

REVIEW AND SYNTHESIS OF ENGINEERED WETLAND TREATMENT  
SYSTEMS WITH APPLICATION TO PHOSPHORUS REMOVAL

by

Diana Lynne Ibarra

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of

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in

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Approval for the Department of Civil Engineering

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Approval for The Graduate School

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## ABSTRACT

Nutrient contamination in point and non-point wastewater sources has led to an increased focus on the removal of phosphorus before reaching receiving waters. Phosphorus, typically a nutrient limiting contaminant is responsible for eutrophication and algae blooms in lakes and streams and the wastewater from agricultural, industrial and domestic sources is under continued scrutiny from the regulatory environment. Constructed wetlands mimic natural wetlands and are used worldwide for the removal of nutrients in wastewater streams but the research and applications for removal of phosphorus has lagged behind other nutrients and contaminants.

This paper is an extensive literature review of construct wetlands and the ongoing applications for phosphorus removal. This review includes recent research on the mechanisms of removal, an evaluation of different plant species, a discussion of phosphorus partitioning in the wetland environment and a look at the use of chemical additives to improve the removal efficiency. Hybrid constructed wetland systems that closely mimic the biological nutrient removal systems for large scale WWTP facilities are being built around the world to improve effluent water quality and take advantage of the benefits of each type of constructed wetland. Maximizing the removal of phosphorus in wastewater will require a multi-pronged approach that includes biological, chemical and physical removal of the phosphorus in both the design phase and ongoing operation of the constructed wetlands system.

Several trends in constructed wetlands phosphorus removal are emerging: the primary removal mechanism for phosphorus removal is accretion and new soil sediments, and the use of chemical additives for precipitate and final removal of phosphorus is required for the removal efficiencies required by regulation. The varied applications and results of constructed wetland systems with respect to phosphorus removal are discussed throughout the paper. Floating island technology, using a buoyant material that supports plants, is a newer unique application of constructed wetlands that can be used to remediate wastewater and remove contaminants. Based on the literature search, a series of experiments to further characterize floating islands and improve the removal of phosphorus from wastewater are recommended using this technology.

## INTRODUCTION

“Wetlands are not wastelands but wealth lands.” Joshua Zake, Uganda.

Constructed wetlands, often referred to as treatment wetlands are used around the world in thousands of locations and a variety of applications to remediate wastewater. Constructed wetlands mimic the natural wetland processes: physical, chemical, and biological, but are engineered for specific applications and more precise control of the effluent water parameters. Typically, constructed wetlands are less expensive, easily sustainable, and require lower maintenance when compared to conventional wastewater treatment facilities. Constructed wetlands allow for on-site treatment and are environmentally sustainable. In the United States, the EPA maintains several resources for wetlands management including the Treatment Wetland Database (TWDB) with design and performance data on over 400 systems (Harrington, Scholz, Harrington & Culleton, 2010).

Because constructed wetlands are mimicking the natural wetland processes, there are often stochastic effects, events that cannot be either planned for or predicted that will impact the performance of the wetland. These include, rain events, drought, animals and birds, etc. The “chatter” in the data when evaluating a single system shows significant differences in the performance of wetlands when systems are compared (Kadlec, 2006) and is be apparent throughout this paper and the literature review of many different systems. Often times these events are difficult to quantify and in designing wetlands the

“recommendation is to adjust the treatment target downward by a factor of two to meet the regulatory requirements” (Kadlec & Wallace, 2009, p. 371).

Constructed wetlands are successful for the removal of ammonia and nitrogen, pathogens, and other contaminants. What is less known and more difficult is the research and application of constructed wetlands for the removal of phosphorus in various types of wastewater. From a research and application perspective, a major focus for communities as they look to further safeguard water resources. “In the last twenty-five years, most of the problems with constructed wetlands have been solved; the outstanding exception is the desire to remove P within the wetland system which largely remains unfulfilled” (Cooper, 2010, p. 21). “Phosphorus reduction is one of the least efficient processes in wetland treatment” (Kadlec & Wallace, 2009, p. 349). Phosphorus is a known nutrient required for plant growth, and is often the rate-limiting nutrient in a natural system. The intensive use of phosphates (domestic, agricultural, food, etc) has resulted in high P concentration levels in surface waters, which in turn leads to eutrophication, algae blooms that deplete the receiving waters of oxygen and prevents sunlight from entering the water. The low dissolved oxygen concentrations in the water do not sustain other organisms and aquatic life (Molle, Martin, Esser, Besault, Morlay & Harouiya, 2010).

Constructed wetlands are used for a large variety of applications and include treatment for the following (Kadlec, 2006):

- domestic wastewater treatment
- animal wastewater treatment
- mine wastewater treatment

- sludge consolidation
- industrial process wastewater
- groundwater remediation
- agricultural crop runoff
- urban stormwater runoff
- drinking water pretreatment.

No literature review or study of constructed wetlands is complete without a review of the two large-scale systems here in the United States: The Houghton Lake system in Michigan and the Everglade Nutrient Removal Project in south Florida. Both of these systems have been studied extensively over a number of years and will be referred to throughout the paper. The Houghton Lake constructed wetland began receiving water in 1978 and the Everglades project started receiving water in 1994 (Kadlec & Wallace, 2009).

The Redfield Ratio of C:N:P, a measure of the nutrient elements required for natural systems is 41:7:1 as represented by molar proportions, but wastewaters do not have this ratio and there is often an excess of phosphorus (Kadlec & Wallace, 2009). Additional treatment of the wastewater is required when any of the contaminants are out of compliance with federal, state, or local laws. The Clean Water Act controls all direct discharge (point sources) into navigable waters throughout the United States. Any facility regardless of type of wastewater, public or private that intends to discharge water into the nation's water system requires a permit that identifies the pollutants in the effluent. The permit sets the parameters and effluent limits for that facility (USEPA 2011). Typically,

in the United States, the regulatory requirement is for a maximum monthly value but in other countries, the maximum contamination allowed is based on a given percentile. (Kadlec & Wallace 2009) An ongoing focus is also non-point source water pollution and the improvement of the waterways (USEPA, 2011).

### Project Background

The Montana State University Bozeman Department of Civil Engineering and Center for Biofilm Engineering has been working closely with Floating Islands International (FII) for several years on constructed wetlands research. Currently, FII has an ongoing project with the wastewater treatment facility in Billings, Montana. Located several miles from the WWTP plant at Rehberg Ranch Subdivision (RRS), a residential subdivision on the Rims in Billings, are two aerated treatment lagoon ponds that FII is currently monitoring and has installed a floating treatment wetland (FTW) in one of the lagoons. The project is in cooperation with the City of Billings, FII, and the Montana Board of Research and Commercialization Technology. The geographical location of RRS requires a stand-alone WWTP and the goal of the FTW is to treat the water so it can then be land applied to less acreage and hence less overall cost of removal. Currently, the FTW is working efficiently at removing chemical oxygen demand (COD) and ammonia-nitrogen contaminants from the lagoon. The FTW has been characterized over an extended period of time and the next phase of the project is to modify the FTW to remove additional phosphorus without compromising the COD and nitrogen effluents levels.

Floating Islands International has successfully designed and patented “BioHaven, a porous mat made of a matrix of 100% recycled polyester and bonded together with marine grade foam to provide buoyancy” (HFI, 2010, p. 2). The BioHaven mat is comprised of “fine (0.007 inch diameter) strands that are intertwined and bonded to provide a three-dimensional non-woven matrix that is highly porous, permeable, and resistant to environmental degradation” (Stewart, Mulholland, Cunningham, Kania & Osterlund, 2008, p.27). In laboratory studies, the phosphate removal in the tank tests using BioHaven was almost 500 mg/d/ft<sup>2</sup> (Stewart, 2007); significantly higher than the removal rates currently recorded in the lagoons at Rehberg Ranch Subdivision. The BioHaven mats were installed on one of the Rehberg Ranch Subdivision in November 2009 and plants were added to the circular FTW in the spring of 2010. A fountain pump was installed to improve circulation. The plants used in the system are native plants, primarily sedges. The second lagoon is similar to the lagoon with the FTW and but does not have a FTW installed on the surface and has served as the control pond (Faulwetter, Burr, Cunningham, Stewart, Camper & Stein, 2010). In 2010, the phosphate removal rate of the FTW at Rehberg Ranch was 54 mg/day/ft<sup>2</sup>, a 27% improvement when compared to the control lagoon but significantly less than the laboratory tests. The FTW covers approximately 6.4% of the lagoon surface area (FII 2010). The challenge is how to improve the current results of 54mg/d/ft<sup>2</sup> PO<sub>4</sub>-P removed to the almost 500 mg/d/ft<sup>2</sup> PO<sub>4</sub>-P removed from the lab studies.

The State of Montana and the USEPA have very stringent laws on the non-degradation of all receiving waters; the challenge for communities is a permitting process

that is complex and requires that both state and federal laws be met. The permit is referred to as the National Pollutant Discharge Elimination System permit. Typically, the permits from the state regulate: BOD, TSS, Total Nitrogen, ammonia, nitrate, E-coli, and Total Phosphorus (TP) as well as other parameters. As communities grow, the total amount of contaminant cannot increase beyond the permit concentrations; often referred to as the Total Maximum Daily Load (TMDL) or a pollution cap. “The US Clean Water Act requires that a TMDL be created for water bodies that fail to meet water quality standards and is essentially a budget establishing the maximum amount of pollution that a water body can accept” (Force 2009 p. 42). Later in the paper, there will be a detailed evaluation of the Everglades Nutrient Removal Project (ENRP) implementing the concept of a TP 12 month rolling average removal rate for the first time with the state of Florida and the USEPA (Kadlec 2006). Closer to home is a typical example for Bozeman, Montana. 252 lbs/day of Total Phosphorus (TP) is allowed and at the current flowrate, equating to approximately 3.4 mg/L TP. As the volume of water through the Water Reclamation Facility (WRF) increases, the allowed concentration (mg/L) will decrease because the total 252 lbs/day cannot increase. It is expected that by 2025 the TP concentration allowed will be in the range of 2.3 mg/L for Bozeman, MT (City of Bozeman 2011); requiring significant change and expense in the Waste Water Treatment Plant (WWTP) and hence the new Biological Nutrient Treatment (BNR) facility that will cost the city 53 million dollars and is currently under construction.

The monitoring of the FTW at the Rehberg Ranch is ongoing and based on the additional research, operational changes are worth exploring that will improve the overall

phosphorus removal in the lagoon ponds while at the same time not compromising the removal of the other contaminants.

### Goals

The goals of my thesis are two-fold. First, an extensive literature search looking at all aspects of phosphorus removal in constructed wetlands was undertaken. Included is an evaluation of the book, *Treatment Wetlands* 3<sup>rd</sup> edition by Robert Kadlec and Scott Wallace, two prominent researchers in the all aspects of constructed wetlands. The textbook is the framework for all topics covered and provided the background material for additional research. The 12<sup>th</sup> IWA International Conference on Wetland Systems for Water Pollution Control, held in Venice, Italy, 4-8 October 2010 Proceedings also provided me with the most up to date and latest research on phosphorus related topics from around the world. The papers presented at the conference are used extensively throughout as well as articles from a broad based literature search via the Montana State University Bozeman library. The literature review addresses the following questions:

- 1) What are the various phosphorus pathways in a constructed wetland environment?
- 2) What are the major mechanisms (natural and anthropogenic) for aqueous phosphorus removal?
- 3) Why is phosphorus more difficult to permanently remove than carbon or nitrogen based contaminants?
- 4) What are the major environmental variables that affect phosphorus removal?

- 5) What bench- scale experiments can be done to assess constructed wetland phosphorus removal in a “site specific” context?

Second, using the Floating Islands International LLC commercial mats, I have suggested a series of experiments that could be undertaken to better understand the phosphorus removal mechanisms and hopefully, improve the ability of the floating mats to remove phosphorus from domestic wastewater based on the research. The Rehberg Ranch Subdivision and a lab setting would be the test locations for most of the experimental work.

## LITERATURE SEARCH

### Overview of Constructed Wetlands

Constructed wetlands systems (CWS) are areas of vegetation and water on the landscape that are designed for a specific treatment of water that is monitored periodically to ensure that the effluent requirements are consistently met within the regulatory environment. CWS are used instead of or along side of other processes for treating wastewater; are considered a viable option because cost of construction and maintenance is less than traditional wastewater treatment facilities. CWS are often built for specific contaminants, in remote areas, in developing countries and for small-scale applications. I have completed a literature search and included all major parameters required to fully characterize and understand the latest research on phosphorus removal in CWS. A brief description of the different types of CWS, a discussion of phosphorus partitioning in the wetland environment, the phosphorus removal mechanisms, associated kinetics, and commonly used plants in the CWS environment are presented. A discussion of phosphorus chemistry in the natural environment is also presented. Applications and lessons learned from CWS around the world are included throughout the paper.

### Types of Constructed Wetlands

A very brief explanation of different types of constructed wetlands follows. Within each of the major types of constructed wetlands, there are also many variations. Schematic diagrams are shown to help visualize the differences. It is important to note

that often hybrid systems and different configurations are used to improve the overall performance of the system and remove all of the required pollutants.

### Free Floating System

Free floating systems (FFS) are typically lined basins with free-floating plants (i.e. water hyacinth) on top of the water. The water flows in from the top of the basin, travels the length of the basin and outflows through the top of the wetland. The floating wetland systems (FWS) are a more sophisticated version of the FFS. Figure 1 below shows the plants are not attached to a floating mat as is the case with the FII BioHaven mats. The primary mechanism for phosphorus removal in the FFS is plant uptake as the water passes through the floating plants and the accretion of organic matter into the sludge layer at the bottom of the wetland. The removal or harvest of the plants is required to keep the growth rate of the plants at an optimum and to ensure continued phosphorus removal (Vymazal, 2007; Crites & Tchobanoglous, 1998). An important consideration for FFS systems is the water depth in order to control vertical mixing. The design is such that the wastewater makes adequate contact with the plant roots and bacteria. If the system is aerated, then the water depth can be increased but it is recommended no deeper than 4 to 5 feet. With aeration, the loading rates can be higher and there is a reduced land area requirement (Crites & Tchobanoglous, 1998).

In Costa Rica a study of five different free-floating systems were evaluated for nutrient removal and overall operational performance; the wetlands all varied in size and application but were compared because of the similarities of plant types, climate and permit requirements (Nahlik & Mitsch 2006). The applications and size of the wetlands

were dissimilar in for this specific study but there were seven similar plant species found in the wetlands, plants were harvested every 2 -3 months and the results relative to phosphorus removal were comparable. Soluble reactive phosphorus (SRP) was measured and compared to the Hydraulic Loading Rate (HLR) for each of the five wetlands. The wetlands retained on average  $3.5 \text{ g PO}_4\text{-P/m}^2\text{-year}$ ; a long-term sustainable rate for these tropical conditions.

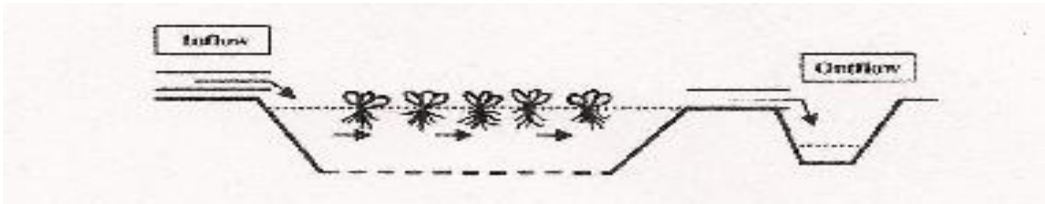


Figure 1: Free Floating System Constructed Wetland Diagram (Vymazal, 2007)

### Horizontal Subsurface Wetland

The Horizontal Subsurface Wetlands (HSSF) are typically basins with an impermeable liner filled with gravel or soil beds and planted with wetland vegetation as shown in Figure 2 below. The substrate is used for the attachment of the wetland plants. The wastewater enters the HSSF at top and flows through the gravel media before discharge at the top of the wetland. HSSF systems are used for a variety of industrial and smaller domestic wastewater systems because there are both anaerobic and aerobic zones (Kadlec & Wallace, 2009; Olsson, Jing & Liden, 2011). High removal of organics and suspended solids for diluted wastewaters makes constructed wetlands with subsurface flow an excellent alternative especially when organics and suspended solids are the major

treatment target (Kropfelova, Vymazal, Chmelova & Sulcova, 2010) Controlling the clogging of the media is an important maintenance requirement for long term performance. The use of recirculation will minimize the clogging and improve the overall treatment efficiencies (Crites & Tchobanoglous, 1998).

It is assumed that absorption of phosphorus in the filter media is the primary mechanism for the removal of phosphorus from the wastewater and an important design parameter. The sorption mechanism requires adequate contact time between the media and the wastewater. Phosphorus from particulate matter is removed from the system by settling, filtration and plant interception (Kadlec & Wallace, 2009). The removal of phosphorus is dependent on the material properties of the substrate and the amount of Fe, Ca, Al, and organic matter in the substrate. If phosphorus removal is a requirement of the HSSF wetland, an appropriate substrate needs to be decided at the design phase of the wetland. Historically, the soil substrates were mixed with metal salts in HSSF wetlands to improve the phosphorus retention but soils are no longer used because they do not have the hydraulic conductivity to support the HSSF water flow. Examples of aggregates used to improve the efficiency of phosphorus removal are mineral aggregates such as calcite, zeolite, iron-rich sands, and shale. (Kadlec & Wallace, 2009) Sorption is better suited for HSSF wetlands when compared to vertical flow (VF) systems because the substrate is continually under water and there is less fluctuation in the redox potential of the wetland (Vymazal 2007). One of the primary advantages to HSSF wetlands is the smaller land area required when compared to free water surface wetlands (FWS) (Crites & Tchobanoglous, 1998).

The higher phosphorus loading rates (PLR of the HSSF to free water surface (FWS) wetlands means that the biomass cycling and the removal of phosphorus because of the biological activity and plant harvesting are not major considerations for the HSSF wetlands. Plant harvesting will only remove approximately 1.5% of the influent phosphorus concentration (Kadlec & Wallace, 2009). If the PLR is too high for the HSSF wetland the influent and effluent phosphorus concentrations will be equal and even if the PLR is decreased by designing a larger HSSF wetland the limit to the amount of removal will depend on the concentration of the influent. While the PLR is a useful measurement if two systems have the same PLR but different influent concentrations, the effluent concentration will be lower for the system with the lower initial concentration (Kadlec & Wallace, 2009).

HSSF constructed wetlands with reed beds are the most common type of CWS installed in northern Europe. However, there is a great deal of variability in the removal rates for these systems; from 90% removal to as low as 11% removal in others for phosphorus (Gill and O’Luanaigh, 2010). An average removal rate for these systems is 35% (Lenntech, 2010). As an example, two HSSF systems were constructed in Ireland and studied over 3 years to fully understand the parameters that impact the performance of the HSSF systems. A couple of important considerations that to consider are: 1) the surface area in the wetland for adsorption is critical and the hydraulic loading rate (HLR) of the phosphorus is linearly related to the final effluent concentration. 2) Removal rates remained relatively constant for both the growing and dormant months of the plants; the total removal of phosphorus for all the plants averages ten percent annually.

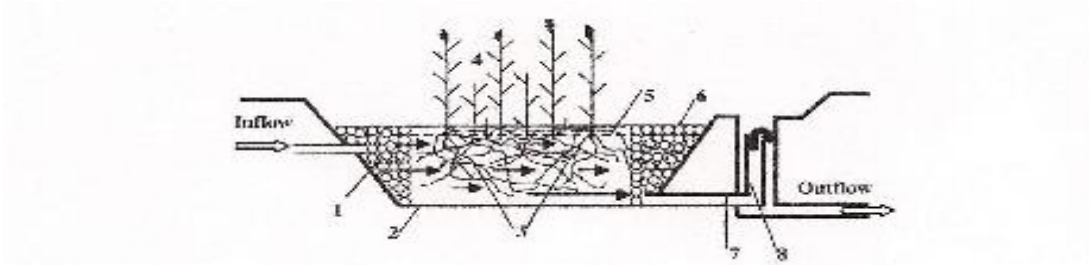


Figure 2: Horizontal Subsurface Flow Constructed Wetland Diagram (Vymazal 2007)

### Vertical Flow Wetland

There are many different types of Vertical Flow (VF) wetlands that have been implemented around the world. Vertical flow wetlands are similar to the planted rapid infiltration (RI) systems used in wastewater treatment for intermittent application and require percolation through the soil. The major difference between the two is that RI systems do not have aerobic processes and the VF can be designed for both aerobic and anaerobic (Crites & Tchobanoglous, 1998). As is the case with HSSF wetlands, VF wetlands historically were not designed to remove phosphorus. If the phosphorus loading rate (PLR) is too high, the internal wetland processes such as plant biomass cycling, and accretion removal mechanisms are not allowed the time required to process the phosphorus (Kadlec & Wallace, 2009). Throughout the paper there are examples of VF wetlands and hybrid wetland configurations being use to treat phosphorus and there is ongoing research to optimize VF wetlands for phosphorus removal.

VF wetlands commonly used in Europe have been used in a variety of applications. The shift from horizontal wetlands to vertical wetlands took place in Europe

in the 1990s because of the nitrification requirements and the importance of improving the Oxygen Transfer Rate (OTR) despite the added complexity of the VF systems and the additional cost of operation (Cooper, 2010). Specifically, they are used to oxidize ammonia in an aerobic environment and can be configured to create anaerobic conditions in a different part of the wetland for denitrification (Kadlec & Wallace, 2009). Realize of course that the increased oxidation can cause the re-release of phosphorus (Vymazal 2007). The average removal rate of phosphorus for VF systems is as high as 70% (Lenntech, 2010) but Kadlec & Wallace (2009) do not think VF wetlands are effective at removing phosphorus beyond the startup periods because the loads are often high and the biogeochemical cycle time is minimal. Again, the primary mechanism for phosphorus removal in the VF wetlands is absorption within the gravel/soil media. As with HSSF wetlands accumulation of organic matter, TSS and associated phosphorus products will negatively impact the porosity and hydraulic conductivity of the VF wetland and can eventually lead to overland flow conditions, typically first seen at the inlet of the VF wetland. The inflow of water is typically from the top as is shown in Figure 3, but the VF can also be designed for water flow from the bottom up through the gravel and sand medium to the plants.

