change in the soil P concentration in the sand soil and a 24% reduction in the field soil over the course of the study. This reduced soil P concentration, coupled with 50% more cattails and 30% more reed canary grass in the field soil tanks suggests that plant assimilation compensated for the P released from the soil column due to the highly-reduced conditions. Low ORP in both soil types would have prevented or reversed precipitation-adsorption reactions and therefore residual organic matter accretion from the biogeochemical cycle was likely the dominant P sink for the 40% TDP that was successfully removed. Once the vegetation has fully colonized the tanks after several years of operation, its role as a nutrient sink may diminish. The field soil may act as a potential source of P due to its tendency to become more reduced than the sand tanks.

(2) The hydraulic retention time was approximately 2.2 days for the tanks in this study. While increasing retention time has been shown to improve P retention, in this case, it may not have improved the removal efficiency because of the reduced conditions. A difference between the field soil and sand soil's ability to remove P may emerge as the CW ages, as the field soil had a larger pool of Melich III extractable iron than did the sand. However, the active volume of the wetland should be taken into consideration as the sand tanks had active volumes ranging from 56 to 74% whereas the field soil tanks were between 29 and 47%. This may indicate that there is more contact between the sand soil and polluted water than there is between the field soil and polluted water which would theoretically lead to the binding of more P.

(3) Acknowledging the fact that these surface-flow CW tanks are still in the process of establishment, the authors of this study would recommend a sand soil for use as a CW wetland substrate in southern Quebec as there is less P to lose from the soil if redox conditions are low enough to reduce iron and there is more water movement within the soil column. While the more prolific plant growth in the field soil tanks translates into a larger uptake of nutrients, once the tanks of both soil types are fully colonized the rapid uptake of nutrients will cease and no longer be an advantage of the field soil.

(4) This study demonstrated that field soil is better at promoting denitrification than sand soil that is planted with cattails and reed canary grass and with an average hydraulic retention time of 2.2 days when flooded with simulation agricultural runoff typical in Quebec.

(5) The field soil tanks outperformed the sandy soil tanks with an overall removal of 63% TDN, compared to 41% TDN removal. It was likely due to the richer soil having been able to support a larger vegetation biomass which was in turn responsible for greater nutrient assimilation, the higher OM accretion rate and greater available carbon for supporting larger microbial populations.

(6) As demonstrated by the dissolved oxygen and oxidation reduction potential within the tanks, the water column conditions were anaerobic after the first month of operation. Denitrification was also apparent in the observation of nitrous oxide emissions coming from both soil types. While there was no significant difference in emission rates between the two soil types, it was likely that more N_2O was being further reduced to N_2 in the field soil tanks, due to the higher carbon availability.

(7) Nitrogen transformations occurred in both soil types; NH_4^+ was produced in the sand soil tanks and the outflow contained 14% more than the inflow. In contrast the field soil tanks removed 28% of the inflowing NH_4^+ probably due to the

higher root-rhizome density and corresponding aerobic microzones where NH_4^+ would have been reduced to NO_3. Dissolved organic nitrogen was also produced in both tanks with 20% more in the outlet from the sand than field soil tanks. This may have been caused by the more severely reduced conditions in the field soil tanks under which OM accumulates more quickly thus sequestering DON.

6. Chapter 6- Recommendations for further study

Following are five recommendations for further study at the Macdonald campus surface-flow constructed wetland for the treatment of agricultural runoff in Quebec:

a. One of the limitations to this study was that it did not address how this constructed wetland design would impact particulate P which is often present in runoff events such as the spring snow melt. Further study of the capacity of this design to reduce particulate P from agricultural runoff would be interesting as the deep zone combined with a slow inflow rate should, in theory, allow for particulate settling.

b. With an overall P removal of approximately 40%, the design of the vegetated tanks used in this research project could be improved in an effort to increase the removal efficiency. A mixing device could be placed in the deep zone to aerate the water column and help increase the oxidation-reduction conditions to a level where Fe^{3+} is no longer reduced, allowing it to react with and immobilize dissolved P. In addition to improving the redox conditions, increasing the hydraulic retention time would allow more treatment within the CW.

c. Future work at this sight should include further testing for iron as well as plant tissue analysis. Outlet water sample analysis for soluble Fe^{2+} concentration as well as soil sample analysis for Fe concentration would confirm that the P loss from the soil was indeed coupled with the reduction of insoluble Fe^{3+} to soluble Fe^{2+}. Plant analysis for P would complete the P mass balance and confirm that the P released from the soil was indeed taken up by the vegetation.

d. DOC concentration increased in the outlet from both soil types in September, 2007. As well as being an indication of carbon loading within both systems, it is an indication of potential BOD_5 being produced. It would be pertinent to monitor this in future studies of this site.

e. Denitrification occurs more readily under anaerobic conditions, and phosphorus adsorption and precipitation occur more readily under aerobic conditions; therefore, further research into creating constructed wetlands that contain both types of conditions would potentially maximize the retention of both nutrients. Linking two of the vegetated tanks in series, with one being aerated and one not, may be an interesting study in the future.

f. Surface-flow constructed wetlands are most often used in the treatment of agricultural runoff because they are less prone to clogging when the runoff contains particulate matter. Despite this, it may be interesting to study a sub-surface flow wetland model because it forces the water through the soil column, providing more opportunity for soil-ion interactions. If this design were incorporated with a pond to settle out particulate matter, it may increase dissolved P removal efficiency as compared to our surface-flow model.