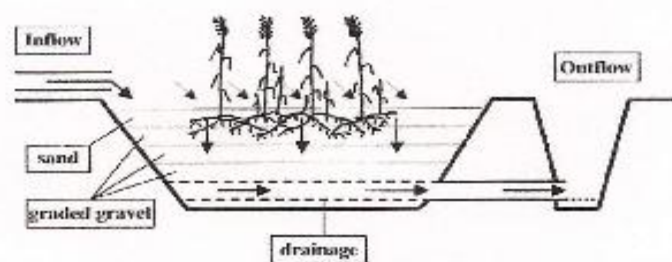


Figure 3: Vertical Flow Constructed Wetland Diagram (Vymazal, 2007)

An excellent paper presented at the 12<sup>th</sup> IWA International Conference on Wetland Systems for Water Pollution Control in Italy that looked at over 16 years of installation experience with VF constructed wetlands (van Oirschot, 2010). Over 250 VF systems have been installed since 1994 by a Belgian firm, RietLand bvba, in the Netherlands and Belgium. The basic design parameters are single bed, 3 m<sup>2</sup> per person equivalent (PE), and a substrate layer at the bottom of the wetland with CaCO<sub>3</sub> and Fe mixed. VF systems have been found to require less maintenance compared to HSSF systems that clog easily. The pipes are laid throughout the second layer of the pea gravel and planted with reed plants and do require occasional cleaning. The primary purpose of the limestone is to add alkalinity, stabilize the pH and remove additional phosphorus. These VF systems are used for a variety of applications and as to be expected in this part of the world, dairy farms are of importance. There is variation between individual farms, and often times the detergents used contain phosphates or phosphoric acid. The use of detergents with phosphorus is discussed later in the paper and an obvious solution to reducing the overall amount of phosphorus is to use cleaning solutions with less phosphorus. The VF constructed wetlands in the study removed over 72% of the TP. The engineering firm has also experimented with other substrates such as a mixture of steel slag and sand, and pure iron. The pure iron gave more consistent results and was easier to manage; removal rates were as high as 90% of TP.

#### Free Water Surface Wetland

“Free water surface (FWS) wetlands have areas of open water, floating vegetation and emergent plants. FWS constructed wetlands closely mimic natural wetlands, and are

typically used for advanced treatment after secondary or tertiary treatment processes” (Kadlec & Wallace, p. 5). A schematic diagram of a FWS wetland is shown in Figure 4. FWS wetlands range in size from 0.1 ha to 2,000 ha and are also used for stormwater events, and mine waters. An advantage to the FWS wetlands is the ability to deal with changing water levels and surge flows and the average removal rate for phosphorus in FWS systems is 51% (Lenntech 2010). Often times the soil at the bottom of the FWS, wetland is selected not only for the rooting media of the plants but also for sorptive capacities. These include soils with high concentration of minerals that have metal salts incorporated into the soil matrix. Examples include laterite, which is rich in iron and aluminum, marl, which is rich in limestone, and spodosols, which are aluminum and iron oxides. Marine sediments are considered another option but are typically only used in constructed wetlands near coastal areas (Kadlec & Wallace, 2009). One of the important considerations when designing a FWS constructed wetland is to ensure uniform distribution of the wastewater stream across inlet side of the wetland (Crites & Tchobanoglous 1998), accomplished by designing the FWS with sinuous cells or compartmental zones that force the water to travel a serpentine path. While increasing the theoretical number of tanks in series (NTIS), improving the phosphorus removal efficiency and providing a system that more closely resembles plug flow. The higher  $k$  values in the removal rate equations (Kadlec & Wallace, 2009) show this as well. The primary mechanisms for removal of phosphorus in FWS are accretion of new soils and sediments. The plants and algae in a FWS will uptake the phosphorus in the wastewater stream quickly and when they decay, the biomass becomes an important constituent of

the new sediments (Crites & Tchobanoglous, 1998). There are over 500 different plant species that are used in FWS wetlands in the United States but there are only 20 that are used commonly (Kadlec & Wallace, 2009).

An example of a FWS that successfully removed phosphorus in Eastern Ontario, Canada showed that operating the system for only a few months each year (May – Oct) and using three cells: the first and third cells were vegetated and had hydraulic retention times (HRT) of 3 and 1.5 days respectively. The second pond was a non-vegetated anoxic pond with a HRT of 10 days. Over the course of 8 years of monitoring the TP cumulative percent removal ranged between 66 and 99% and the discharge criteria of 0.3 – 0.5 mg/L was maintained (Crolla, Kinsley & Higgins, 2010).

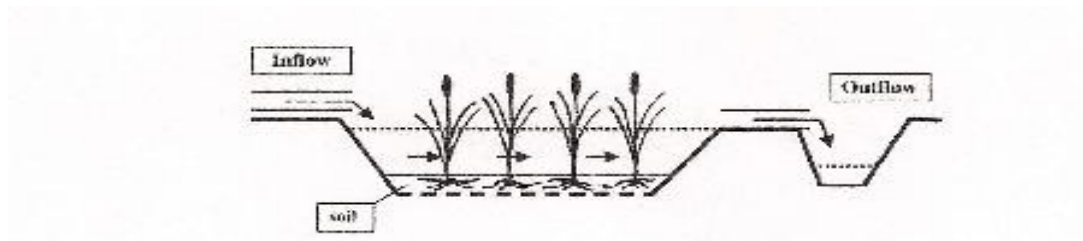


Figure 4: Free Water Surface Constructed Wetland Diagram (Vymazal, 2007)

### Floating Treatment Wetland

The Floating Treatment Wetlands (FTW) has been used with the FWS to improve the quality of the effluent with the Floating Islands Rehberg Ranch installed at the Subdivision (Faulwetter et al., 2010). An example of a FTW is shown in the Figure 5 below. The FTW also referred to as floating plant mats (FPM) are considered an emerging technology in environmental engineering and constructed wetlands design.

“They are an innovative variant on the constructed wetlands concept that uses emergent wetland plants which are grown on a hydroponic floating mat on the water surface” (Hendrickx & Meire 2010 p. 1321). As is the case with the BioHaven design, the newest version of the matrix is only 5% fibers and 95% pore space. The wetland plants embedded in the matrix provide additional buoyancy and more opportunities for microbial growth and nutrient removal because the plants are in direct contact with the wastewater rather than in the soil of the traditional CWS; allowing for a smaller surface area for the constructed wetland because the platforms improve the efficiency of the wetland with the addition of the FTW. The fiber composite has a larger internal surface area that can be used for attachment by the microbes (Stewart et al., 2008; Kania & Stewart, 2011). The water enters a lined water basin below the water level; the plants are in the water and attached to a rooting media. The effluent volume is controlled based on the receiving water requirements. As pointed out by Hendrickx & Meire (2010), the deeper pond-like system allows for more accommodation of large and rapid fluctuations in water depth and because the plants take up more of their nutrient requirements from the water than soil, there is the potential for more nutrient removal. An adequate retention time is required for the root system of the plants and the water to make contact. The most important phosphorus removal mechanism in the FWS is soil accretion but the FTW provides additional removal of the phosphorus.

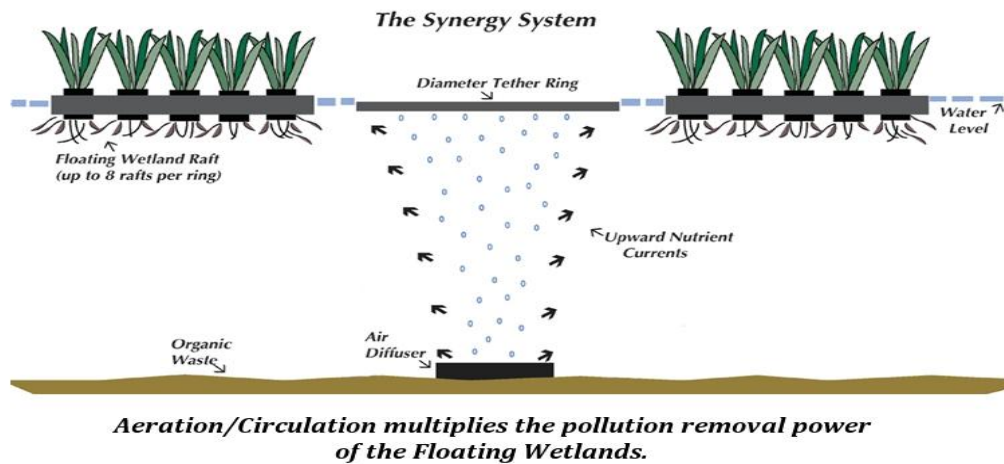


Figure 5: Floating Treatment System Diagram (CAN, 2011)

### Hybrid Systems

Hybrid Systems are combinations of HSSF, VF, and FWS wetlands placed in either series or in parallel and designed to improve the overall effluent water quality. The development and use of the hybrid systems started to take off commercially in the early 1990s (Cooper 2010). Typically, the wastewater needs to meet the effluent requirements of several different contaminants and the use of a combination of the constructed wetlands allows for the flexibility and possibility of meeting all necessary parameters. Within the context of the latest research at the 12<sup>th</sup> IWA International Conference on Wetland Systems for Water Pollution Control, most if not all research looked at hybrid constructed wetland systems. Again, some of the most interesting hybrid systems are referenced further in the paper.

In the Walloon region of Belgium, phosphorus removal is currently not required for smaller systems but will eventually have to meet the EU effluent standards. A study looked at the difference between four different small-scale systems side by side for

comparison (Fonder, Defays, Wauthelet & Xanthoulis, 2010). Horizontal systems (HS) have generally been preferred because there is no energy consumption and gravity flow of the water; however, the direct flow (DF) or vertical flow systems while requiring energy for pumping require less area. The four system configurations (I– DF, II– HF, III - DF+HF, VI - HF+DF) showed that the system II, the single HF had the best removal rates for phosphorus. While the hybrid systems presented in the study did not improve the phosphorus removal it did improved the overall quality of the effluent water for other contaminants.

An example of a hybrid system is called an Ecological Treatment System (ETS), which is a series of aerobic reactors, clarifiers, wetlands and relies on the biogeochemical processes to create value added products of which water is one (Lansing & Martin, 2006). This system is reviewed later the paper because the ETS is a hybrid system with several components that mimic Biological Nutrient Removal (BNR) systems used in standard WWTP facilities and uses components similar to the floating islands for plant and water exposure.

### Phosphorus Partitioning

#### Background Chemical Information

Phosphorus is multivalent nonmetal element, atomic number 15, in the nitrogen group of the periodic table. The phosphorus cycle is different from the nitrogen cycle however, because there are no valency changes during the biological processes of assimilating phosphorus or the decomposition of organisms (Vymazal, 2007). In the

natural world, phosphorus is not found as an element but rather as phosphates, which is typically a negatively charged ion,  $\text{PO}_4^{-3}$  that occurs in most minerals.

Municipal wastewater will contain 5 – 20 mg/L of total phosphorus (TP – defined as the sum of all phosphorus in the wastewater stream) of which 1 – 5 mg/L is organic phosphorus (defined as phosphate ions attached to hydrocarbon molecules) and the rest is inorganic (defined as phosphate ions attached to non-hydrocarbons). The organically bound phosphorus can be as high as 30 -60% of the TP concentration in natural waters (Snoeyink & Jenkins 1980). On average, a person contributes 0.65 g/day to 4.8 g/day of phosphorus with an average of about 2.18 g into a wastewater stream from all activities (Lenntech 2010; Tchobanoglous, Burton & Stensel, 2003). Of the inorganic phosphate, approximately 50% is orthophosphate, 30% is tripolyphosphate and 20% is pyropolyphosphate. The tripolyphosphate has three O-P-O molecular links and the pyropolyphosphate has two O-P-O molecular links (Snoeyink & Jenkins, 1980).

Microorganisms play a major role in the phosphorus cycle. They convert inorganic phosphorus to the organic phosphorus. Polyphosphate is taken up by the phosphorus accumulating organisms (PAO) in the anaerobic conditions and converts it to organic phosphorus in the cell biomass under aerobic conditions. All organic phosphorus is comprised of dead plants and animal tissue that is converted through a series of steps into the orthophosphate ion. The insoluble forms of phosphates such as Ca-P solids are also converted back to soluble forms with the help of microorganisms, and changes in the redox environment.

Cleaning agents are a major source of phosphates in domestic and some agricultural cleaning processes. Synthetic detergents have condensed polyphosphate salts that are used to control water hardness. These detergents historically contributed as much as 50 to 60 % of the total phosphorus in domestic wastewater (Snoeyink & Jenkins, 1980) and while the percentage has dropped (closer to 19% presently) it is still in a variety of cleaning agents. Sixteen states, including Montana and Canada have state laws that strictly limit the amount of phosphorus allowed in the automatic dishwashing detergent (ADD). The response from the industry was to “voluntarily” comply with these laws for all fifty states and Canada. Phosphorus used in commercial operations and agricultural fertilizers play a bigger role to the overall phosphorus loading in receiving waters. There is ongoing research and implementation to use products that have less phosphorus from the beginning.

Phosphorus in the environment cycles between the organic and inorganic forms, referred to in the literature as the biogeochemical cycle. The wetland environment provides for the transformations of phosphorus and there is a dynamic interconversion of the phosphorus throughout the system (Vymazal, 2007). While there are different processes (chemical, biological, sorption, etc) happening simultaneously, the phosphorus is cycling between a number of various forms and there are continual rearrangements of the phosphorus. Each of these processes has a different kinetics rate and as the water progresses through a wetland and phosphorus is removed from the system the different fractional components of phosphorus will change, termed “weathering” of the wetland.

The concept has not been studied in detail but the complexity of the wetlands system and the phosphorus cycle lends itself to further study (Kadlec & Wallace, 2009).

The phosphorus cycle in natural settings is one of the slowest matter cycles. Phosphorus cycles more quickly through plants and animals when compared to soils, sediments and water (Lenntech, 2010). The latest research on the different types of phosphorus and the measurement techniques used to determine the different types of phosphorus are summarized. Robert Kadlec and Scott Wallace summarize the challenge quite succinctly: “It is certain that differences in sampling and laboratory protocols have contributed significantly to the data scatter for wetland performance parameters” (Kadlec & Wallace, 2009, p. 945).

The literature search has allowed me to piece together the following Figure 6, a representation of the different types of phosphorus found in wetlands, both constructed and natural. The basic premise for the diagram is from the Kadlec and Wallace textbook, *Treatment Wetlands*, 2<sup>nd</sup> edition. Using that framework, I designed Figure 6 to show the major components of the different phosphorus fractions. There are five major categories: Total Dissolved Phosphorus (TDP) and Total Suspended Phosphorus (TSP) represent the water column of the wetland. Total Soil Surface Phosphorus (TSSP) and Soil Stored Phosphorus (SSP) represent the phosphorus in the soil and sediments of the wetland. The Total Biomass Phosphorus (TBP) is found in both the water column and the soils of the wetland and is made up of the phosphorus found in all biological activity of the wetland, including plants, algae, and microbial activity. The primary advantages to knowing the fractionation of the different phosphorus concentrations in the wetland allows for

optimization of the process and a detailed understanding of the mass balance of the phosphorus. Around the world, these different fractions of phosphorus are given different names, and so throughout the paper, other commonly used names for these different phosphorus types are referenced. A second word of caution, typically the measurements of phosphorus used in constructed wetlands engineering are Total Phosphorus (TP) and orthophosphate, but evaluating Figure 6 shows that many different types of phosphorus are referred to as “Total. At times confusing and a bit of a misnomer it is seen throughout the literature. In this thesis, TP concentrations refer to the analytical methods requiring a full acid digestion of the water or soil sample, which will be explained later.

While the most common phosphorus fractions measured in the water column are total and dissolved phosphorus and total and dissolved orthophosphates; the polyphosphate concentrations, particulate phosphorus and organic phosphorus all play significant roles in determining the primary removal mechanisms and the final effluent concentrations (USEPA, 1993). Equally important are the phosphorus concentrations in the soil and sediment environment of the wetland and the phosphorus in all biologically active species.

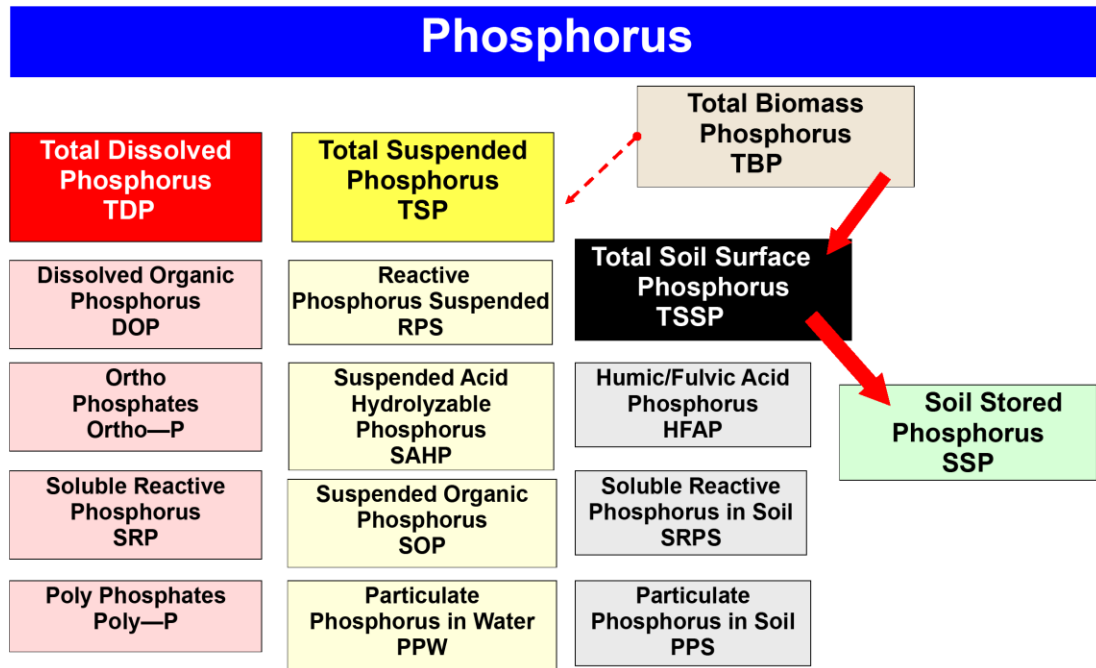


Figure 6: Phosphorus Partitioning Diagram: the TDP and TSP fractions are in the constructed wetland water; the TSSP and SSP are located in the constructed wetland soils. The TBP is all phosphorus located in the constructed wetlands biomass in both the water and the soil.

The methods for determining the concentrations for the fractional phosphorus components in the wetland requires different analytical chemistry techniques for the water and soil concentrations. The methods are approved by the USEPA and originated from two different branches of analytical chemistry: soil science and water chemistry. The analytical methods for determining phosphorus in the wetland soils are more complex. The digestion of water-based phosphorus into the different fractions is a multistep acid digestion. There are three different acid digestions that are used for determining the concentration of TP in all water samples including surface waters,

domestic wastewater and industrial wastewater: 1) perchloric acid (most aggressive), 2) sulfuric-nitric acid 3) sulfuric acid and persulfate digestion (most common). There are two colorimetric methods for determining orthophosphate: 1) molybdovanadate method (yellow method) and 2) ascorbic acid method or the molybdenum blue method (WEF 2006; Sawyer & McCarty 1978). While the yellow method is simpler, most of the literature refers to the molybdenum blue method, also referred to as the Murphy and Riley procedure. The methods here are the persulfate and sulfuric digestion (USEPA, 1974) for TP and the molybdenum blue method (Method 365.1) for orthophosphates; the Standard Methods for the Examination of Water and Wastewater, 4500-P by the American Water Works Association supports these methods. Essentially, all of the phosphorus in the water converts to orthophosphate by an acid digestion made up of strong acids and ammonium persulfate as a catalyst and then it is titrated with sodium hydroxide until light pink color develops. After which the methods for orthophosphate are used (WEF, 2006; USEPA, 1993; USEPA, 1974; APHA, 1999).

Method 365.4 is method for digesting the phosphorus in the water to convert it to the orthophosphate for measurement. In order to completely digest all forms of phosphorus, the water is heated to a temperature of 160 °C in a sulfuric acid,  $K_2SO_4$ , and  $HgSO_4$  solution for 2.5 hours (USEPA, 1974). If the acid hydrolysis is at a temperature over 100 °C, converting all dissolved and particulate condensed phosphorus to soluble orthophosphate. The persulfate,  $(NH_4)_2S_2O_8$  a strong oxidizing agent, oxidizes all organic phosphorus.

Method 365.1 is the method for determining the orthophosphate concentrations in the water; in the literature there are frequent references to the ammonium molybdate/antimony potassium method that complexes the phosphate ion to an intensely blue colored solution that is proportional to the orthophosphate concentration in an acid solution. The organic phosphorus and polyphosphates in the water will not react with these chemicals. The colorimetric method is used for also determining the TP in the water column after the acid digestion of Method 365.4. Hexavalent chromium, nitrite and high iron concentrations interfere with Method 365.4 (USEPA, 1993).

Standard Method 4500 – P is an eight part analytical method for water and wastewater determination of phosphorus, referred to in the literature as 4500-P. Maintained by the American Water Works Association it includes all procedures for the different digestions and methods for determining the phosphorus concentrations as dissolved and suspended with respect to the organic, reactive and polyphosphate fractions. Sulfuric acid and infrequently nitric acid are used to hydrolyze the water samples and the ammonium persulfate is both a catalyst and a strong oxidizing agent (APHA, 1999).

Table 1 summarizes the different acid digestions used for each of the different types of phosphorus in the water. The importance of each phosphorus fraction is explained in more detail. All measurements for the water column are mg P/L measured as  $\text{PO}_4\text{-P}$ .

<b>Fractional Component of Phosphorus</b>	<b>Quick Summary of the Methods Used to Convert all Phosphorus in water to Orthophosphates for Measurement using the Molybdate Blue Method for Determining Concentration in mg/L</b>
<b>TP</b>	TP requires the unfiltered sample to be digested with both the sulfuric and persulfate solutions to hydrolyze and oxidize all phosphorus to Ortho-P.
<b>TDP</b>	After filtration, digested with sulfuric acid and persulfate solution
<b>SRP, Ortho-P, TRP</b>	No acid digestions required, test with molybdate after filtration, the SRP and Ortho-P require filtration, TRP does not require filtration.
<b>DOP, TOP</b>	DOP after filtration, TOP without filtration, persulfate oxidation only
<b>Poly-P, TAHP</b>	Poly-P after filtration, TAHP without filtration, hot sulfuric acid only
<b>PPW</b>	PPW is based on TSS, dry ash, sulfuric, and persulfate solution digestions
<b>SOP</b>	$SOP = TOP - DOP$
<b>SAHP</b>	$SAHP = TAHP - Poly-P$
<b>RPS</b>	$RPS = TRP - SRP$ or Ortho-P
<b>TSP</b>	$TSP = TP - TDP$

Table 1: Quick summary of methods used to determine phosphorus in wetland water.

In the wastewater treatment industry, there are analytical tools that allow for continuous monitoring of the process in real time. Total phosphorus monitors for continuous measurement are more complex because the TP (including polyphosphates and organic phosphates) must first be converted to orthophosphate with the acid digestion and then measured the same way as the orthophosphates. Instrumentation based monitoring is possible for the orthophosphate concentrations because the acid digestion is not required (WEF, 2006).

#### Total Dissolved Phosphorus

Total Dissolved Phosphorus (TDP) in the water column is made up of four different fractions: Dissolved Organic Phosphorus (DOP), Orthophosphates (Ortho-P), Soluble Reactive Phosphorus (SRP), and Polyphosphates (Poly-P). The start of these phosphorus fractionations requires the water to be filtered with a 0.45 $\mu$ m pore size filter (USEPA, 1993). The DOP and the Poly-P require an acid digestion and conversion to

orthophosphate before the concentrations can be analyzed. The dissolved phosphorus in the wetlands system is one of the major components that are adsorbed on the sediments and soil surface and taken up by the biological processes (Maynard, O'Green & Dahlgren, 2009).

Dissolved Organic Phosphorus: There are many different types of dissolved organic materials that contain phosphorus that are classified as Dissolved Organic Phosphorus (DOP) and is classified as the organic phosphorus that is smaller than the 0.45µm pore size filter.

Organically structured phosphorus, both DOP and the organic phosphorus in suspended particles (SOP) can be re-released into the water column as soluble phosphorus if the organic matter is oxidized (Vymazal, 2007) or because the life cycle of these tiny organisms is short and the turnover is quick, the uptake is returned as DOP and Particulate Phosphorus (PP). DOP does not sorb as well as other phosphorus fractions to substrates in constructed wetlands (Kadlec & Wallace, 2009). Some DOP will sorb onto the surfaces of the wetland media but not as readily as the orthophosphate ions (Kadlec & Wallace, 2009).

An important component of the DOP is Phosphorus Accumulating Organisms (PAO) that use polyphosphates for growth and eventually remove the phosphorus from the water ; these organisms become a part of the system as TSS, biomass and sludge by products. The cell mass of the PAO will have organic phosphorus contains as much as 30% TP (MPCA, 2006).

Xia, Tao, Lu & Shayya (2010) showed that the addition of phosphatase enzymes can also be added in an alkaline solution to the vertical flow wetlands to enhance the conversion of organic phosphorus, both Total Organic Phosphorus (TOP) and DOP, to orthophosphate and the orthophosphate was recovered and used as struvite, a natural mineral that is a slow release fertilizer.

The methods for determining organic phosphorus require that the organic matter be destroyed with the oxidation of the water sample with persulfate (Sawyer & McCarty, 1978). The “severity” of the oxidation required for conversion to orthophosphate will depend on the type of organic substances that are in the wastewater stream. The organophosphates used in synthetic pesticides will require several hours of oxidation (APHA, 1999). When determining the DOP analytically the recommendation is to use glass filters as to not contaminate the sample (Zhang & Oldham, 2001). More often the DOP is calculated from the subtraction of  $TP - (SRP + Poly-P) = DOP$  (MPCA, 2006).

Orthophosphates: Orthophosphates are soluble and are the inorganic phosphorus in the wastewater stream; the generic term used through the literature for the orthophosphate ion concentrations is  $PO_4\text{-P}$  (Crites & Tchobanoglous, 1998; Kadlec & Wallace, 2009). Orthophosphates are designated Ortho-P on Figure 6 above.

Orthophosphates are thought to be the only form of phosphorus utilized directly by biological processes and “thus represents a major link between the organic and inorganic cycling of phosphorus in the wetlands” (Vymazal, 2007, p. 58; Crites & Tchobanoglous, 1998). However, there is ongoing research that plant P adsorption is possible in small quantities for the simplest linear polyphosphate, pyrophosphate that has

two P-O bonds (Torres-Dorante, Claassen, Steingrobe & Olf, 2005). In addition, the molybdate method of determining the orthophosphate concentration is thought to be the best indicator of the amount of bioavailable P. (bio-P)

In the orthophosphate molecule, the P atom is centrally bonded to two oxygen atoms in the form of O-P-O (Snoeyink & Jenkins, 1980). Orthophosphate refers to several different ionic compounds:  $\text{PO}_4^{-3}$ ,  $\text{HPO}_4^{-2}$ ,  $\text{H}_2\text{PO}_4^{-}$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{HPO}_4^{-2}$  complexes and all are biologically available without further breakdown. The phosphate species in the water is dictated by the pH in the water. Figure 7, shows the relationship. Typically, the pH of wetland systems is in the range of 4 to 9. The predominate orthophosphate species are the inorganic, dissolved forms:

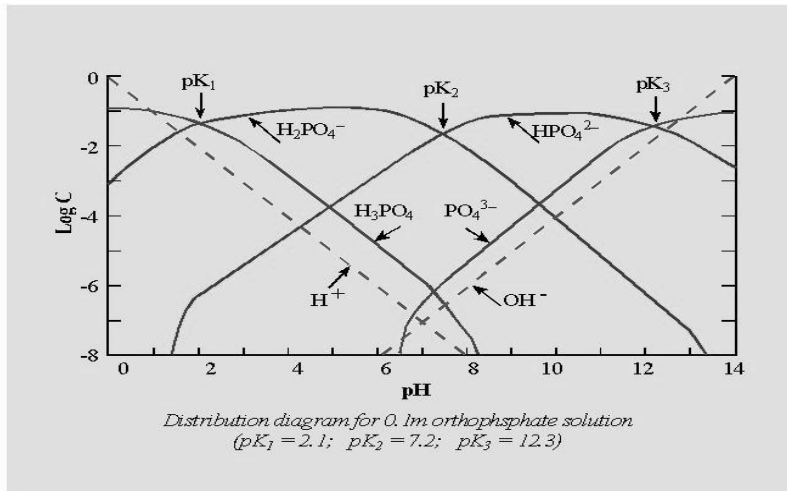
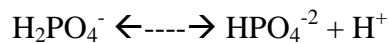


Figure 7: pH vs. Log C for orthophosphate in Water (Kafkafi, 2011)

The molybdate analytical test determines the concentration of the orthophosphate ions but also detects the exchangeable phosphorus and the colloiddally bound phosphorus (Kadlec & Wallace, 2009). The complication to the analytical method is some colloidal phosphorus (TCP) may be in the orthophosphate fraction and occurs in both organic and inorganic forms. Examples of colloidal material are iron hydroxide complexes and the iron hydroxide dissolved humic substances (DHS) found in the water-soil interface. It is well documented that the molybdate test overestimates the amount of orthophosphate available in the system for bioavailability.

An excellent paper by Zhang & Oldham (2001) looked at an ultrafiltration technique to determine only the orthophosphate concentration. While the paper is challenging to understand because all of the acronyms used are different than the industry accepted acronyms for phosphorus partitioning the recommendations for determining orthophosphate independent of the other fractions are compelling. Zhang & Oldham (2001) defines the reactive phosphorus as the filterable reactive phosphorus (FRP) and considers it a chemical indication of the orthophosphates in the wetlands. There is considerable variation in phosphorus fractions between wetlands when evaluating the FRP, TP, total filterable phosphorus (TFP), and orthophosphate between and within 17 wetlands in Western Australia that the University of Western Australia studied. The key experimental method was to filter the water through an ultrafiltration technique with the goal of separating the colloidal phosphorus from the orthophosphates with a filter that separates molecules larger than 1500 Daltons. A Dalton (Da) is a molecular measurement of approximately one proton and one neutron. The average particle size of the colloidal

phosphorus was between 1.0 nm and 0.5  $\mu\text{m}$  and greater than 1500 Da. By setting the limit at 1500 Da, the orthophosphate filters through but not the colloidal particles that have phosphorus incorporated into them. The colloidal phosphorus (TCP) is the difference between TFP and orthophosphate. One of the interesting findings is that the amount of filterable organic phosphorus (FOP), referred to as Soluble Organic Phosphorus (SOP) in most literature, and is an important source of the regeneration of FRP at the end of the growing season. Wetlands with higher dissolved organic carbon (DOC) also showed higher TFP concentrations, suggesting that the DOC and orthophosphate formed complexes. Another important conclusion is the DOC/TFP ratio is critical to regulating the amount of orthophosphate in the wetland water system and the amount of DOC in the water regulated the Fe-P precipitation. The amount of filterable Fe concentration in the presence of the DOC was also a factor in determining the precipitation of Fe-P. The key finding specific to the 17 wetlands evaluated was that on average 82% of the Total Filterable Phosphorus (TFP) concentration was Filterable Colloidal Phosphorus (FCP) indicating that the orthophosphate available for biological uptake by algae and other microbial processes is significantly less than if the molybdate test was performed. The FCP concentration will experience seasonal changes, which in turn will cause variability as to how much the FRP actual overestimates the orthophosphate concentrations (Zhang, 2001; Zhang & Oldham, 2001).

Soluble Reactive Phosphorus: Orthophosphates are a subset of Soluble Reactive Phosphorus. In some literature referred to as the Molybdate Reactive Phosphorus (MRP), Dissolved Reactive Phosphorus (DRP) or as the labile P in water.

It is worth noting that the Ortho-P and SRP are often confused in the literature, and the SRP includes the Ortho-P and some condensed Polyphosphates (Poly-P) that can be used directly by biological processes and some organic phosphates. The organic component of SRP moves readily into the soils and sediments and is often associated with the suspended particulate phosphorus in water (PPW). The Poly-P used in biological processes is for the phosphorus accumulating organisms (PAO) and a small fraction of the simplest polyphosphate, pyrophosphate for plant uptake (Kadlec & Wallace, 2009; Vymazal, 2007).

The actual organic phosphorus in the influent wastewater is not a major constituent in domestic wastewaters but can vary in industrial wastewater and some activated sludge. As the larger organic phosphorus compounds are processed to dissolved organic phosphorus (DOP), a fraction of the DOP will be hydrolyzed by soil enzymes and fractioned into soluble reactive phosphorus (SRP). Moreover, the SRP can be used for biological processes or can cycle into particulate phosphorus (PP) with additional processes or be sorbed directly to wetland soils and sediments (Crites & Tchobanoglous, 1998; Vymazal, 2007).

The SRP contribution to the overall phosphorus concentrations in the wetland cannot be underestimated. As an example, the influent storm water event to the Everglades Nutrient Removal Project (ENRP) had 60% TDP of which SRP concentrations were 55% of the total concentration of the phosphorus, which is typical of runoff waters. Essentially the SRP was between 25 and 50% of the TP entering the system. The SRP fraction was eliminated in the ENRP wetlands but in contrast, a WWTP

will have much higher concentrations of SRP in the range of 70% (Kadlec, 2006). As stated earlier it is the SRP that is used first in the wetland by the biological processes, all other phosphorus forms will require processing in the wetland before they are available for biological activity or precipitation with the metal salts at the water-soil interface.

Poly Phosphates: The polyphosphates are molecules with more than one phosphorus atom, and oxygen atoms in complex molecules. Examples of the polyphosphate ions are  $\text{P}_2\text{O}_7^{-4}$ ,  $\text{HP}_2\text{O}_7^{-3}$ ,  $\text{H}_3\text{P}_2\text{O}_7^{-}$ ,  $\text{H}_4\text{P}_2\text{O}_7$ , and the corresponding complexes with metal ions.

Polyphosphates are often referred to as molecularly dehydrated phosphates or condensed phosphates (Sawyer & McCarty, 1978; Crites & Tchobanoglous, 1998). Polyphosphates (Poly-P) is referred to in the literature as the acid-hydrolyzable phosphorus because enzymes in the wetlands environment hydrolyze it.

The condensation of two or more orthophosphates will form polyphosphates with the bond structure of P-O-P. Polyphosphates are both linear and circular molecules, the metaphosphate of which trimetaphosphate (TMP) is the most common are the cyclic polyphosphate molecules and are more difficult to breakdown into the orthophosphate ion for uptake (Snoeyink & Jenkins, 1980). The literature refers to all Poly-P as condensed phosphates seldom distinguishing between the different types of Poly-P. As expected, the linear Poly-P molecules are easier to break down to orthophosphate ions than the circular Poly-P molecules, such as trimetaphosphate (TMP) and the most difficult to breakdown are the synthetic organo-polyphosphate fertilizers (Snoeyink & Jenkins, 1980; Torres-Dorante et al., 2005). Condensed Poly-P includes the organically

bound phosphorus found in nucleic acids, nucleoproteins, phosphorylated sugars, and other condensed organic enzymes. These condensed Poly-P molecules decompose at very different rates with the nucleic acids, lipids and sugars decomposing much faster than the other organic compounds (Vymazal, 2007).

Determining the amount of polyphosphates in the water column is not a simple process. There are several factors complicating the measurement and often the fraction of polyphosphate is either a calculated value or estimation. 1) The SRP will contain some polyphosphate molecules, so in essence the Poly-P is double counted. 2) The Poly-P is also incorporated into the Total Suspended Phosphorus (TSP) fraction because it is a part of the Total Suspended Solids (TSS). 3) The Poly-P will form complex molecules at the soil-water interface that are also a part of the particulate phosphorus (PP), and 4) the reactions with sulfuric acid at high temperatures separate Poly-P fraction but there is often contamination and will include some organic phosphorus (USEPA 1993; APHA, 1999).

One method for determining the Poly-P in the water column requires looking also at the soil-water interface. At the soil-water interface, water (no soil) is extracted and a portion of that sample is analyzed for orthophosphate. A second portion of the sample is tested for TP with the sulfuric acid digestion and the molybdate blue method of orthophosphate determination. The difference between these two measurements is assumed the Poly-P concentration (Torres-Dorante et al., 2005). While not an ideal method because it can overestimate the amount of Poly-P in the wetland with the inclusion of some Particulate Phosphorus (PP) and it does not take into account the rest

of the Poly-P higher up in the water column that is available for Phosphorus Accumulating Organisms.

The second method, as described by the Standard Method 4500-P is the digestion of the water sample with hot sulfuric acid for several hours to convert all of the different condensed polyphosphates to orthophosphate, realizing of course that there is cross-contamination from organic phosphorus that are also hydrolyzed (APHA, 1999). As we know, the (PAO) use the polyphosphates bonds as an energy source, the ideal method would be to determine the amount of phosphorus in the PAOs themselves or to calculate the amount of Poly-P used by the PAOs based on the uptick in the orthophosphate concentrations between the anaerobic and aerobic cells of the wetland. Determining the amount of phosphorus in the PAO is not possible because PAOs are difficult to separate and have not been identified but there is research showing the uptick in phosphorus concentration between anaerobic and aerobic cells of WWTP. The uptick in concentration can almost double (Crites & Tchobanoglous, 1998) the concentration of the orthophosphates in the system. Measuring the idelta between the cells is probably the best estimate for determining the amount of Poly -P in the wastewater stream; it would be a Poly-P as Ortho-P measurement but would still be useful in determining the amount of Poly-P in the wastewater stream because the PAO used Poly-P for growth.

Within the wetlands environment, several other processes with Poly-P molecules are happening simultaneously. These include the hydrolysis of polyphosphates to orthophosphate and the precipitation of Poly-P with the metal ions in the soil and water of the wetland. Hydrolysis, a slow reaction, converting the polyphosphates back to the

orthophosphates in the water but is a function of both the pH and the temperature of the wastewater (Crites & Tchobanoglous, 1998). As an example, the hydrolysis of 5% of the pyrophosphate is 1 year at a pH of 4, and at a pH of 10, it is over a century (Snoeyink & Jenkins, 1980). What typically happens at a faster rate is the hydrolysis of Poly-P by enzymes called phosphatase and is slower in natural systems than wastewater treatment processes. The pyrophosphates (2 P linear chain) hydrolyze faster than tripolyphosphate (Sawyer & McCarty, 1978; Snoeyink & Jenkins, 1980). The hydrolysis for the cyclical Poly-P molecules require additional hydrolysis to open up the ring structure. The hydrolysis of Poly-P in the soil environment happens more quickly and it assumed that the soils have their own and different enzymes to promote the conversion to orthophosphates (Torres-Dorante et al., 2005). It is worth noting that one of the reasons the digestion of Poly-P is in acidic conditions with heat at boiling temperatures for the 2 hours or more is because of the difficulty completely hydrolyzing the sample.

When removing phosphorus from the wastewater with metal ions, the polyphosphates and organic phosphorus are not easily converted to orthophosphate, which is the phosphate ion that reacts with Fe, Al, and Ca. The metal ions will react first with the orthophosphates, and the organic phosphorus and polyphosphates by reactions that are more complex and by adsorption onto metal salt floc particulates. The flocs, precipitates and TSS are a sludge product. (Tchobanoglous et al., 2003) It is important to note that TSS is a lumped parameter based on particle size, and seldom is the chemical composition of the TSS confirmed. The TSS concentration is dependent on the type of filter used (Crites & Tchobanoglous, 1998). The Particulate Phosphorus (PP) in the Total

Suspended Phosphorus (TSP) is considered to be a component of the TSS in the wetland waters.

#### Total Suspended Phosphorus

The Total Suspended Phosphorus (TSP) is the phosphorus in the water column that does not pass through the 0.45 µm filter and comprises of the four fractions: Reactive Phosphorus Suspended (RPS), Suspended Acid Hydrolyzable Phosphorus (SAHP), Suspended Organic Phosphorus (SOP), and the Particulate Phosphorus in Soils (PPS). The analytical chemistry methods for determining the fractional proportions of these different types of phosphorus are the same acid digestion/molybdate colorimeter measurements used for the Total Dissolved Phosphorus fractions. Essentially these samples are digested without the 0.45 µm pore filters.

Reactive Phosphorus Suspended: The Reactive Phosphorus Suspended (RPS) includes all suspended phosphorus in the water column that is easily available for use by the biological processes and precipitation with the metal salts that is larger than the 0.45 µm diameter pore size filter and referred to in the literature as a part of the labile P in water.

The molybdate colorimetric analysis is performed on unfiltered water from the wetland and the difference between the Total Reactive Phosphorus (TRP) and the Soluble Reactive Phosphorus (SRP) is the Reactive Phosphorus Suspended (RPS) (USEPA 1993). It is worth noting that the RPS will include the reactive colloidal phosphorus (both inorganic and organic).  $RPS = TRP - SRP$ .

Suspended Acid Hydrolyzable Phosphorus: The Suspended Acid Hydrolyzable Phosphorus (SAHP) is the polyphosphate concentration that is suspended in the water. Interestingly, the literature refers to this typically as Poly-P for dissolved polyphosphates but more clearly defines it for the suspended polyphosphates as the acid hydrolyzable phosphorus. Because, enzymes in water and wastewater hydrolyze polyphosphates slowly, the digestion speeds up the hydrolyzation and allows for the determination of the polyphosphate concentrations.

The SAHP is determined by acid hydrolyzing the water sample without filtration for an extended period of time. The research suggests anywhere from 90 minutes to several hours depending on the chemical makeup of the wastewater. The organic polyphosphates will require a long digestion time but eventually the hot sulfuric acid will convert the polyphosphates to Ortho-P and the concentration of the Total Acid Hydrolyzed Phosphorus (TAHP) can be calculated. The  $SAHP = TAHP - Poly\ P$ .

Suspended Organic Phosphorus: The Suspended Organic Phosphorus (SOP) is made up of organic organisms that are not a part of the Total Biomass Phosphorus (TBP) but larger than the 0.45  $\mu\text{m}$  pore filter. The determination of the SOP concentration is the subtraction of the Total Organic Phosphorus (TOP) – Dissolved Organic Phosphorus (DOP). The water sample is oxidized with persulfate and then tested for Ortho-P with the molybdate colorimetric method.

Organic structural phosphorus is released as organic phosphorus if oxidized from the tissue and cells structures of the plants and biological species (Vymazal, 2007). Another source of organic phosphorus is the phytoplankton that is often present in FWS

wetlands. Phytoplankton eventually become Particulate Phosphorus in Water (PPW) that drops to the bottom of the wetland (Kadlec & Wallace, 2009). Phosphorus in organic matter being decomposed can be incorporated into growing cells through the mediation of enzymes called phosphatases (Grady & Lim, 1980).

It is estimated that 15 to 25 % of the organic phosphorus in the constructed wetlands is microbial, in phosphorus forms suspended in water, soils and flocs. Other studies place this value as high as 50%, and because the life cycle of these microbial organisms is short, the phosphorus is returned to the system as Suspended Organic Phosphorus (SOP), Dissolved Oxygen Phosphorus (DOP) and Particulate Phosphorus in Water (PPW) and to a lesser extent the Particulate Phosphorus in Soils (PPS). Very little of these microbial organisms are permanently buried (Kadlec & Wallace, 2009).

Organophosphates are organic molecules attached to the oxygen molecules of the phosphate ion. The synthetic organophosphate pesticides are the most difficult to decompose and will pass through a constructed wetlands system without altering composition. When oxidized for an extended period of time (several hours) and tested for the orthophosphate concentration, indicating the phosphorus contaminants not taken up by any removal processes in the system. The organophosphate compounds are one example of why there is always a background concentration of phosphorus in the wetland. The background concentration,  $C^*$  is referred to extensively later in the paper because of the importance of the understanding the kinetics of the constructed wetland.

The research by Turner & Newman (2005) shows the interrelationship between the soil-water as the organic phosphorus concentrations in the water impact the long-term

sequestration of the phosphorus in the soil. Additional emphasis and research is required to identify the unextractable fraction of the soil P, which is critical for understanding long-term sequestration of P in wetland soils, including a better understanding of the phosphodiesterase activity and the turnover of phosphate diesters in wetlands (Turner & Newman, 2005). Phosphorus diesters are the dominant organic P compounds in plant and microorganisms in wetlands and the hydrolysis of these compounds in tropical environments like the Everglades is a limiting step in soil organic P turnover. These phosphate diesters are the dominant organic P contribution to the alkaline extracts of the soil of the Everglades Nutrient Removal Project (ENRP).

Particulate Phosphorus in Water: The Particulate Phosphorus in Water (PPW) is a spectrum of particle sizes and types and is often seen in the Total Suspended Solids (TSS) in the water that has not dropped to the surface of the constructed wetlands (WEF, 2006). PPW is between 5 and 20% of the TSS in wastewater effluents (MPCA, 2006). The nonreactive particulate phosphorus (NRPP) in the water is a subset of the PPW fraction that eventually settles to the bottom of the wetland. TSS is difficult to measure in wetlands but is typically in the range of 5-10 mg TSS/L. The sulfuric acid digestion and persulfate oxidation of the TSS is required to determine the amount of phosphorus in the TSS. The amount of phosphorus in the TSS is often referenced as the % by dry weight (DW) of TSS.

TSS flocs are a major challenge that requires management and proper design. The flocs can occur anywhere in the wetland and increase the overall removal rate constants. The actual rate constant that describes the flow of TSS is changing through the wetland

and both axial dispersion and retardation need to be taken into account when designing a constructed wetland (Crites & Tchobanoglous, 1998). Non-rooted macrophytes (SAV) help to eliminate elevated TSS levels in constructed wetlands (MPCA, 2006). As Phosphorus Accumulation Organisms (PAO) use Poly-P for growth, the biomass produced is a part of the TSS in the water column. In WWTP, the TSS is a part of the activated sludge but for wetlands, the TSS eventually drops to the bottom surface of the wetland.

#### Total Biomass Phosphorus

The Total Biomass Phosphorus (TBP) is the phosphorus found in all biological processes of the wetland, including all phosphorus found in all living and dead biomass that has not begun to incorporate into the soil surface. As examples, all parts of the standing plants including roots and rhizome, algae, microbial activity, phosphorus accumulating organisms, and biofilms. The method of determination is complete ashing of the biomass, the oxidation of the sample in persulfate and the re-dissolution of the dry ash for testing with the molybdate blue method. Throughout the paper, this is referred to as the % P in the dry weight (DW) of the plants and algae. The method is straightforward for the plants and algae but it is more difficult for the phosphorus in the microbial species. The microbial fraction is typically a part of the Suspended Organic Phosphorus (SOP) in the water sample. As shown in Figure 6, as the plants decay, the phosphorus is cycled through the water column and returns as Total Suspended Phosphorus (TSP) often in the form of Suspended Organic Phosphorus (SOP) and Particulate Phosphorus in Water (PPW). The remaining TBP settles to the bottom of the wetland as Particulate

Phosphorus (PP) and begins to incorporate into the soil sediments becoming a part of the Total Soil Surface Phosphorus (TSSP) and eventually as Soil Stored Phosphorus (SSP).

#### Total Soil Surface Phosphorus

The Total Soil Surface Phosphorus is made up of three different fractions: the Humic/Fulvic Acid Phosphorus (HFAP), the Soluble Reactive Phosphorus in Soils (SRPS), and the Particulate Phosphorus (PP). The top soil layer and the most active soil in the wetland is the first 20 cm, including the zone of soil where most of the roots of the plants are located. In the literature, the top layer of the wetland substrate is often referred to as the benthic layer of the wetland and includes the not only the soil but also the plant and algae detritus that has fallen to the surface (Turner & Newman, 2005). The methods for collecting soil samples and not disturbing the soil surface involves cylinders carefully placed on the soil surface. Often referred to as Mortimer cylinders, these methods have evolved over the years and the techniques have been refined by Robert Kadlec and other wetland scientists with the majority of the work at the Houghton Lake, Michigan wetland and the Everglades Nutrient Removal Project in South Florida. The collection methods include using dry ice and instantly freezing the soil samples before transporting or disturbing the soil column. (Kadlec & Wallace, 2009; Kadlec, 2009b)

The techniques required for digesting and determining the different fractions of P in the soil, have changed and been refined, “this is not an exacting, science .... It must be kept in mind that these are rather crude methods” (Moore & Coale, 2000). While the water chemistry methods for determining phosphorus are straightforward, the analytical methods for determining the concentration of phosphorus in soils are not straightforward.

There are many different acid digestions used to breakdown the soil, and convert the phosphorus to orthophosphate and the final concentration of each fraction is reported as orthophosphates by use of the molybdate blue method. These sections of the paper will synthesis the methods most often seen in the literature. Phosphorus extraction from the soil requires several different acid digestions and in order to fully understand the fractionation of the different types of phosphorus they need to be done in a sequential format.

Several studies recommended starting with saturated samples and looking first at the amount of phosphorus in the pore water (Moore & Coale, 2000; Sherwood & Qualls, 2001). The saturated soil sample is centrifuged and filtered with the 0.45  $\mu\text{m}$  pore filter and then acidified with sulfuric and oxidized with persulfate. The molybdate blue method determines the TP that is water-soluble and in the pore water of the soil (Moore & Coale, 2000).

Evaluating the phosphorus in the soil requires several different extractions and acid digestions because of many different the mechanisms by which the phosphorus is held in the soil and the sedimentation. As stated by Bender & Wood (2000), “Underestimation of TP by acid digestion in soils is thought to be due to the inability of these methods to extract P from the apatite” (p. 43). As an example, just one of the challenges to completely converting all phosphorus to orthophosphate for measurement by the molybdate blue method. Also stated by Pierzynski & Sharpley (2000), “Laboratories today must deal with the analysis of a wider range of sample types for more diverse agronomic and environmental uses. Often leading to confusion over the

selection of the most appropriate method for specific need and inappropriate recommendations for P management” (p. 1).

The methods and order of the different acid and alkaline digests are based on the differential solubilities of the forms of phosphorus in the soil matrix. Within the SRPS, there are four different acid digestions to ensure that all of the Fe-P, Al-P, Mg-P Ca-P and loosely held P are extracted. Within the HFAP, there are three different digestions to ensure that all of the organic P is removed from the soil. Finally, the PPS is by calculation. Table 2 shows a summary of the different acid digestion methods for each of the TSSP fractionations (Zhang & Kovar, 2000; Moore & Coale, 2000; Bender & Wood, 2000; Sharpley & Smith, 1985; Wen & Recknagel, 2006; Lowen & Piirtola, 2000; Borovec, Sirova, Mosnerova, Rejmankova & Vera, 2010). Each of these methods is detailed and if there are alternatives that give reliable results, they are mentioned.

One of two methods is used for establishing the Total Soil Surface Phosphorus (TSSP). The research recommends either the nitric acid/perchloric acid ( $\text{HClO}_4$ ) digestion or NaOH digestion (Bender & Wood, 2000; Wen & Recknagel, 2006). With all of these digestions, the soil is finely ground to less than 0.5 mm diameter. The acid digestion does not take as long as the NaOH method but the NaOH method has been used historically.

As an example, Wen & Recknagel (2006) looked at using a method designed by Hieltjes and Lijklema, and consisted of five different fractionations of the soil phosphorus similar to the Table 2. Specific to the wetland used in the study, the fractioning of the phosphorus in the soil led to several key conclusions. The control area

was a hillside near the wetland. 1) The TP (NaOH extraction) was high in the topsoil for the wetlands that had originally been used for agricultural purposes. 2) The P held to the Fe and Al (NaOH extraction) was sensitive to the redox potential of the soil. The Fe and Al bound phosphorus can re-release into the water depending on either the pH or anaerobic conditions. The result was 62% of the TP for the soil in the wetland. 3) The residual phosphorus (Res -P) was the resistant organic P and was a calculated value. 4) The bioavailable phosphorus (bio-P), referred to in the literature, as the loosely held P was less than 0.8%. 5) The organic phosphorus (org-P) or HFAP is determined by subtraction from two different digestions: NaOH for TP and another NaOH extraction for the Fe and Al held P.

<b>Fractional Component of Phosphorus</b>	<b>Quick Summary of the Methods Used to Convert all Phosphorus to Orthophosphates for Measurement using the Molybdate Blue Method for determining Concentration in mg P/kg soil</b>
<b>TSSP</b>	There are two methods used: NaOH for 18 hours, or nitric/perchloric acid digestion.
<b>HFAP</b>	<b>Loosely held organic P</b> – extraction is with NaCO <sub>3</sub> . At this point, the microbial biomass can be determined by chloroform fumigation. <b>Moderately held organic P</b> – extraction is with HCl and NaOH. This will separate the humic and fulvic acid components. <b>Resistantly held organic P</b> – extraction is NaOH and H <sub>2</sub> SO <sub>4</sub>
<b>SRPS</b>	<b>Loosely sorbed P</b> – extraction is with either NH <sub>4</sub> Cl or KCl <b>Ca and Mg sorbed P</b> – extraction is with HCL <b>Al sorbed P</b> – extraction is either with NaOH, or NH <sub>4</sub> F <b>Fe sorbed P</b> – extraction is with NaOH <b>Reductant soluble P</b> – extraction is with SCDB The alternative method for determining Ca, Fe, and Al bound P is the NaOH – EDTA test
<b>PPS</b>	PPS = TSSP-HFAP-SRPS

Table 2: Quick summary of methods used to determine phosphorus in wetland soil.

The biogeochemical cycle means that the biological activity on the surface of the wetland will impact the removal of phosphorus in subtle ways. As examples: 1) when determining the importance of the macrophytes in the phosphorus removal and fractionalization in the soil, the plants promote the removal of P by enhancing the capacity of P adsorption of the sediment. 2) The plankton algae increases the pH of the water and 3) if the major mechanism for the removal of P is with the Ca cation, the capacity of sediment P adsorption decreases (Kadlec & Wallace, 2009).

The Everglades Nutrient Removal Project (ENRP) looked closely at the different fractionations of phosphorus in the wetlands soil. The different phosphorus fractions in the vertical profile of the soil were evaluated. In the ENRP wetland most of the phosphorus, both organic and inorganic forms, was biologically not available phosphorus. At the soil surface including the first 10 cm into the soil, the following measurements were taken: SRPS was 30% of the TSSP, HFAP was 35% of the TSSP, and PPS was 32% of the TSSP. Closer evaluation of these new sediments (low-density flocs) shows that there was little of the loosely held P, Fe and Al phosphorus precipitates. The largest percentage of P in the SRPS on the top layer of the wetland was calcium bound phosphorus and organic P (Kadlec, 2006).

There is ongoing research as to the amount of phosphine gas in the soil and sediments of constructed wetlands. The gaseous forms are phosphine ( $\text{PH}_3$ ) and diphosphine ( $\text{P}_2\text{H}_4$ ) are found in wetland soils with very low-redox potential

The phosphorus in soil occurs primarily in the +5 valency state, because all lower oxidation states are thermodynamically unstable and readily oxidize back to the  $\text{PO}_4$  ion even if the soil environment is reduced (Vymazal, 2007).

Humic/Fulvic Acid Phosphorus: Humic substances are a heterogeneous mixture of naturally occurring organic materials that arise from the decay of plant and animal residues, and the fulvic substances are humic substances of lower molecular weights. HFAP fraction includes all organic phosphorus in the top layer of the soil.

A complicated three-step digestion, separates out the loosely held organic P, the moderately held organic P, and the resistantly held organic P. As with the other soil digestions, these need to be performed in series. The loosely held P is extracted with  $\text{NaHCO}_3$ ; it is worth noting the first digestion is a 16-hour process. If required, some of the residual can be used to determine the amount of microbial biomass with a chloroform fumigation procedure. The second digestion is to remove the moderately held organic P with HCl and is much shorter at only 3 hours for the digestion. To further separate the fulvic acid organic P from the humus acid organic P, a portion of the sample needs to be acidified to a pH of 0.2. In the highly acidic solution, the humic acid will precipitate out and the fulvic acids will stay in solution (Zhang & Kovar, 2000). Finally, the third digestion is to determine the concentration of the resistantly held organic P with NaOH. The residue is ashed and dissolved in  $\text{H}_2\text{SO}_4$  before measurement. As the case with all other phosphorus determinations, the orthophosphate concentration is determined with the molybdate blue method. The HFAP is equal to the addition of all three of these organic P digestions (Zhang & Kovar, 2000; Sharpley & Smith, 1985).

While a large percentage of the phosphorus in soils and sediments is present in the organic fraction and typically consists of easily decomposable organic phosphorus such as nucleic acids and phospholipids, and slowly decomposable substances such as inositol phosphates and phytin, the (HFAP) does not provide the full description of the organic phosphorus at the soil surface. There are other considerations and Kadlec & Wallace (2009) clearly state “the importance of knowing the bioavailability of the organic phosphorus in decreasing order: microbial biomass phosphorus, labile organic phosphorus, fulvic acid-bound phosphorus, humic-acid bound phosphorus, and residual organic phosphorus.” The conclusion is that organic phosphorus is immobilized in the soils and only a small percentage of it is bioavailable, the major portion of the organic phosphorus is stabilized in the soil environment (Kadlec & Wallace, 2009).

The organic phosphorus concentrations in the upper most layers of the soil can be as much as 1000 to 2000 mg P/kg of soil. There are often times a vertical profile with diminishing concentrations of the organic phosphorus at the lower depths beyond the 20 cm where plant roots can extract phosphorus from the soil and porewater or add more phosphorus to the system with the decay of the plant roots (Kadlec & Wallace, 2009). The importance of the organic phosphorus to the accretion of new soils and sediments is a common thread throughout the research, but it is also worth pointing out that the organic matter in the wetland can be a major source of clogging for HSSF and VF wetlands.

If the wetland design, typically HSSF or VF systems dries out the surface of the wetland and the wastewater is intermittently applied to wetland site, the organic

phosphorus on the top of the surface will be oxidized and the mineralized phosphorus can become soluble again upon rewetting (Kadlec & Wallace, 2009). The sorption and desorption of phosphorus on the substrate surface is still under review; other researchers suggest that the mineralized phosphorus provides additional sites for sorption of phosphorus to the wetlands, extending the sorptive lifetime of the wetland.

Soluble Reactive Phosphorus in Soil: The Soluble Reactive Phosphorus in Soil (SRPS) is bound to the aluminum, iron, calcium, magnesium within the soil particles. The loosely bound labile phosphorus is on the soil surface and still available for reaction at the soil-water interface. The importance of the metal salts and precipitates with phosphorus in CWS are an important consideration that needs to be taken into account when evaluating a constructed wetland.

The SRPS the total of of five different acid digestions done in sequence, as step functions. These digestions are performed in a serial format. The first digestion is with either  $\text{NH}_4\text{Cl}$  or  $\text{KCl}$  to remove the loosely held inorganic P from the soil. The rest of the residual is used to separate the Al-P from the Fe-P with  $\text{NH}_4\text{F}$  and then the Fe-P is removed with  $\text{NaOH}$ . Removing the Fe -P is a 17 hour process. The fourth extraction is for the non-reductant-soluble P is removed with sodium citrate dithionite bicarbonate (SCDB) at  $100^\circ\text{C}$ . The Ca-P and Mg-P is finally extracted with  $\text{HCL}$  or  $\text{H}_2\text{SO}_4$ . Because these extractions are done in series, it is important to begin the sampling with amply amounts of soil. The final concentrations of each digestion can be tested for orthophosphate with the molybdate blue method. Another important point is if the soil has a lot of  $\text{CaCO}_3$ , the recommendation is not use  $\text{NH}_4\text{F}$  to separate out the Al and Fe

and rather just perform the NaOH digestion to determine the Al and Fe held phosphorus together (Zhang & Kovar, 2000; Bender & Wood, 2000; Moore & Coale, 2000; Borovec et al., 2010). It is worth pointing out that there is no discussion of the reductant soluble P specifically in the literature studies, except for Borovec et al. (2010) who points out P bound to Fe hydroxides and compounds is sensitive to the redox potential of the system; this includes P bound to organic compounds that are sorbed onto Fe hydroxides. The digestion protocol requires that it be accounted for in this manner, but in wetlands studies this is often referred to organic phosphorus Fe precipitates. As seen from the digestion process, the phosphorus in these fractions, while some is readily available, the concept of soluble reactive phosphorus in soils is a misnomer. The digestions require the dissolution of the mineral precipitates such as apatite and struvite in order to release all of the phosphorus from these minerals. The SRPS is the addition of all five of the different digestions: loosely held P + Al -P + Fe -P + reductant P + Ca/Mg -P.

The other method referenced for determining the amount of phosphorus attached to polyvalent metal ions is the NaOH – EDTA digestion, often used in the activated sludge technology. Lowen et al. (2000) and Turner & Newman (2005) both recommend this method of determination for wetlands science. The EDTA, ethylene diamine tetraacetate reacts directly with the metal ions and the soluble P is digested to determine the orthophosphate concentration.

The loosely held P is the most bioavailable and is for the most part a small percentage (0.8%) of the overall phosphorus held in the soil (Wen & Recknagel, 2006). The loosely bound P was extracted by  $\text{NH}_4\text{Cl}$  solution. The  $\text{NH}_4\text{Cl}$  digestion is

commonly used but there is a preference to use KCL solutions because then the same extract is used to determine the amount of  $\text{NH}_4$  in the soil co-currently. (Vymazal, 2007; Zhang & Kovar, 2000; Moore & Coale, 2000)

Another chemical used for digestion is  $\text{MgCl}_2$  by Borovec et al. (2010) for loosely held inorganic P. The  $\text{Mg}_2\text{Cl}$  digests the extracellular polymeric substances (EPS) of which loosely held P is a major component. The study looked at the amount of phosphorus in the cyanobacterial mat (CBM) at the bottom of the wetland. A very detailed study looked at the CBM through the depth profile. There are several interesting results: 1) The  $\text{Mg}_2\text{Cl}$  was used instead of KCl because of the nature of the CBM, it is predominately organic and 96% water. 2) The loosely held P contained other inorganic and organic components. 3) There was a nighttime release of the loosely held P at night by the upper CBM layers. 4) There is no universally accepted method for extraction P from the EPS. 5) There were large amounts of loosely P phosphorus available (average 58% of TDP in the CBM) and 6) EPS appear to bind significant amounts of P at the soil-water surface.

Sherwood & Quall (2001) looked closely at the ferric chloride precipitate with phosphorus as a possible long-term removal mechanism for the wetlands in the Everglades, Florida. Using the  $\text{NaHCO}_3$  extraction method, by use of phosphorus isotopes it was determined that the Fe -P settled in the top 0.5 cm depth of the wetland. The acid digestion also included the addition of oxalic acid to improve the removal of the Fe from the soil particles. The study also showed the translocation of P from the lower depths of the soil profile back up to the surface of the wetland; the theory behind the

movement of phosphorus is twofold, the mass flow of low-density colloidal precipitates and the release of P in the lower depths as dissolved phosphorus that moves to the surface. The primary focus of the research was to determine if the Fe-P precipitates are stable enough for ferric chloride to be considered for permanent burial of the P in the wetland soils.

The biogeochemistry of the wetland keeps the metal- phosphorus complexes in continual flux, the metal - phosphorus salts and precipitates all respond differently to changes in the redox environment. As pointed out by Kadlec & Wallace (2009), the Fe-P will respond to lower redox changes by re-releasing the phosphorus but the calcium-P will not release the P under lower the redox conditions. While the Fe-P complexes are sensitive to changes in redox, the Ca-P complexes are sensitive to changes in the phosphorus concentration of the influent wastewater. Any desorbable phosphorus is the re-release of the P from the more loosely bound Ca-P precipitates. The soil-water equilibrium is reestablished if a lower influent concentration of P enters the system. The test procedure used wetland soil cores and exposed them to water with zero phosphorus. The phosphorus leached out of the soil to reestablish the equilibrium. Some studies show that 15 % of the sorbed phosphorus is re-released and other indications are that the system can give back as much as 1 year of the phosphorus stored in the soil (Kadlec & Wallace, 2009).

Particulate Phosphorus in Soil: As with the Particulate Phosphorus (PP) in the water column (PPW), the Particulate Phosphorus in Soil (PPS) is made up of phosphorus particles attached to the TSS, organic matter and mineralized solids, which have settled to

the top of the soil surface. The PPS will contain organic phosphorus complexes and metal salt – phosphorus complexes but needs to be taken into account because while the PPS is in the soil it is still cycling through different phosphorus configurations as it becomes a part of the soil matrix long term. The PPS will also contain the residual phosphorus in the wetland soils that are not digestible by the different acid fractionations; often referred to in the literature as the non-reactive phosphorus (NRP). Because the metal-salt complexes in the soil are a part of the Soluble Reactive Phosphorus in the Soils (SRPS), and the organic phosphorus is in the Humic/Fulvic Acid Phosphorus (HFAP), the PPS fraction will only contain the residual phosphorus and is calculated determination:  $TP - SRPS - HFAP = PPS$  (Wen & Recknagel, 2006).

There is ongoing research to understand the role of PPS in the accretion of new soils in FWS wetlands. Kadlec & Wallace (2009) point out that, while an important phosphorus removal mechanism, it will depend heavily on the hydrology of the system and the composition of the soil. The understanding of the PPS floc layer, which is on the surface of the wetland, still loose and mobile is still an active area of research. The floc is referred to as “grey gelatinous material” and is easily disturbed with water movement, the thickness can be as much as 20 to 30 cm, and with further decomposition, the re-release of phosphorus is possible (Kadlec & Wallace, 2009). As with the WWTP facilities and the removal of phosphorus with particulates, the same holds true for wetlands, the mineral PP that falls to the bottom of the wetlands form a major portion of the overall phosphorus removal in the system.

There is one consideration that is still under review in soil science phosphorus studies: polyphosphates, mostly commonly pyrophosphates, are detected in the TSSP and based on the fractional determinations, they are incorporated into the PPS fraction (Turner & Newman, 2005). The polyphosphates are decomposed in the soil but the mechanisms are not fully characterized but what is known is that type of soil in the wetland plays an important role. In the silty-loam soils less of the polyphosphates were completely hydrolyzed when compared to sandy soils. The polyphosphates are considered non-reactive for the most part. As Turner & Newman (2005) states, "emphasis should be placed in identifying the unextractable fraction of soil P, which is critical for understanding the long-term P sequestration in wetland soils."

#### Soil Stored Phosphorus

The phosphorus that is stored in the soil in long-term permanent storage is the Soil Stored Phosphorus (SSP) and no longer available for further reactions or phosphorus cycling. It is important to point out SSP is less likely to happen with HSSF and VF wetlands and typically is in reference to FWS wetlands. Measurement is at soil depths beyond the root zone of the plants i.e. 20 cm. The key parameter for the final storage of phosphorus in the wetland is a system that is stable relative to the influent phosphorus concentrations, a stable water chemistry environment and a redox system that does not change. Providing stability for the metal-salt phosphates minimizes the re-release of phosphorus, and allows the accretion of the soils to steadily remove phosphorus from the organic matter without a major pulse of phosphorus to the wetlands system water. The amount buried is very dependent on all the overall biogeochemical processes and the soil

composition in the wetland; the values can range from 0.18 g P/m<sup>2</sup>·year to 13.7 g P/m<sup>2</sup>·year. The highest value is at the Houghton Lake, Michigan wetland where accretion of new soils is also higher than most wetlands (Kadlec & Wallace, 2009). Houghton Lake wetland system is reviewed in more detail through the paper but much of the research proving that accretion of new soils is the primary removal mechanism was done at the Houghton Lake wetland site.

Often predicted, the amount of phosphorus reaching the burial stage or deep sediments of the FWS wetlands is 50% of the phosphorus in the root zone of the wetland (Kadlec & Wallace, 2009). Measuring the amount of phosphorus in the SSP is looking at the TP at different depths of the wetland soils and sediments and not evaluating the different fractions of phosphorus. The TP is determined with either the NaOH digestion for as long as 17 hours or the double acid digestion of sulfuric and persulfate. The soil was tested at different depths for the Everglades Nutrient Removal Project (ENRP) at different depths. The evaluation of the buried phosphorus was in-depth and did quantify the different fractions of phosphorus along the different depths. The key results showed that the TSSP was 427 mg P/kg soil; and dropped to 193 mg P/kg soil at a depth of 30 cm into the soil. Almost 50% percentage of the SSP at this depth HFAP – the organic phosphorus in the soils and 36% was the PPS or residual phosphorus (Kadlec, 2009b).

As an example when evaluating the SSP along a vertical profile, one of the relationships looked at, is the change in carbon and phosphorus concentrations because if they are both decreasing along the same trend line that indicates that the phosphorus being buried was organic in nature (Kadlec & Wallace, 2009).

The ongoing research of evaluating soil sequestration of phosphorus has shown that polyphosphates do not reside in the deep sediments; it is in the TSSP but decomposes before it reaches the final burial. The actual origin of the polyphosphates, the function in the soil and the decomposition processes are not well understood (Turner & Newman, 2005). Within the soil matrix both the SSP and the TSSP, there are polyphosphate concentrations that are not reactive, extracting the polyphosphate fraction from the soil requires yet a different acid digestion, most often a long, boiling hot extraction with a combination of nitric and sulfuric acid. The importance cannot be underestimated because as much as 25% of nitrogen - phosphorus - potassium (NPK) fertilizers is made up of polyphosphates (Torres - Dorante et al., 2005).

#### Phosphorus Removal Mechanisms

Phosphorus removal from wastewater is accomplished by several different mechanisms in the wetlands. They are complex processes that are dependent on many different characteristics of the wastewater stream and the surrounding environment. In the past few years, a major focus of research evaluate the different mechanisms are for both long and short-term removal efficiencies.

The literature supports the importance of determining how much phosphorus is removed from each of these mechanisms, quantifying the overall mass balance of the phosphorus system and being able to predict the outcome of constructed wetlands effluent waters at the design stage. The key phosphorus removal mechanisms are accretion/sedimentation of new soils, sorption/desorption, biological/microbial removal,

mineralization, fragmentation, leaching, chemical precipitation and final burial (Vymazal, 2007). These different mechanisms are referred to as saturable if there is a limited capacity (i.e. sorption and biological) and sustainable if there is no capacity limits (i.e. accretion). The secondary processes referred to in the literature are particulate setting and movement/reconfiguration between different storage compartments (Kadlec & Wallace, 2009). It is important to note and the literature confirms, these phosphorus removal mechanisms are happening simultaneously and there are interactions. For example, the accretion of the new soils is due to biomass decay; sorption of phosphorus onto the existing soils is dependent on the chemical reactions and the concentrations of the metal ions in the soils. The combination and interactions between processes is referred to in the literature as biogeochemical cycling (Kadlec, 2006).

Other considerations, such as pH, temperature, and alkalinity of the system will influence each of these removal mechanisms. Yousefi, Jowhari & Nasiri (2010), clearly state the challenges faced with the research of all removal mechanisms in wetlands, constructed and natural.

Radioisotope P studies have shown that 10 to 20% of P is controlled by the biotic uptake initially. Inorganic phosphorus transformations, subsequent complexes and P retention in wetland soils and sediments are controlled by the interaction of redox potential, pH values, Fe, Al, Ca minerals organometallic complexes, organic matter content, clay minerals, hydraulic loading, and the amount of native soil P. (p. 1592)

Of minor consideration is the role of animals and birds in the wetland environments.

Some research shows large enough muskrat populations will “eatout” the majority of the standing crop during the unfrozen season, essentially accomplishing the same percentage of phosphorus removal as plant harvesting would accomplish. Birds on the other hand

add phosphorus to the wetland; based on the population of the birds and directly related to the amount of fecal matter of which 2% is phosphorus. Essentially large flocks of birds will affect the performance of the constructed wetland if ultra-low phosphorus concentrations are required (Kadlec & Wallace, 2009). Very few studies in the literature search mentioned this; however, the floating islands technology BioHaven mat has been used for attracting birds and fowl and could prove to be counterproductive if phosphorus removal is required for the wetlands system.

Matos et al. (2010a), concludes that as much as 97% of TP removed is by physical mechanisms, 2.1 % by microbial activity and as little as 0.3% by extraction of phosphorus from plants. The physical mechanisms account for the chemical processes if there are cations available or the shorter-term mechanism of sorption to the sediment soils. Kadlec & Wallace (2009) point out many times, the periods of initial adaptation for a CWS can take years to reach steady state. The process responses to additional changes in the wetland environment require adaptation, often times slow, approximately 1 to 2 years.

### Accretion

The most important removal mechanism for phosphorus in natural and constructed wetland systems is accretion but the least studied and is the creation of new soils and sediments from the partial decomposition of plants, algae and microbial organisms but not all of it decomposes and some form new stable accretions (Kadlec & Wallace, 2009). Accretion is most effective for wetlands with high biomass production, when the substrate is always covered with water, specifically free water surface (FWS)

wetlands (Olsson et al., 2010). Vymazal (2007) points out that accretion occurs only in free water surface (FWS) wetlands and emergent plants are required. With burial of plant residuals, 10 –30 % of the phosphorus is permanently stored. Of the percentage in the accreted soils, 50% is from the above water line plants, 15% is from the below plant parts and 35% is from algae and microbial activity.

The soil in the wetland will play an important role in determining the actual amount of phosphorus that is permanently buried in the sediments as well as the influent concentrations. The actual burial percentages are also dependent on climate and there is less plant decay and burial in tropical climates. It is also important to note that the burial of phosphorus happens in cold climates during the unfrozen season of the wetland. P concentrations in the wetland soils will show a 10-fold range from 200 mg P/kg soil to 2000 mg P/kg soil around the world equating to a range of 0.01 – 20 gm P/m<sup>2</sup>·year. The accreted fraction is in the range of 0.05 to 0.5% DW of the biomass in the form of new soils. (Kadlec, 2006; Kadlec & Wallace, 2009). Determining accretion values in cm/yr of new sediments and the amount of phosphorus buried is difficult and often times estimated by mass balance calculations. “Once the system is in a steady-state the net uptake of phosphorus that is buried as recalcitrant residual phosphorus is a very small fraction of the gross uptake” (Kadlec & Wallace, 2009, p. 363). The net uptake is on average 13% (Kadlec & Wallace, 2009). We have seen in the literature, accretion values, as high as 7 cm/year but typically the numbers are less.

Bays & Jordahl (2010) did a survey of many different types of construct wetlands for agricultural runoff and found Integrated Constructed Wetlands (ICW) in Ireland had

new soil sediments as high as the 7 cm/year and the sediment deposited annually between 4 and 12 % of the Irish farms surveyed annual phosphorus requirement. In Houghton Lake, Michigan, the accretion is estimated at 2 cm/year and the phosphorus burial is 2 gm P/m<sup>2</sup> year. Other studies have looked at the sedimentation rates but are also concerned with the re-release of the phosphorus as the nutrients cycle in and out of the soils. New sediments are formed but the phosphorus is not permanently buried in the sediment. With the new sediments, the soil environment can be divided into active and inactive compartments or deep sediments (Kadlec & Wallace, 2009). The sedimentation also needs to be monitored in CWS because it can result in reduction of bed porosity, cause hydraulic problems and lead to overland flow situations. One of the chemical elements that need to be considered carefully is calcium. If the soil or wetlands are iron deficient, the calcium biogeochemical processes are dominant. The sediments in these environmental conditions will be calcium carbonate rich and often called calcitic mud or marl. The Everglades in South Florida are a wetlands system that contains extensive areas of Ca –P precipitation. These materials are dense, low in organic and typically low in phosphorus content (Kadlec & Wallace, 2009). Three different models for determining the amount of phosphorus in the sediment layers of the constructed wetlands are reviewed.

Accretion will change the flow patterns of the wetland over time in all types of constructed wetlands (Kadlec, 2006). Sediment accretion in the front- end of the wetlands caused hydraulic problems during parts of the year for a wetland in Orlando Florida. After 15 years of operation, the sediment was dredged and TP removal again met

regulatory requirements. The new soils will not be uniformly distributed and hydraulics will probably be impaired before the TP concentrations are no longer within the permit values. As has been pointed out the accretion of soils is less sustainable for HSSF and VF systems, not only from a process point of view but because the oxidation of the soil and re-release of the phosphorus. There is a decrease in hydraulic conductivity and loss of porosity in these types of wetlands because of the solids deposition on the substrate media.

There is ongoing research as to the amount of phosphine gas in the soil and sediments of constructed wetlands. The gaseous forms are phosphine ( $\text{PH}_3$ ) and diphosphine ( $\text{P}_2\text{H}_4$ ) are found in wetland soils with very low-redox potential, and are often emitted from the soil alongside methane gas. There has been  $\text{PH}_3$  found in the wet sediments of the Everglades and as the amount of P in the soil increased so does the concentration of the phosphine gas. Most of the phosphine is matrix bound in the soil even though it is water-soluble, it can also be found in rice-paddy soil (Kadlec & Wallace, 2009).

As stated earlier, removal of phosphorus by accretion requires the constructed wetland to be covered in water all year; however, it is not always possible for wetlands used for stormwater (STA) events such as the Everglades Nutrient Removal Project (ENRP). As the water draws down, oxygen reaches the soil and there will be a rearrangement of the phosphorus in the soil. The dry-out will decrease the overall sorption capacity of the soil and the phosphorus in the accreted flocs will be mineralized. When re-flooded the mineralized inorganic phosphorus is re-released to the water as the

case with the ENRP wetlands, the phosphorus concentrations in the water spiked after a flood event for the STA systems. If the wetland is completely dried out and the soils are “burned” even the organic phosphorus will be mineralized and then solubilized when the wetland is re-wetted. If all of the new soils and accretions are compromised, it is termed, “hydrologic burnout” and no further net phosphorus accumulation will occur. The recommendation for accretion of new soils to permanently remove phosphorus from the wastewater is that the wetland system be continually under water (Kadlec, 2006).

Matos, Freitas & Lo Monaco (2010a) looked at the removal mechanisms of phosphorus in CWS for swine waste in Brazil. There were 4 planted CWS and 1 unplanted CWS for control. The plants used were cattails, tifton 85 grass, and alligator grass. The hydraulic retention time in the systems was 4.8 days and at a flow rate of 0.8 m<sup>3</sup>/day. The prefilter was chopped sugarcane stalks. The total phosphorus (TP) removal efficiency was between 30 and 55 % for all 5 CWS. One of the conclusions Matos et al. (2010a) concluded is that the plant uptake of P did not have a major impact on the removal of the phosphorus. The primary removal mechanism was accumulation of organic phosphorus and due to its immobilization by microorganisms in the sediment. Matos et al. (2010a) quotes CY Lee from Taiwan who observed 97.3% of TP is purely by physical mechanisms, 2.1% by microbiological mechanisms and only 0.3% by extraction from plants.

Mechanistic Model for Determining Phosphorus Removal: This paper presents a model that looks at the removal of phosphorus removal from detritus accumulation in wetland environment.

The model by Hafner & Jewell (2006) is included because of its approach to identifying the key parameters to predicting the phosphorus removal in constructed wetlands. Given the premise that the most important phosphorus removal mechanism in wetlands is detritus accumulation, the P removal can be predicted by determining the storage of P in the refractory detritus. The model assumes that the P uptake is from the biotic processes of removing P from the influent wastewater and not the sediments. The key premise is that the detritus accumulations in the wetlands are defined by the rate at which they are broken down by the decomposer organisms. Other models reviewed did not take into account the role of the decomposer organisms. The decomposer parameters have been determined in aerobic and anaerobic wastewater treatment systems. Six parameters are required model for determining the P retention rate: 1) NPP, the net primary productivity of the organic matter. Estimates of wetland NPP are available for wetlands and include the production of all plant material with numerical values in the range of 5000 g/m<sup>2</sup>·year. 2)  $f_1$ , a fractional unit that is the mass of the decomposer organic matter per unit of algae biomass is in the range of 0.5 g decomposer/g biomass. 3)  $f_{pd}$ , phosphorus concentration of the decomposer biomass with values in the range of 0.02 g P/g biomass. 4)  $f_{po}$ , the initial phosphorus concentration of plant or algae biomass in the range of 0.005 to 0.02 g P/g biomass. 5)  $f_2$ , the fraction of decomposer organic matter that is refractory; a typical value is 0.2 g decomposer/g biomass. 6)  $f_3$ , the fraction of plant or algae biomass that is refractory. While  $f_3$  has variability within a wetland systems and it is often set at 0.5 g/g. Testing the model with data from a nutrient film technique (NFT) the results were measured in g P/m<sup>2</sup> day and were quite good when compared to the

observed results. The plants grown at the study site in Ithaca, New York reach steady state for 52 months before the measurements were taken. The model has limitations that are not accounted for, pH and temperature variations, and other environmental conditions where decomposition is inhibited.

Sedimentation Rates: The cycling of the nutrients in and out of the sediment is also an important consideration. It is important to know both the rate of sedimentation and the rate of re-release back into the wetland waters.

A study on the equilibrium of the phosphorus in the wetland, Ahn, Choi & Oh (2010) investigated the sedimentation rate of a pollutant to better understand the moving characteristics of the pollutant at the Shingal Reservoir in Korea. The Sediment Oxygen Demand (SOD) was also estimated as the removal of the pollutant from the sediment. The sedimentation rate was calculated by:

$$SR = C \times M / (A \times T)$$

where: SR = sedimentation rate ( $\text{g}/\text{m}^2 \cdot \text{day}$ )  
 C = concentration of pollutants ( $\text{g}/\text{kg}$ )  
 M = sedimentation mass ( $\text{kg}$ )  
 A = sedimentation area ( $\text{m}^2$ )  
 T = time (day)

Using the model, Ahn et al. (2010) showed that the sedimentation rate (SR) of TP was significantly higher for shallow water sites when compared to deep-water sites, 2.47  $\text{g}/\text{m}^2 \cdot \text{day}$  and 0.457  $\text{g}/\text{m}^2 \cdot \text{day}$  respectively. The second measurements taken were to determine the release rate of the contaminants from the sediment because the degradation of the organic matter in the sediment relates directly to the eutrophication of the waters by the nutrients, of which phosphorus is one. The re-release rate of the nutrients will vary

with the Dissolved Oxygen (DO) and pH of the sediment. There were two findings worth noting: there is a correlation between pH and release of phosphorus. The lower the pH of the soil, the more phosphorus released for most of the soil sites and more importantly, there is a strong correlation between the amount of DO in the soil and the release of phosphorus. The phosphate release increased to a maximum once the conditions were anaerobic (low DO) and the release rate of phosphorous is greater than the sedimentation rate of new soils.

Wetland Ecosystem Model: Constructed wetlands are dynamic ecosystems and this paper evaluates the removal of phosphorus by looking at four different submodels: hydrology of the wetland, the primary productivity of the biological processes, sediment submodel, and the phosphorus submodel.

Wang & Mitsch (2000) looked at the phosphorus cycling in wetlands and modeled this using three years of data from four different wetlands in Illinois, USA. This detailed model used four submodels to fully simulate the system: hydrology of the wetland, primary productivity of all biological activity (phytoplankton, macrophytes and periphyton), sediment accumulation and phosphorus concentration. The primary purpose was to develop an ecosystem model that explored the various components of the wetland to phosphorus retention and integrated the data to predict the sediment and phosphorus retention under different hydrologic conditions as a whole system.

The hydrology submodel was the simplest of the four sub models and looked at the overall water balance of the system: inflows, outflows, evapotranspiration, precipitation and seepage. The water volume of the four wetlands ranged between 7750

$\text{m}^3$  and  $19,250 \text{ m}^3$ . The key conclusion when correlated to the other submodels was that TP retention is linearly related to the inflows into the wetland by the equation:  $\text{TP} = 90.997 - 0.274 \times \text{inflow}$ .

The primary production submodel looked at the biological activity in the wetlands by measuring the gross primary productivity (GPP) in the water columns for the phytoplankton and periphyton and the macrophyte production using aerial photography and biomass data. A few important points were confirmed with the modeling simulations. “The macrophytes overwhelmingly depend on the soil in the wetland for their phosphorus uptake instead of the phosphorus in the water” (Wang & Mitsch, 2000, p. 121). The dead plant litter re-release of phosphorus annually in the late fall and early spring creates an environment that should be designed for by eliminating outflows of the water in late fall and early spring. The standing dead detritus (SDD) was defined as plants that are no longer living but have not fallen into the water. The SDD is at its highest in October and lowest in August of each year. It is important to note that they provide a substrate for the periphyton and biofilms in the system. Harvesting the macrophytes impacts the phosphorus removal in two different ways: 1) it removes the phosphorus from the system in the actual plants themselves and just as importantly, 2) it reduces the phosphorus in the upper level sediments and drives the phosphorus movement deeper into the soil (root zone) and creates a higher phosphorus sorption capacity and lower phosphorus desorption. With respect to the algae, the TP removed was directly proportional to the net growth of the biomass at a rate of  $0.8 \text{ g P/g DW}$  of algae. The use of phosphorus by plankton and periphyton was around 14% of the TP in the influent.

The sediments submodel was important because it looked at the five different components that affect overall phosphorus cycling in the wetland. The parameters evaluated were the standing dead detritus (SDD), the bottom detritus (BD), the active sediment layer (AS), the deep sediments (DS) and suspended solids (SS), all of which will have phosphorus in them. For the SDD 80 -90 % of the SDD will fall to the wetland bottom surface annually. The BD is the organic matter that is decomposing at the bottom of the wetland and will either be lost because of respiration and assimilation of OM by microorganisms or the fragmentation of the OM into small particles and then incorporated in the AS. The BD accumulates during the winter months and decomposes the following summer. For the purposes of this model the AS, was defined as the layer of sediment 4 cm deep and there was the assumption that no decomposition of OM takes place in the deep sediments (DS). The SS in the water column included the sediments from the inflow and the outflow. The submodel clearly showed that the new soils, for these four wetlands, were between 6 and 2.9 cm/year. Looking at both the autochthonous and allochthonous sediments (indigenous and transported sediments from other locations), the allochthonous suspended sediments contributed to over 58 % of the total sediments for fast or high flowing wetlands and autochthonous suspended sediments and OM contributed the most to the new sediments of low-flow wetlands. Overall, high flow wetlands have higher sediment accumulation rates.

The phosphorus submodel combined all of the parameters of the other three models and looked closely at where the TP came from and where it ultimately resided. The parameters used were total phosphorus bottom detritus (TPBD), total phosphorus

active sediment (TPAS), and total phosphorus deep sediment (TPDS). The nomenclature in for this model is different from the nomenclature used in other literature studies and the section on phosphorus partitioning but it is apparent that goal is the same: to determine the amount of phosphorus in the wetlands soil that is available for re-release and to estimate the amount of phosphorus that is permanently buried. The initial steady state values for each of these different types of phosphorus ranged between 78 and 274 gm/L for TP in the water columns, between 1862 and 3440 grams TP/kg soil for TPBD, between  $4.47$  and  $8.26 \times 10^5$  grams TP/kg soil for TPAS and zero TP for the TPDS. The overriding amount of phosphorus is in the active sediment layer (AS) by orders of magnitude.

For the purpose of the submodel, the sedimentation rate constant was the same one used in the sediment submodel at a value accepted by the industry at  $5.5 \times 10^{-5}$ /week. The model confirmed that the decomposition of the OM at the BD and AS layers re-releases phosphorus into the water column. The decay is a rapid process and over 50% is re-released within 12 days for these systems. The TP in the BD layer and AS layers reach an equilibrium. The AS layer is a short-term storage place for the phosphorus and it can take weeks for the phosphorus to reach the DS and then it is available for the macrophytes to use. The model calculated that the macrophytes decreased the overall TP retention by about 5% and is referred to as the phosphorus pumping effect in the literature. There are two different mechanisms: the sediments are lifted from the bottom of the wetland and in the process re-release the phosphorus into the water and the macrophytes use the phosphorus that is in the DS of the wetland during the growing

season, cycling it back through the system. Despite these events, physical sedimentation is still the predominate mechanism for phosphorus removal in the wetland systems. By eliminating the sedimentation on the bottom of the wetlands for macrophytes and managing the flow rates such that the sedimentation is not re-released, the wetland performance will improve with respect to phosphorus removal; both of these parameters are minimized with the floating islands wetland systems. The macrophytes take the phosphorus from the water and the inflow water velocity can be controlled in the design phase of the system to ensure that suspended solids are kept to a minimum.

Houghton Lake, Michigan: First established in the late 1970s, the Houghton Lake wetland is a 700 ha constructed wetland, often referred to as Porter Ranch, and has been monitored for over 40 years. Of the 700 ha, 100 ha of irrigated areas has been used historically for nutrient removal. There is no physical boundary between the two areas; the regulatory requirements are for the system as a whole and the hydraulic studies have included 400 ha during the different study times because of water overflow caused by beaver dams and remnant agricultural drainage. It is worth noting that after 30 years of operation, the system is not saturated as predicted, and continues to successfully remove phosphorus (Kadlec & Wallace, 2009; *Ecological Engineering*, 2009).

The wetland receives wastewater from the city of Houghton Lake's aerated lagoons and the effluent water from the wetland is released into the Muskegon River (Kadlec, 2009a; *Ecological Engineering*, 2009). The journal, *Ecological Engineering* devoted the entire September 2009 edition to articles discussing in detail the Houghton Lake wetland system. The primary investigator is Robert Kadlec of Wetland

Management Services in Michigan. The journal included articles on the soils and sediment, vegetation, energy balance and hydrology of the system. All of these different parameters are referenced here in the paper because they are interrelated to the primary removal mechanism of phosphorus in this system: accretion and new soils. The discussion of the natural floating mat at that Houghton Lake wetland and other natural floating mats are later. Because the wetland has been in operation and monitored extensively for so many years, there are long-term studies available; the techniques and methods for monitoring system have evolved. The modeling used for these studies is called biomachine modeling and is very similar to the dynamic model for stormwater areas (DMSTA) used in the Everglades Nutrient Removal Project (ENRP). The biomachine model leads to a kinetics Monod removal expression for phosphorus removal: first order reaction at low concentrations of phosphorus and zero order reaction at higher levels of phosphorus (Kadlec, 2009a; Kadlec, 2009c).

The Houghton Lake wetland is a natural peatland that treats over 600,000 m<sup>3</sup>/year of wastewater that is then discharged seasonally between the months of May to October. During the winter months, the water is stored in the two lagoons and a holding pond and then released gradually during the summer months. The wastewater is distributed across the width of peatland through 100-gated openings to ensure that the wastewater is spread throughout the system; defined throughout the studies as the 100 ha irrigated area. The lagoons have a phosphorus concentration in the range of 3.5 mg TP/L. The irrigated areas under close consideration have historically removed 95% of the phosphorus (53 metric tons over a thirty-year period out of a total of 56 metric tons) before discharge to the

receiving water. The effluent phosphorus concentration is in the range of 40 µg TP/L; calculated to an average of 5.41 g P/m<sup>2</sup> ·year in the influent and 0.4 g P/m<sup>2</sup> ·year in the effluent. However, it is important to note that the annual amount of phosphorus released has increased over the length of time because of increased population in the surrounding town and for the first few years of operation, the area of the wetland increased (Kadlec, 2009a).

Initially based on pre-project studies, soil sorption was thought to be the primary sink for phosphorus but long term mass balances shows that the major removal mechanism is newly created soils, and the additional soil over the extended length of operation for the wetland has allowed for measurement of the accretion of the new soils. During the first 8 years of operation, the sorption and biomass content increased because the area of the irrigated land increased but long-term accretion is the dominant storage mechanism. After a 30 year period of reporting (POR) the removal mass balances are 7.68 g P/kg of soil is from biomass; 2.91 g P/kg soil is from sorption, and 45.6 g P/kg soil is the accretion of new soils. Essentially the continued accretion of news soils because of changes to the plant community was not understood at the time of design. The ecosystem changes are more complex than expected. (Kadlec & Wallace, 2009; Kadlec, 2009) issues a word of warning that using measurements take in short-term settings is not useful for long-term forecasts of wetland behavior and performance.

Evapotranspiration of the 100 ha segment has been determined to be 3.7 mm/day during the irrigation season and has accounted for 82% of the water pumped into the system during that same period but rain added an average of 59% of back into the system.

Because there is approximately a 20% loss of water during the pumping season, there is a longer HRT and the water flow rate decreases allowing more time for reactions to occur; the evapotranspiration causes there to be an increase in evaporative concentration of the nutrients. Closely related is the temperature of the wetland system, both water and soil, because it affects the pH, dissolved oxygen, and respiration responses of the plants. During the summer, the water temperature is higher and creates a heat transfer to the soil, and during the winter, the energy is released by the soil back to the water. The soil heat release is important when considering the operation of a constructed wetland under cold conditions. Specific to the Houghton Lake wetland, the temperatures were measured to fully characterize the wetland even though it was not processing water during the winter months. The temperature of the water dictates biological processes and was challenging to measure and fully quantify because of the floating mat and water under-flow. It was pointed out that the altered thermal regime should be accounted for in design of the wetland (Kadlec, 2009c).

The plant population has changed drastically over the last 40 years. The wetland started out primary with a diverse population of different plants: sedges, willow, bog birch, leatherleaf and isolated patches of cattail. As expected, the plants near the discharge pipe had more biomass and the results showed Monod kinetics could be used to predict the amount of phosphorus removed. In the area around the effluent discharge pipes, the phosphorus concentration in the water was higher and the removal rate was determined to be zero order compared to the other areas in the center of the wetland where the removal rate is first order (Kadlec, 2009c). The primary plant, considered an

invader plant, is now cattails ( 85 ha of the 100) and by 2002 there was a floating mat mainly made up of cattails that is up to 27 ha out of the 100 ha irrigated area. The floating mat has water, around 20 cm deep below the bottom of the floating mat. The wastewater is exposed to the roots zone of the plants instead of the stem zone of the plants. Because of the changes in temperature and climate throughout the year, there is a growth and decomposition cycle of the plants; cattails have more biomass than the plants initially in the wetland, it is estimated that over 14% more of the phosphorus has been sequestered in these newer larger standing plants over the last 30 years. The change in plant species took over 9 years near the influent of the wastewater and is still occurring 30 years later at the downstream edges of the wetland. As the plant species changed to the high standing crop of cattails, the phosphorus removal was enhanced (Kadlec & Wallace, 2009; Kadlec & Bevis, 2009). The litter from all of the biota: algae, biofilms, plants and bacteria contribute the accretion and the sediments of the newly formed soils. The most important message concerning the plant ecosystem and the long-term stability of a wetland is: “No short term study (i.e. a year or two) can hope to quantify biological effects that take years to manifest” (Kadlec & Bevis, 2009, p. 1331).

The methods and equipment designed to measure the sediments and the phosphorus in the soils have evolved over time and are important to the study of new soils and sediments by accretion. The total amount of phosphorus buried in the soils over time is 2000 mg P/kg of soil and over 30 cm of sediments have been added to the bottom of the Houghton Lake wetland (Kadlec, 2009b). Determining the suspended solids in the water without disturbing the underlying soil required the design of a passive sampler that

was activated after the surrounding disturbed soil had resettled. The added complexity was the ice and floating plant mat in the wetland. Frozen water added to the device was used to help settle sediments. Soil cores were also collected throughout the wetland with large aluminum pipe and dry ice was used to freeze the peat, plant litter, and water to get an accurate core of soil. The different core and sediment samples were modeled to determine the settling rate, generation rate, and resuspension rate of each contaminate.

The evaluation of the TSS is important but not mentioned in many of the literature studies. In the wetlands system, there are algae in areas of the wetland but not in the area of the floating vegetation mat, the algae leads to an increase in the TSS. The TSS also contains polyphosphates from fertilizer and pesticide runoff. The TSS in the wetland is also a major input to the new soil sediments. The Houghton Lake wetland removed approximately 80% of the incoming TSS. Given that the new soils were approximately 2 cm/year, equating to 800 t/year of accumulated solids. A mass balance of all solids determined that the TSS contributed 382 t/year, and the remaining came from the undecomposed macrophytes and death or roots in the shallow soils.

There are several other important considerations when evaluating the Houghton Lake wetland: 1) the sediments on the top of this wetland are referred to as flocs because they are unconsolidated material when compared to the underlying soils. The floc was analyzed with the frozen soil cores and large amounts of mobile material showed the importance of both the settling and resuspension of the material in a dynamic wetland system. 2) In the pre-study and design phase, it was determined that the amount of extractable Ca was at least 5 times greater than Fe, Mg, and Al. The core samples Ca

concentrations were between 16,135 mg Ca/kg soil to 30,084 mg Ca/kg soil. Despite the minerals in the soil, it is estimated that Ca sorbs only 3% of the phosphorus. 3) The soils and sediments in the root zones of the plants were studied to determine the amount of phosphorus in the vertical stratification of the soil; the goal was to determine the amount of phosphorus in the soil from the nutrient rich root necromass and the sorption of porewater phosphorus. Evaluating this phenomenon proved that the accretion of new soils is not a simple layering as originally assumed. As shown because of the resuspension of the soils it was also determined that there is the injection of accreted roots and rhizome residuals into the different layers of the soil. 4) The accretion of new soils was caused by both the macrophyte litter and the microdetritus. 5) The resuspension of the soils was caused by a variety of different mechanisms: advective flow, suspension caused by bioturbation, gas release at the soil-water surface, and shear-induced release of the particulates. It was estimated that the distance traveled because of these phenomena was only 10 m – 100 m (Kadlec, 2009b).

### Sorption/Desorption

The sorption of phosphorus onto existing soils of a wetland is an important process for the removal of phosphorus in the wastewater. However, it is important to note that the sorptive capacity is finite and is not an instantaneous process. Sorption is thought to be two-step process:

- Phosphorus exchanges between the soil porewater and the soil particulates or mineral surfaces. Called adsorption it is the adhesion of the soluble inorganic phosphorus molecules on an extremely thin layer at the surface of the soil. The

process establishes an equilibrium between the solid phase and the P in the soil porewater (Vymazal, 2007). The rate of adsorption is on the order of minutes (Maynard et al., 2009).

- Phosphorus penetrates slowly into the solid phases of the soil. Called absorption it is the process where the phosphorus molecules become part of the soil matrix (Kadlec & Wallace, 2009). The rate of absorption is on the order of days to months to years (Maynard et al., 2009).

Sorption of the nutrients into the soil is a mass diffusion process at the molecular level and continues to occur until the soil has reached full capacity or the soil and water reach an equilibrium concentration. The mass transfer time ( $t_{MT}$ ) is defined as the time required for the sorption process to be completed and takes into account the length of the wetland that is actively sorbing the phosphorus and the flow velocity of the water.

$$L_{MT} = t_{MT} \cdot v$$

where:  $L_{MT}$  = the mass transfer zone length (m)  
 $t_{MT}$  = the mass transfer time (d)  
 $v$  = the water velocity (m/d)

As the mass transfer zone is diminished from the inlet to the outlet of the wetland, a sorption front develops and little phosphorus removal occurs. If the systems have slower sorbing bed conditions then the effluent concentrations will gradually increase as the wetlands substrate reaches saturation (Kadlec & Wallace, 2009).

The three primary components of mass transfer equilibrium for phosphorus sorption in HSSF wetlands are advection, mass transfer and accumulation in both the water and solid phases. The model analyzed the HSSF wetland and the sorption of

phosphorus until the break through occurs and the influent and effluent phosphorus concentrations are the same. In actual field applications, the phosphorus concentration is not zero at the exit and other processes influence the sorptive capacity of the wetland, including plant uptake, biocycling processes, and the mineralization of some sites will free those sorptive sites for re-sorption, and biological solids on the substrate surface (Kadlec & Wallace, 2009).

There are several other considerations taken into account when determining the sorptive capacity of substrate and if an additional aggregate will be effective. Phosphorus sorption is an endothermic reaction requiring heat and colder water temperatures will decrease the sorptive capacity of the bed aggregate. The historical mineralogy of the aggregate also strongly influences the surface chemistry and the possible reactions over time. Phosphorus removal requires the aggregate size to be small enough to provide the largest number of sites per unit volume but cannot be too small as to cause a hydraulic failure; often times of greater concern for HSSF wetlands because of the water flow requirements. Often times the sorptive capacity is over-estimated and it is recommended that a 50% reduction be used during the design phase of the constructed wetland. Long-term study results are better than the short-term batch tests that are often used to determine aggregates and substrates. In the field, only a small percentage of the theoretical maximum sorptive sites are utilized. When designing a wetlands system if sorption is the primary removal mechanism for phosphorus removal, the system will require refurbishing periodically and the size of the wetland is dictated by the specific sorptive capacity of the selected substrate materials. Phosphorus is in many forms,

organic, particulate and inorganic, and all have different rates degrees of sorption (Kadlec & Wallace, 2009).

Kadlec & Wallace (2009) reference over 40 FWS and natural wetlands and show that the “median time to saturation is about one year” (p 388). The sorptive process will reach saturation and stabilize but is still an active process with an exchange of ions at the water soil surface. It is important to note, “...phosphorus can be washed away from the constructed wetlands when sorption capacity is saturated and thus outflow concentration of TP may increase” (Chmelova, Sulcova, Kropfelova, Baxa & Pechar, 2010, p.1243).

Much of what we know about the interactions of phosphorus removal in soils of wetland soil is based on our experience with slow-rate (SR), and rapid infiltration (RI) and overflow (OF) land treatment systems. The key reactions are the adsorption processes onto the soil and chemical precipitation. Typically, the sorption on the surface of the soil is a faster process than the chemical precipitation. From the design of overflow systems, there is also research that shows the phosphorus removal will not be more than 40 to 50 % because there is not enough contact time between the soil and water. Soils usually have very active surfaces with Fe, Al, Ca. Acidic conditions favor the Al and Fe complexes and alkaline conditions favor complexes with Ca. The USEPA, using the basic 1<sup>st</sup> order kinetics reaction, establishes the short term-adsorption to the soil but it is also known that actual removal of phosphorus in the field will be 2 to 5 times higher because of the slower chemical precipitation processes that renew the adsorption sites (Crites & Tchobanoglous, 1998). The reactions with the water and the soil are anaerobic for the most part because of the isolation from atmospheric oxygen (Wanner & Mlejnska, 2010).

Wolfe & Lind (2010) looked at the sorption of phosphorus in the presence of suspended clay particles in constructed wetlands. An interesting study because it took into account the role of periphyton in this process, and looked closely at use of clays for sorption of phosphorus in natural systems. Use of clay-like materials in constructed wetlands while important, most studies focus on the specific chemical composition of the materials and less on the mechanism or clay in a general sense. The two clays used were bentonite and kaolinite. The bentonite is 2:1 expanding clay and the kaolinite clay is representative of 1:1 non-expanding clays. Soluble reactive phosphorus (SRP) was chosen for measurement because of the use of SRP by biotic organisms. The SRP sorptive maximum capacity of the clays was determined with the Langmuir isotherm model. For the bentonite clay, the calculated maximum was 125 mg SRP/kg clay and the actual results were 75 % SRP/kg clay of the maximum in 60 minutes. For the kaolinite clay, the calculated maximum was 58 mg SRP/kg clay and the actual results were 68% mg SRP/kg clay of the maximum in 60 minutes. Structural differences in the clays have been studied previously and kaolinite adsorbs anions only on its broken edges and bentonite with more surface area and exchange sites adsorbs almost twice as much phosphorus in the same amount of time. The second parameter looked at the role of periphyton in the system. The results showed that neither of the suspended clay particle types influenced the uptake of phosphorus by the periphyton. The short-term uptake of SRP was in the range of 89 – 95% for the two clays and control sample. Secondly, the turnover of phosphorus back to solution by the periphyton was slower than the uptake and as a percentage of the total was in the range of 21 – 45%, and again the presence of

clays did not adversely or positively impact the results. It was also thought that the species of periphyton is less important than other system characteristics such as temperature and velocity of the water. I did not find research that correlated this research with clay particles in wastewater streams to the total suspended solids (TSS) often measured as an effluent parameter in wastewater treatment, but a correlation is probable.

There has been research on the desorption of phosphorus and there are different theories as to what is happening: 1) there is a loosely bound fraction of phosphorous. A study of sediment chemistry in Minnesota showed increased depths of water above the soil surface increased the P concentrations in the porewater and the release Dissolved Reactive Phosphorus (DRP) from the iron oxyhydroxides because of the reduction of  $\text{Fe}^+$ . Additionally an increased partial pressure of  $\text{CO}_2$  in the calcium carbonate predominant soils caused the release of the carbonate-bound P (Bays, et al., 2010). 2) Treatment wetland soils might give back something like 1 year's storage of phosphorus if exposed to low phosphorus content water. Most of the P in the soil is structurally bound organic or inorganic P compounds and very little is in the pore water at equilibrium (Kadlec & Wallace, 2009). 3) If the soil pore water has low phosphorus concentrations, there will be a net movement of P from the soil to the water. Vymazal (2007) states the "balance between P absorption and desorption maintains the equilibrium between the solid phase and the P in the soil water. Defined as phosphate buffering capacity it is analogous to the pH buffering capacity of a soil" (p.60). While the phosphate buffering capacity of the soil is an important concept for the equilibrium of the water-soil interface, there has been research to show that the diffusional transport of the

phosphorus is less than the movement of phosphorus caused by the transpiration of the plants in the wetland (Kadlec & Wallace, 2009).

The overall sorption in the wetland is dependent on the pH of the soil and the concentrations of the ionic metals in the substrate. The metals in the soil most likely to be measured are Al, Fe, Ca and the P sorption capacity can be predicted “solely from the oxalate extractable (amorphous) aluminum content of the soil” (Vymazal, 2007 p. 60). In anaerobic conditions (soil reduction), the soil phosphate is solubilized at the surface of the gel-like reduced ferrous compounds and increases the concentration of phosphorus in the wastewater (Vymazal, 2007). As pointed out by Kadlec (2009b), the oxidation of the organic matrix that holds the newly sorbed organic phosphorus reverses the process slowly due to exposure of the upper soil horizon to air or rapidly in the case of a peat fire; in either case the mineralized P could be easily transported.

Wanner & Mlejnska (2010) looked closely at not only constructed wetlands in the Czech Republic but also at other non-traditional technologies, specifically soil filters for the removal of phosphorus from small municipality systems. Soil filters use porous soils and other materials to improve the removal efficiencies. Different than constructed wetlands, the chemical reactions are anoxic (low oxygen) to aerobic; while for most constructed wetlands, the soil water reactions are anaerobic. The other important reaction mechanism is the microbial reactions and decomposition taking place in the soil environment under oxic conditions. Soil filters work best in an aerated mode and a fill and drain operation. While analysis of systems showed that overall there was a 24% removal of TP for most constructed wetland systems, the TP removal for the soil filters

was 47% and the removal rate for phosphates was 31%. These results were better than just gravel and sand filters because there was an additive to the soil that improved the removal efficiencies. The application of these techniques relative to the floating island technology are aerating of the system, and the growth of the microbial activity at the surface of the materials in an aerobic environment. By carefully determining the filtration material, the floating island technology will operate as a soil filter on top of either the lagoon pond or constructed wetland.

Maynard et al. (2009) looked at the sorptive capacities of wetland soils in California and came to very different conclusions on the wetland soils that are alternatively wetted and dried. The alternating cycles changed the oxidation state of the Fe, changed the crystalline structure of the surface of the wetland, resulting in an increase in the surface area available for sorption and hence the P sorptive capacity. Recall that other studies have shown that the crystalline structures that occurred during the dry cycle are dissolved when wetted. The research stands out because it also looked at the Fe-polyphosphate precipitates whereas most research looks at the Fe-orthophosphate precipitates. Referred to throughout is the bio-available phosphorus (BAP) in the soil; phosphorus readily available for biological uptake, i.e. orthophosphates. The studies show that the BAP phosphorus in the soil averages 5% of the TP in the soil. The BAP was highest in the areas of the wetland where there were active sediment-deposition zones and less BAP in the areas where Fe-oxidation was taking place. Maynard et al., (2009) suggests that active sedimentation indirectly promotes P sorption with the continual influx of new materials and sorption sites.

Langmuir and Freundlich Sorption Models: Both models are used frequently in a variety of environmental engineering applications, including sorption of contaminants in soils and sediments in CWS.

These models are referred to throughout the literature on constructed wetlands when evaluating phosphorus removal mechanisms, specifically the sorption of phosphorus to the soils and sediments when Fe, Al, and other metal ions are a part of the process. These models are not without controversy and as pointed out earlier, Kadlec and Wallace do not think the models are that useful (Kadlec & Wallace, 2009). The parameters for these models are determined in bench tests and are useful for the design phase and operation of the constructed wetlands. These models are used for determining the sorptive capacity of the sediments for a specific CWS (Wiedemeier, Rifai, Newell & Wilson, 1999). These sorptive characteristics of the soil- water can be determined with bench tests at constant temperature (isotherm); the relationship between the amount of contaminant adsorbed and the concentration of the contaminant still in solution. There are typically three different scenarios: 1) The Langmuir model describes sorption where the sorbed concentration increases linearly at low concentrations and approaches a maximum constant value at higher concentrations because there is a limited number of sites available for sorption.

The equations for the Langmuir model can be expressed in a couple of different forms (Wiedemeier et al., 1999):

$$C_a = (KC_1b)/1 + KC_1$$

where:  $C_a$  = sorbed contaminant concentration (mg P/kg soil)  
 $K$  = equilibrium constant for the sorption reaction (mg/g)  
 $C_1$  = contaminant concentration still in solution (mg P/L)  
 $b$  = number of adsorptive sites.

Another form of the same model is (Kadlec & Wallace, 2009):

$$C_a/C_{\max} = C_1/(C_1 + 1/k)$$

where:  $C_{\max}$  = maximum sorbed phosphorus (mg P/kg soil)  
 $1/k$  = half saturation concentration (mg/L).

Typical values for  $1/k$  are in the range of 0.3 to 5.6 but have been to be as high as 74.6 mg/L (Kadlec & Wallace, 2009).

The model presented is a general sorption model and it has been determined for the  $C_{\max}$  in a soils and phosphorus environment, it is dependent on the Al and Fe concentrations in the soil.

$$C_{\max} = a(C_{\text{Fe}} + C_{\text{Al}}).$$

where:  $a$  = proportionality constant ( mg P/mol)  
 $C_{\text{Fe}}$  = extractable iron concentration in the soil (mmol/kg)  
 $C_{\text{Al}}$  = extractable aluminum concentration in the soil (mmol/kg).

2) The Freundlich model is the Langmuir model for an infinite number of sorption sites. (Wiedemeier et al., 1999; Kadlec & Wallace, 2009) The model assumes dilute contaminant concentrations.

$$C_a = K_d C_1^{1/n}$$

where:  $C_a$  = sorbed contaminant concentration (mg P/kg soil)  
 $K_d$  = distribution coefficient  
 $C_1$  = contaminant concentration still in solution (mg/L)  
 $n$  = chemical specific coefficient.

As an example, the Freundlich model for sorption has been used extensively when studying the Houghton Lake wetland to calculate the amount of sorbed phosphorus for mass balance calculations (Kadlec & Wallace, 2009; Kadlec, 2009b).

3) The linear sorption isotherm is a special form of the Freundlich where  $n = 1$ , typically in situations where the dissolved concentration is less than  $\frac{1}{2}$  of the solubility. References of isotherm are seen in the literature because it has been well established that the sorption of phosphorus is a finite removal mechanism.

Yoo, Ro, Choi, Yoo & Han (2006) looked at phosphorus adsorption in sediments, using the Langmuir isotherm for five constructed wetland marshes in Korea. The use of the Langmuir isotherm allowed for the calculation of the equilibrium P concentration ( $EPC_o$ ) in the soil at a point where there is no net P adsorption or desorption; the  $EPC_o$  is also the solution concentration where the solid phase is at its maximum sorption capacity. The question for the research was to determine whether the sediment was a sink or a source of P for the constructed wetland, knowing that depends on the flux of P across the sediment- water interface. The batch and columns tests were designed using sediment samples in five sub-marsh locations in the constructed wetland. Using the Langmuir equations, the relationship between  $EPC_o$ , Phosphorus Sorption (PS) and a variety of external parameters (pH, Al concentration, Fe concentration, degree of soil saturation with phosphorus (DSSP), organic matter (OM), and clay) were determined. Several key results confirmed and proved the validity of the Langmuir isotherm. 1) There is a linear relationship between the P sorbed (mg P/kg sediment) and the P added (mg/L) by the wastewater, shown by a correlation between the TP concentrations and the  $PS_{max}$

determination of the soil samples. 2) As the pH went up the  $PS_{max}$  was lower. 3) The higher the organic matter (OM), and the metal ion concentrations the higher the  $PS_{max}$ . The relationship between OM in the sediments and the removal of phosphorus by sorption is not agreed upon research and it is thought that the OM competes with the phosphorus for sorption sites. 4) However, the  $EPC_o$  correlated positively to increased pH and negatively with Fe, Al, Ca concentrations and amount of OM. 5) By also studying the sediments in a floodwater situation, it was shown that the equilibrium P concentration ( $EPC_w$ ) is different than the steady state  $EPC_o$ . 6) This study clearly demonstrates the complexity of the system and concludes that the increase in pH over 6.5 will enhance Ca-P precipitation at the same time countering the decrease in  $PS_{max}$  because of dissolution of the Fe-P and Al-P complexes. The Fe-P and Al-P complexes are assumed amorphous and poorly crystallized in the sediment. 7) The usefulness of this data is in determining the estimated lifetime of the constructed wetlands bed and in the case of these marshes; the range is between 6.6 years and 23 years (Kadlec & Wallace, 2009).

#### Biological/Microbial Mechanisms

The biological activity of constructed wetlands is of paramount importance and an integral part of the overall constructed wetlands processes. This includes the actual plants used in the constructed wetlands, the microbial activity (biofilms on the plant root zone and in the water and soil), and the algae that forms in the wetland systems. The biological activity in the constructed wetlands is very specific to the climate and the surrounding environment and the uptake rates of plants, algae and microbes are all different for phosphorus (Kadlec, 2006). Appendix B lists the plants that commonly used in

constructed wetlands throughout the world; the list is a compilation of the plants researched and mentioned throughout this paper as a part of the literature search. A very basic concept that was in many of the articles on biological activity and removal mechanisms in constructed wetlands was the N: P (Nitrogen: Phosphorus) ratio in the system and the importance of knowing that ratio when evaluating a CWS. The chemical composition of the cell biomass used in WWTP is  $C_{12}H_{87}O_{23}N_{12}P$ ; this is 2.3 P for every 100 gm of cell biomass (Tchobanoglous et al., 2003). Zhang, Rengel & Meney, (2010) looked at different ratio combinations relative to the plant, *Canna indica* and showed that in wetland systems there is an interactive relationship between the nitrogen and phosphorus concentrations. The best performance for the growth of the plants was in a high N, high P setting; and the lowest relative growth rate (RGR) was in the low N environment regardless of the P concentration. With respect to phosphorus removal efficiencies, the lowest removal efficiency for  $PO_4\text{-P}$  was in a low N, high P environment (63%) and the  $PO_4\text{-P}$  removal efficiency increased with N additions regardless of the P concentrations. An importance consideration often overlooked in the research because the study of nitrogen removal is separate from phosphorus removal research. One of the papers showed that with an excess of both nitrogen and phosphorus the ratio is less important for algae and macrophytes growth.

The role of all biological activity in constructed wetlands and then highlights of research that is either promising new research or presented excellent removal results relative to phosphorus removal in a constructed wetlands application are discussed. When evaluating the biological processes it is important to take into account the net removal of

phosphorus to permanent storage because over the course of the year the uptake and re-release of phosphorus will differ. The seasonal patterns of vegetation growth and phosphorus storage are a complex system that is interconnected to the influent wastewater stream, the soil, climate and many other factors (Kadlec & Wallace, 2009). Biological oxidation of phosphorus within the red beds of constructed wetlands will convert most P species to the soluble orthophosphate over time for use by the biological components of the wetland and adsorption to the substrate media (Gill & O’Luanaigh, 2010).

Specific to the application to the floating islands technology, it is worth noting that another Montana company in Hamilton, MT received grants in 2008 from the Montana Board of Research and Commercialization Technology to develop “new techniques for the production of wetland species with exacting germination requirements” that can then be marketed throughout the western states (GBR, 2011; MBRCT, 2008). Included is over 1.2 million seedlings and 20 different species of which the beaked sedge is native to Montana and could be tested with the floating island technology.

Plants: Plant selection for constructed wetlands requires careful consideration and the suitability of the plants depends on the following parameters: 1) ecologically acceptable with no significant weed or disease risks, 2) tolerance of local climate, 3) tolerance of the pollutants in the wastewater stream, 4) rapid establishment and growth, 5) high pollutant removal capacity and 6) the type of constructed wetland where the plants will be established (Tanner, 1996).

Kadlec & Wallace (2009) points out that when comparing vegetated wetlands to unvegetated lakes and lagoon ponds, the removal rates for lakes and lagoons are minimal. It is assumed then that plants of all types, submerged, emergent and floating do remove a major fraction of the phosphorus from the wetland. There are several removal mechanisms of phosphorus for plants.

The three primary functions for all plants in constructed wetlands are: 1) The root system creates channels for the water to pass through in the water-soil environment. The absorption through leaves and shoots is typically only for submerged plants. The phosphorus uptake is highest at the start of the growing season (Vymazal, 2007; Kadlec & Wallace, 2009). On a seasonal basis, the plant uptake can be a large part of the phosphorus removal during the growing season but as has been pointed out, the majority of the uptake is re-released to the water during the autumn senescence except for the small percentage that is permanently buried with the accretion of new soils. The autumn turnover is an important consideration for wetlands design but the processing of phosphorous by microbial and plants in the soil continues beyond the senescence of the above ground plant parts (Kadlec & Wallace, 2009; Kadlec & Bevis, 2009). 2) The plant roots also provide oxygen into the soil for the aerobic bacteria, which breakdown many types of compounds. 3) The plants themselves will use nutrients from the wastewater stream. Plants will have different rates of phosphorus uptake; the differences are related to both the difference in species and the turnover of the plants themselves. Compared to plant species in northerly climates, the plants in the Everglades Nutrient Removal Project (ENRP) turned over the standing above ground crop five times more often per year.

Much of the literature looks at the amount of P in the dry weight of the plants; the range will be between 277 to 3000  $\mu\text{g P/kg}$  of biomass. In terms of dry weight, the phosphorus percentages are 0.14-0.30% for emergent plants, 0.14 to 0.40% for floating plants and 0.12 to 0.27% for submerged plants. Because wastewaters are nutrient rich, the plants in constructed wetlands respond and uptake more phosphorus than in an environment that is not phosphorus rich; the uptake can be double in the nutrient rich system relative to a nutrient poor system. Verified in the plant tissue studies and the case for all biological activity including plankton, periphyton and algae (Kadlec & Wallace, 2009). The rates of decomposition and re-release also vary between plant species and the half live of these plants ranges from 15 days for submerged aquatic vegetation (SAV) to 200 days for floating aquatic vegetation (FAV) (Kadlec, 2006). The estimate is that 15 – 20% on average of the nutrients from the influent is consumed by the plants in the growing season of the plants. As an example of plants commonly used in constructed wetlands, *Phragmites australis*, common reed, has the most extensive root system, which plays an important role in the overall removal rates of phosphorus (CIWEM, 2011).

There are differences in the removal mechanisms for plants for different types of constructed wetlands. In the FWS wetlands, the plant detritus returns to the water column because water is always present. The amount of water in a FWS to complete the decomposition and accretion of new soils in the FWS is unlimited. The process of decomposition of the plants in HSSF and VF wetlands is much slower because the systems are not always loaded with water and the decomposition happens partially in a dry air environment. The detritus is deposited directly onto the substrate of the HSSF and

VF wetlands. The environment is unsaturated or will have intermittent water flow. There is often times a larger standing crop of decaying plants. The phosphorus is eventually leached out of the detritus but the process is much slower than for FWS wetlands and there is often a buildup of refractory material that will not decompose and contains residual phosphorus (Kadlec & Wallace, 2009).

Translocation of phosphorus in the plants is a response to the temperature and seasonal variations of wetlands. The ions/nutrients (including phosphorus) in the plants move from the shoots to the roots and rhizomes before the start of the cold season. These nutrients are stored there until the start of the early spring growth cycle. For moderate climates, approximately 1/3 of the phosphorus in the aboveground part of the plant will move to the belowground plant storage annually (Kadlec & Wallace, 2009) indicating that the phosphorus storage in the above ground biomass is short-term. As the plants decay, the phosphorus is re-released back to the wetland water. The abiotic leaching removes the soluble phosphorus from the decaying biomass, and as much as 30% of the nutrients are loss in the first few days of decomposition. Some of the re-released phosphorus is then incorporated into decomposer organisms that need nutrients to decompose the rest of the decaying plants and release more phosphorus. The decaying dead roots decompose underground. The aboveground plants return P to the water and the belowground parts return phosphorus to the soils (Vymazal, 2007).

Plant harvesting typically yields on the order of  $2 - 4.9 \text{ g P/m}^2 \cdot \text{year}$ , a very small percentage except for lightly loaded systems. An average wetland might see influent loads of  $150 - 300 \text{ g P/m}^2 \cdot \text{year}$  but a lightly loaded system can be as low as  $30 - 50 \text{ g}$

$\text{P}/\text{m}^2\cdot\text{year}$  (Kadlec & Wallace, 2009). Macrophyte harvesting is widely proposed in some constructed wetland applications but the nutrient removal from harvesting is only around 10%; however, with free-floating plants, the harvesting is often required (typically tropical climate) to maintain open areas and allow for increased oxygen exchange in the wetland (Nahlik & Mitsch, 2006). The removal of water hyacinth can remove 62% of the TP in lightly loaded wetlands; the average is closer to 20%. While harvesting is possible for free-floating plants it is very difficult with rooted emergent macrophytes and if harvesting only the above ground standing crop, the removal will be between 1 and 5  $\text{g P}/\text{m}^2$ . It is important to point out the cost of plant harvesting is expensive but can be beneficial to the local communities if either the phosphorus can be recovered or the biomass can be used (Nahlik & Mitsch, 2006).

There are important differences with plant decay and the different CWS systems. For the FWS, a portion of the plant detritus is returned to the water column but for HSSF and VF wetlands it is deposited on the top of the wetland soil at the bottom of the CWS. The phosphorus is returned back to the water more quickly for FWS than the slower processes of the HSSF and VF as a result (Kadlec & Wallace, 2009). Water depth affects the growth of macrophytes because if too deep, inhibits macrophyte growth and colonization of the wetland cells and therefore plants require shallower water for most of their growing season. As is noted in the different types of CWS, the FWS systems are have deeper water depths and can negatively affect the plant environment (Harrington et al., 2010).

Submerged aquatic vegetation (SAV) such as waterweed, coontail and naiads have been used in wastewater treatment but are not as common as emergent plants and floating plants in constructed wetlands; these plants are suspended in the water, rooted in the sediment and grow to just below the water surface. These types of plants are more common in natural wetlands and are often seen as invaders in constructed wetlands (Kadlec, 2006). Ongoing research suggests that aeration is required for long-term use in constructed wetlands (Crites & Tchobanoglous, 1998). The SAV plants have extremely high rates of orthophosphate uptake but cannot be sustained for long periods of time. The orthophosphate is converted to the organic particulate phosphorus (Kadlec & Wallace, 2009; Kadlec, 2006). SAV wetlands seem to work better at lower concentrations of phosphorus and are more effective at the 100 µg P/L range than emergent vegetation and are less effective at phosphorus concentrations above 1000 µg P/L.

There is ongoing research into different plant species used around the world; macrophyte diversity in the CWS improves the overall functioning of the CWS and there are cultural and geological differences throughout the world. The Singaporean government has worked closely with private companies in building their constructed wetlands and floating wetlands. They have clearly identified which plants work best for each application in a tropical climate (Sim, 2010). Fardin, Holle, Gautier, Da Lage, Molle & Haury (2010) looked at over 226 different plants used in constructed wetlands and determined that 4 plants are used consistently more than others: water hyacinth, common reed, cattail, and water lettuce. It is important to know that in some regions these plants are considered invasive and a threat to the natural ecosystems. In developing countries,

the plants used in the constructed wetlands need to be considered for their economic, cultural, and social concerns in addition to the ecological benefits to the communities.

However, it is also important to note the tradition of plants used in constructed wetlands is “not based on rigorous comparative assessment of efficiency among different species of macrophytes but rather on established practice” (Mburu et al., 2010, p. 663). The authors point out the many roles the plants serve in the wetland environment. Macrophytes need to do the following things in a wetlands environment: 1) uptake of the nutrients, 2) provide a large surface area for attached microbial growth, 3) add oxygen to the water, 4) provide a carbon source for other microbial activity, 5) filtration via the roots of the plants, 6) regulate velocity of the water, 7) insulate the wetland against frost, and 8) often times provide economic activity for the local community. There are differences between the different aquatic species, emergent, free floating and submerged, but there has been less study done to differential between aquatic species and the potential wastewater treatment potential. Mburu et al. (2010) goes on to point out that *Cyperus papyrus* is a plant species that does well in a variety of subtropical and tropical environments, and is a productive plant relative to both height above water and root structure below water. It is important to review all of the potential removal mechanisms for a plant species and they found studies that support the selection of this plant with removal efficiencies as high as 76% for TP and 73- 83% for orthophosphate.

Ongoing research looking at plants for the dewatering of anaerobic sludge in Brazil (Magri, Suntti, Voltolini & Philippi, 2010) proved that the common plants used in constructed wetlands are not necessarily the best for the dewatering sludge application.

The *Typha domingensis* performed significantly worse than the other plants in the study: *Cyperus papyrus* and *Zizaniopsis bonariensis*. The study looked at nutrient removal using vertical flow constructed wetlands with influent phosphorus concentrations as high as 150 mg/L and a standard deviation of 104 mg/L. There is ongoing research on the removal of phosphorus, but the preliminary research shows the importance of plant selection for the application and local environment.

*Qualitative Assessment of Plant Species:* Tanner (1996) evaluated eight emergent plant species in wetland environments for five different characteristics in a qualitative scoring system to determine the best plants overall for constructed wetland systems.

The wastewater was from a dairy operation and had average TP concentrations of 14.6 mg/L and Dissolved Reactive Phosphorus (DRP) concentrations of 11.4 mg/L. One of the shortfalls of this experiment was that it only ran for 124 days and did not take into account the entire growth and decay cycle of the plants and steady state of the system was probably not reached. The wetland plots were lined with gravel and batch fed weekly with the wastewater. The phosphorus removal percentages were in the range of 79 – 93% for TP and 86- 93% for DRP; these removal percentages were irrespective of the plant species. While one of the older studies reviewed for this literature search and is included is because of a few important points. The characteristics of the plants were evaluated and given a score of 1 to 3 are: 1) standing biomass, 2) harvestable biomass production, 3) seasonality of aboveground growth, 4) tissue nutrient levels, and 5) potential for root-zone aeration. An overall score of these parameters showed that the *Glyceria maxima*, reed sweetgrass, was the best plant for New Zealand where this study

took place. Reed Sweetgrass is not used often in constructed wetlands and is a creeping aquatic grass that will either root into the soil or form a floating mat and grows actively year round. The plant with the maximum uptake rate of phosphorus removal was the *Zizania latifolia*, Manchurian wild rice, and was over 9% faster compared with the other plants in the study but is not ideal for constructed wetlands because it poses a serious weed risk in areas where it is not already present.

*Extraction of Pollutants from Plants:* Matos, Abrahao, Lo Monaco, Sarmiento & Matos (2010b) looked at the extraction of different nutrients from the plants in a HSSF constructed wetlands system.

The experiment had 11 beds of HSSF, five were planted with elephant grass and five were planted with tifton 85 commonly referred to as bermuda grass and designed for secondary and tertiary treatment of dairy products wastewater. The hydraulic retention time was 4.8 days. The plant material collected looked at the concentration of the nutrients in the plant tissue after drying. The TP extraction for the tifton grass was in the range of 15.7 to 37.8 kg/ha and for the elephant grass the extraction averaged 30.17 kg/ha. If extended to an annual extraction, the range would be 5-15 g/m<sup>2</sup>·yr for tifton and 18 g/m<sup>2</sup>·yr for elephant grass. Because of the other nutrients also extracted from the plants, it was concluded that tifton grass is an important source of protein feed when grown in CWS that are used to treat dairy waste.

*Willow Bed Treatment Systems: O'Hagain, McCarton, Reid, Turner & Fox (2010)* modified an existing hybrid constructed wetland with the addition of willow beds (added in 2008) to improve the removal of nutrients, nitrate and phosphate.

These hybrid willow bed treatment systems (HWTS) were used first in Denmark and are now being implemented in several countries. A unique design feature of these systems is that there is zero discharge to a receiving body of water. The location of the pilot HWTS was in Dublin, Ireland; and the final design was four different configurations in series: two VF systems at 2 m<sup>2</sup>/PE (people equivalent), followed by a 1 m<sup>2</sup>/PE HSSF wetland, and finally a willow bed treatment area of 3 m<sup>2</sup>/PE. The addition of the willow bed component meant that there was no discharge and the mechanisms of removal included: passage through the soil in the HWTS, absorption to the roots of the willows, and evapotranspiration. The layout of willow bed systems is normally a long narrow bed perpendicular to the prevailing wind direction. Based on the June 2007 updated wastewater regulation, only 2 mg/L of TP is allowed in effluent water. The results showed that the zero discharge of water to a receiving body is a possible solution to contaminate pollution from individual wastewater treatment systems (IWTS).

Another study also looked at the use of wooded buffer zones (WBZ), willow and alder trees, as an alternative to releasing water into the natural environment. The objective was to look at nutrient uptake and exportation of different species of willow in four WBZ in various locations of France (Koenig, Reeb & Werckmann, 2010). The existing wetlands were all different sizes (area allotted/PE) and had different hydraulic loading rates (HLR), different soil types, and different effluent permit requirements.

Willows were chosen specifically because they have a high rate of evapotranspiration ( $27.2 \text{ L/m}^2$ ) in summer months and the capacity to export nutrients and to resist groundwater contamination in wastewater flood situations. The four different willow species were *Salix viminalis*, *S. caprea*, *S. fragilis*, and *S. alba* and the hybrid willow, *S. rubens*. It was also verified that the type of soil influences the overall performance of these WBZ. A complex study with many variables that were not well defined or controlled during the study, it was concluded that the WBZ did remove phosphorus in the wetlands between 12 and 89 % in the four systems. The phosphorus uptake by the different willow species did vary with *S. fragilis* removing the most phosphorus at 5.4 mg/g DW of the leaves and *S. viminalis* was the lowest with 2.65 mg P/g DW. The effluent concentrations still did not meet the 2007 requirement for France, but did show that the WBZ would protect the natural environment during periods of low water levels, and reduce the possibility of wastewater contamination into groundwater.

*Subsurface Riparian Buffer Zone Pilot Study:* Water quality pollution regulations in Korea are for point sources only, but an ongoing problem is the non-point source pollution caused by rain events, and other runoff events.

(Jung, Choi & Oh, 2010) designed a pilot riparian buffer zone (RBZ) along a bank of the Han River. The experimental design of the pilot was to have five different plots each of them 15 x 20 meters in size with different plants to determine which plants worked the most effectively at removing nutrients and other pollutants. The nutrient concentrations, including phosphorus were tested at different depths in the soil environment to determine the role the plants roots had on the overall removal efficiency

of the system. Specifically looking at the TP measurements, the depth of soil where the most phosphorus was removed was 30 cm and greater, and the removal efficiency improved along the length of the subplots as well. The removal mechanisms in the subsurface were adsorption and, filtration by the soils and plant roots. Of the different plants tested, the grass subplot removed the most phosphorus because of the dense distribution of the grass in the subplot; however, the grass species was not identified in the study. Ongoing work is to model the flow-path length of artificial RBZ to meet water quality requirements from the non-point source pollution.

*Ornamental, Edible and Useful Plants:* Throughout the research, there has been an ongoing discussion on using plants with large biomass production rates and then harvesting the plants for either economic or aesthetic value.

The following study by Zurita, de Anda & Belmont (2010) at the Universidad de Guadalajara took a different approach to the plants used in subsurface flow wetlands (SSFW). By using the wetlands for growing and harvesting ornamental plants that are commercially valuable and at the same time, not compromising the effluent standards required for the wastewater, this would be a way to encourage the use of constructed wetlands in developing countries. Five different ornamental plants were evaluated for nutrient removal at both a lab scale and a pilot study for both VF and HSSF constructed wetlands. The results were encouraging; the average TP removal percentage as 70% in the lab test and 50% in the pilot study. The plant growth varied between the different ornamental plants but the study showed that in warmer climates the use of ornamental plants should be considered. The study was concerned with the flowering and growth of

the ornamental plants, it did not report the amount of phosphorus removed when the plants were harvested.

A second study evaluated 20 different plants, 13 terrestrial plants and 7 different aquatic species for nutrient removal, including phosphorus. The plants and wetlands system design were chosen for resource recovery (substrate and plants) and reuse of the systems. The plants are used for food, paper products, flowers, and handicrafts and more recently are being looked at for their biofuel potential (Abe & Ozaki, 1998). One of the older studies in the literature search, many of the concepts presented are being reevaluated at in constructed wetlands research and application. The design of the plant bed filters were long trenches that contained baskets filled with zeolite filter material as the substrate. Zeolite is a naturally occurring mineral that is mentioned later when evaluating different materials for phosphorus removal by chemical precipitation and is reusable as a soil conditioner. The zeolite baskets held six plants in each and weighed between 26 – 29 kg for the terrestrial plants and 22 kg for the aquatic plants. The plants tested included food (rice, wheat, canola, sorghum, barley), cut flowers (hoary stock, hanana, iris, lily, safflower, marigold), and handicrafts (hemp, rush, kenaf, papyrus). Some of these plants were perennials and others had a July to September growth seasons and others had December to April growth seasons. These plants were chosen over the typical constructed wetlands plants such as reed and cattails because of their utilization by the rural communities where the constructed wetlands would be located. The artificial wastewater had 3.3 mg/L of TP. The results looked at both the biomass production rate and the phosphorus removal rate for the each plant (P absorbed by the above ground part

of the plants) and the basket (including the adsorbed phosphorus by the zeolite). A few conclusions worth noting: 1) the plants with the high biomass production rates showed the higher P removal rates. With regard to phosphorus removal, the papyrus, sorghum, and kenaf plants had the best results and were the most productive during the summer months. 2) The Italian rye grass and barley were the winter plants that removed the highest percentages of phosphorus. 3) The zeolite removed almost half of the phosphorus in the wastewater. 4) The amount of zeolite required for a 200 PE wetland e would be an area of 1200 m<sup>2</sup> and the system would removal approximately 70% of the phosphorus in a secondary treatment effluent. There is flexibility in choosing the plants for the wetlands system beyond the cattail and reed plants typically planted and the importance of choosing a substrate that contributes to the removal mechanism.

Algae: Algae are commonly found in natural and constructed wetland systems; more often than not, and it indicates an excess of nutrients and adversely impacts the overall balance of the system. The algae use the phosphorus for growth, but when the algae decompose it causes a reduction in the dissolved oxygen of the water which negatively impacts other biological processes.

Algae is referred to in the literature as the phytoplankton (suspended plankton), the epipelon algae (bottom sediments), the epiphyton algae (on the submerged plant parts), and the metaphyton (mats of algae). The non-plankton forms of algae are termed periphyton (Kadlec & Wallace, 2009). It is fair to say that some of these algae types would also be referred to as biofilms and the literature does not always distinguish the differences clearly.

Reduction of algae blooms in receiving waters has been successful if the internal phosphorus cycling is kept to a minimum; most often seen in aerobic waters (Pontius, 1990). For growth the algae use the soluble reactive phosphorus (SRP) but when algae decay the phosphorus is returned to the wetland water either as particulate phosphorus (PP) or dissolved organic phosphorus (DOP) (Kadlec, 2006). On the other hand, there is ongoing research to better understand the role various algae species and maximize the use of algae in the overall removal of contaminants. Algae differ from the macrophytes because they obtain the bulk of their nutrients directly from the water column and their rapid growth responses to nutrient loads (McCormick, Shuford & Chimmney, 2006). The chemical formula of the organic matter in plankton is often given as  $C_{106}H_{263}N_{16}P_1$  (Drever, 1982).

In the 1970s, the US Department of Energy funded research looking at algae as both a biofuel and removal mechanism for nutrients in wastewater. The study of secondary and tertiary wastewater treatment with algae served two purposes, both as a potential energy source and as a means of eliminating an environmental concern (Wang, Min, Li, Chen, Chen, Liu, Wang & Ruan, 2010). Locally at Montana State University, the Energy Research Institute is currently looking at the use of algae as a biofuel and at ways to increase the productivity of the oils in various algae with the addition of sodium bicarbonate as a chemical trigger during the growth of the algae. An added benefit to using algae that is gaining traction is algae assimilates  $CO_2$ , which is a greenhouse gas, and the process becomes “a perfect candidate for  $CO_2$  sequestration and green house gas reduction” (Wang et al., 2010, p. 1175).

*Algae-based Ponds:* This is interesting study, from Palestine on the uptake of phosphorus in algae, evaluating the use of algae-based ponds (ABP). Isayed & Zimmo (2008) looked at (ABP) as a cost effective alternative to traditional WWTP given the economic and political situation in Palestine. A pilot study was designed to test the removal efficiencies of nutrients and TSS for ABP at different pond depths.

This simple but well designed study clearly showed the relationship to the depth of the pond and the removal of the nutrients. ABP are low cost and efficient in producing a high-quality effluent that can be reused for irrigation purposes, but ABP have a high land requirement (LR) per person in the range of 5 to 7 m<sup>2</sup>/person. The depth of the ABP is critical to the performance; the higher surface area to depth ratio influences the removal mechanisms because of the light available per volume measurement, and more light leads to more algae which favors different treatment processes. The experimental setup was a septic tank for settling and then three different depths of ponds, 30, 60 and 90 cm in triplicate. The HRT (28 days) was the same for all three depths and the influent TP concentration was 12.8 mg/L. The key result is that there is an inverse relationship between the depth of the pond and the effluent concentration relative to phosphorus. The removal of efficiencies of the 90, 60 and 30 cm were 37.6%, 46.9% and 57.6% respectively. There are three considerations besides the uptake of the phosphorus by the algae for growth: 1) the higher surface/area volume allowed for more algae growth per unit of wastewater, 2) the lower water velocity in the shallower pond helped improved the sedimentation, and 3) the TP removal by sedimentation of particulate phosphorus (PP) in the decayed algae itself.

*Use of Algae in Different Process Steps of a Wastewater Treatment Plant:* This study evaluates the use of algae in a wastewater treatment facility, looking closely at the location in the process stream where the green algae (*Chlorella*) is most effective.

Evaluating the efficiency of the algae to remove nutrients in different stages of a municipal wastewater treatment plant (MWTP) in St Paul Minnesota was the primary objective (Wang et al., 2010). At four different points in the MWTP, algae growth was evaluated as to how well it removed nutrients, of which one was phosphorus. The four locations were: #1 before primary settling, 2# after primary settling, 3# after activated sludge, and 4# centrate (water from the activated sludge). The removal efficiencies for total phosphorus from, #1, #2, and #4 were 83.2%, 90.6%, and 85.6% respectively. There were several key points applicable to the general information of biological processes in the removal of nutrients, including constructed wetlands. 1) The primary measurement method determining the growth rate of the algae was a measurement of optical density over time. 2) The optimal N: P ratio was in the range of 6.8 – 10.0 based on previous literature but, the algae grew in all four of the wastewaters where the ratio varied between 53 and 0.36; with the ratio of 0.36 in the centrate there was the most algae growth. Because the amount of nutrient was greatest in the centrate, the imbalance in N:P ratio did not adversely affect the growth of the algae or the removal of either nitrogen or phosphorus. 3) At the stage in the wastewater where the N: P ratio was 53, only 4.7% of TP was removed. A severe phosphorus limitation for algae growth impacted the removal of the all nutrients, including the removal of phosphorus. 4) The phosphorus concentration in the centrate was 30 greater in stages 1 and 2, but all 3 stages showed

approximately 90% removal of TP in around 3 days of algae growth, indicating a rapid luxury uptake of phosphorus by the *Chlorella* algae to polyphosphates. 5) An additional study parameter was the evaluation of different metal ions in the same wastewater streams by the algae. The algae removed over 95% of the Ca in the centrate solution. The conclusion here is: “that the Ca/P ratio and the pH (range of 10) of the wastewater are two controlling factors for the phosphate recovery by precipitation, an increase in either can enhance the thermodynamic driving force by calcium phosphate precipitation as well as the removal of the phosphorus by the algae” (p. 1183). The ability to precipitate and remove the calcium phosphate from the centrate would be an added benefit to the process.

*Algae Transformations:* The phytoplankton species changed from *cyanophyceae* to *bacillarophyceae* during the restoration work of a watershed area in Japan.

The change in plankton type significantly improves the water quality of the Tone River and Lake Tega in northern Japan. Two points worth considering, but neither were considered in detail: The agricultural runoff was paddy fields and Lake Tega went from being eutrophicated to a P-limiting, non-eutrophicated lake. There was no discussion on the details of the rice fields (Murakami, 2010).

*Comparison of Cyanobacterial Mats to Chlorophycean Mats:* Using the Everglades Nutrient Removal Project (ENRP) as a test site, a comparative study looked at different periphyton mats to determine the capacity of the mats to remove phosphorus

from the water and the re-release of phosphorus back into the water during decomposition of the periphyton.

There were a couple of parameters that had been determined prior concerning the role of algae in wetland systems. The prior work established that phytoplankton decomposition and re-release of P is rapid when compared to macrophytes but not take into account is the fraction of P associated with periphyton that is in a recalcitrant form like the carbonate rich wetlands of the ENRP. Some of the P precipitates are insoluble inorganic complexes (McCormick et al., 2006). It is also been shown that a pH over 6.5 enhances Ca-P precipitates and algae enhances this process (Yoo et al., 2006). Both the short-term and long-term phosphorus removal processes with two different algae types: cyanobacterial and chlorophycean mats were evaluated. Cyanobacterial mats are defined as bacteria on the bottom of the marsh and a part of the sediments of the wetlands; the chlorophycean are different types of green algae in fresh water systems. In the laboratory, the mats were isolated and each was spiked with soluble reactive phosphorus (SRP) in the range of 50 – 120  $\mu\text{g P/L}$ . The level of contamination was selected because it is the range of phosphorus contamination seen in the ENRP. The short-term results showed that the cyanobacterial mats had almost double the P uptake and was twice as fast when compared to the chlorophycean mats. The long term studies showed that the phosphorus uptake rates decreased by five fold during the 40 day study. More importantly, the decomposition of the cyanobacterial mats released substantially more P than the chlorophycean mats; and the amount of P released was considerably lower in aerobic conditions for both mats. Algal decomposition is also faster than macrophytes. Other

conclusions show that the algae are not quickly saturated even if dosed with large pulses of P to mimic repeated storm water events. The decomposition of the algae and the re-release of P in the system are dependent on the type of algae. As pointed out, the sediment sorption is a major sink for the P, but the Everglades wetlands have been restored on areas of highly oxidized soils used in agriculture and the P sorptive properties of the soil impacts the overall sorptive ability of the system. Also, as has been pointed out in other studies, there are 2 mechanisms to keep in mind: 1) The accumulation of P in the intracellular storage of the algae in the form of polyphosphates related to the growth of the algae and 2) the precipitation of the P with carbonates onto the actual surface of the algae mats; this form of phosphorus removal is irreversible compared to the life cycle of the algae and the re-release of the P. “The form of accumulation by all periphyton determines its fate within a wetland and may influence P retention efficiency” (p. 287).

Microbial: The microbial activity in the constructed wetlands environment is globally described as one of two processes:

The biofilms on the plants and surfaces of the wetland that use phosphorus for microbial growth, and the phosphorus accumulating organisms (PAO) that uptake phosphate when using the energy of the polyphosphate bonds. Microbial uptake of phosphorus is fast relative to the other processes because these organisms grow quickly and multiple at high rates but the amount of phosphorus stored is low. What is clear is that the uptake also depends on the eutrophic status of the wetland. The more eutrophic the wetland, the less phosphorus will be stored by these organisms and algae (Vymazal, 2007). The use of P tracer tests have shown that the “first line of interaction for biological

processes with phosphorus in the wetland is the microorganisms and not the macrophytes...they store significant amounts of phosphorus and place the intercepted phosphorus in the sediment-soil systems where other processes can operate to convert it to recalcitrant forms” (Kadlec & Wallace, 2009, p. 360). What is less understood and researched is the role that soil microorganisms play in overall process of phosphorus burial. While they do help with the final burial of P in the soil by decomposing and mineralizing organic P, it is also believed that they regulate the P flux between the soil – water interface and solubilize the soil P back into the water (Vymazal, 2007).

*Biofilms:* At the microbial level, the degradation of pollutants takes place close to the solid surface interface in wetland systems. The roots and rhizome areas of the plants as well as the soil water surface are the locations for the biofilms to grow in the CWS environment.

One of the more interesting studies was a comparison of the biofilm communities of a HSSF wetland and a VFCW to determine if they are the same or different based on an inlet environment that was similar. Martin, Salas, Sardon, Pidre, Parrado & Garcia (2010) looked at the microbial communities of the two systems and also demonstrated that in the HSSF wetland the microbial species is also dependent on the water depth and kind of medium used as substrate. The VF wetland did not show the same variations in microbial types between wet and dry parts of the system. The outlet effluent concentrations for COD and nutrients were also similar between the two systems. The two most prevalent bacteria associated with the HSSF were anaerobic bacteria:

*Lysobacter sp.* and *Clostridium sp.*; and in the VFCW, the bacteria were *Pseudomonas*

*sp.* and *Sphingiminas sp.* This article was of interest because it suggests additional research for the floating islands technology. Extensive work has been done to evaluate the microbial activity with respect to the nitrification and de-nitrification processes by Montana State University researchers and the research staff of Floating Islands International. The extension of the research lends itself to identifying the phosphorus accumulating organisms (PAO) that are in the different wetlands environments and determining which are more prevalent and efficient at removing phosphorus from the wastewater stream.

*Phosphorus Accumulating Organisms:* The basic premise with phosphorus accumulating organisms (PAO) is that the phosphorus will be incorporated into the cell biomass which is then removed from the wastewater in the sludge process (Tchobanoglous et al., 2003). For constructed wetlands, cell biomass becomes a part of the new sediments and soils on the bottom surface of the wetlands. Creating an environment for the growth of PAO requires that there be a selective advantage for them to grow by putting other groups of bacteria at a temporary disadvantage with respect to substrate (WEF, 2006).

The three basic requirements for PAO to thrive and consistently remove the phosphate from the wastewater are: 1) available carbon and polyphosphate in the influent; 2) the anaerobic zone of the system precedes by zones that have electron acceptors of either nitrate or oxygen. The PAO that use nitrate are referred to in the literature as DPAO, denitrifying PAO and 3) sufficient number of other cations such as magnesium and potassium to assist in the uptake of the phosphate. The metal ions are

required to neutralize the negatively charged phosphate ion, so that it can pass across cell membranes (WEF, 2006).

By alternating the anaerobic and aerobic stages of the process, a favorable environment for the production of bio-phosphorus (bio-P) or Phosphorus Accumulating Organisms (PAO) is created. The process requires an initial anaerobic stage for the PAOs to convert readily available organic material, often times volatile fatty acids, to polyhydroxyalkanes (PHA); energy is used in the process step and there is actually an increase in the phosphorus concentration during the anaerobic stage. The high-energy phosphate bond releases approximately 8 kcal/mole per bond (Grady & Lim, 1980). It is important to point out; the phosphate concentration has now changed from a polyphosphate concentration to an orthophosphate concentration and will as much as double in the anaerobic stage (Crites & Tchobanoglous, 1998). When determining the carbon source, methanol is a one carbon compound that will not be taken up by PAO. Volatile Fatty Acids (VFA), acetate, propionate are all used commercially to facilitate the growth of the PAO (WEF, 2006). It is important to note that while there is decaying biomass in the CWS and this is a large carbon supply, only a fraction is usable in the process (Kadlec & Wallace, 2009). In the wastewater stream available VFA include raw wastewater if the retention time is long enough, and breakdown of more complex carbon molecules by fermentation. Often times there are supplemental additions of VFA in the anaerobic stage of the system. The required energy is from the phosphate bonds in polyphosphate molecules. Because of the uptake of polyphosphate, the PAO are often referred to as PPAO, polyphosphate-accumulating organisms. In the aerobic stage, the PAOs oxidize

the previously stored PHA and the energy is restored with the orthophosphorus uptake and reformed as polyphosphates. The poly-phosphorus is now located in the biomass and can be removed (WEF, 2006). These two process steps can either be done in two separate cells of the process or operated in a sequencing batch reactor operated under alternating conditions (Lemos, Serafim, Santos, Reis & Santos, 2003). As we have seen throughout the research, the nutrients and energy sources (COD) are interconnected and one of the ways to estimate the amount of phosphorus that can be removed by the PAO is by looking at the bsCOD in the wastewater stream. bsCOD is the fraction of COD that is the biodegradable soluble COD. In order to have enough bsCOD, acetate is often added to the wastewater stream (Tchobanoglous et al., 2003; Linntech, 2010).

The ongoing research is looking at which PAOs are typically found in wastewater streams, how to isolate these PAOs and better understand the mechanisms in the mixed culture environment of constructed wetlands. Lu, Oehmen, Viridis, Keller, & Yuan (2006) looked at the *Candidatus Accumulator Phosphatis* PAO and the role that glycogen accumulating organisms (GAO) play in competing for limited carbon sources with the PAO. The research Lu et al. (2006) have been working on is for WWTP and not constructed wetlands, but better understanding the microbial environment overall will positively impact the understanding for constructed wetlands. They were successful in creating an environment where the PAO bacteria were at 90% in the lab samples and the GAO bacteria were eliminated. The goal was to design a method where the GAO bacteria were eliminated from the system because while they consume the carbon source they do not remove phosphorus from the wastewater stream. In the past, even if favorable

conditions exist for the PAO to remove phosphorus from the water, if the GAO bacteria are present in the system the overall efficiency of the system is negatively impacted. The experimental method used two different carbon sources, acetate and propionate, that were alternated every 1 to 2 sludge ages and the pH was maintained between 7 and 8. The PAO bacteria use either acetate or propionate at comparable rates and higher pH than the GAO. There are several GAO bacteria in the system and some prefer acetate and others propionate. In order to isolate PAO, the two carbon sources were alternated over a period of 20 months in order to slowly remove the GAO organisms from the system. After the lab bench system reached steady state, the effluent phosphate concentration was 0.2 mg/L. The amount of phosphorus in the volatile and total suspended solids (TSS) determined that the higher amount of phosphorus is stored in the sludge per gram of biomass at the lower COD/P ratio.

There is also ongoing research into the different metabolic pathways for different carbon sources by PAOs. Often times the laboratory studies will use one carbon source, but it is clear that the wastewater will contain a diverse mixture of substrates and the consumption of these produces different PHA compositions. Lemos et al. (2003) looked at the use of propionate acetate, and butyrate as the carbon sources in a sequencing batch reactor where the anaerobic residence time was 2 hours, the aerobic was 4 hours followed by 1 hour of settling time. The total sludge P content was 5.2% by weight. By using carbon isotopes, a key result showed that the PHA polymer formed was different for each of the carbon sources.

As has been pointed out elsewhere, the removal of phosphorus as one of the nutrients in excess is seldom in isolation, the removal of ammonia is also required. Ongoing research is looking at the denitrifying phosphorus accumulating organisms (DPAO) and their role in the microbial phosphorus removal processes. Filipe & Daigger (1999) looked at why DPAO are not always observed in biological excess phosphorus removal (BEPR) systems. As stated earlier, with the BNR systems for phosphorus removal in WWTP, the anoxic stage is for denitrification and does not impact the removal of phosphorus from the waste stream. However, ongoing research has looked at DPAO and the conditions required for phosphorus removal in the anoxic stage of BNR systems. The experimental design and results showed very clearly the Monod kinetics necessary to characterize the system. The Monod kinetics model clearly demonstrated the switching between the oxygen and nitrate in the overall process and the conclusion that the fraction of PAO available will be higher for aerobic process compared to the anoxic stage. There are several other important conclusions: 1) timing is critical, DPAO bacteria need to be exposed to anoxic conditions while they still have a high content on PHB and recirculation of the biomass between the anaerobic and anoxic zones will favor DPAO selection. Because the timing is critical, DPAO are not always in the system even if an anoxic stage is a part of the process. 2) The return of activated sludge will introduce nitrate and oxygen back into the system and strongly affect the accumulation of the DPAO. 3) There are stoichiometric differences between the PAO and DPAO because of the different phosphorus to oxygen requirements, referred to as the P/O ratio. There is also a difference in the energy efficiency of the different PAOs. The DPAO use the stored

PHB less efficiently when the P/O is anoxic. So while they exist, they will never be as efficient as the PAO that uptake phosphorus in the anaerobic-aerobic process. 4) Within the research on PAO, it is thought there are two different types of PAO, one that uses either nitrate or oxygen as the terminal electron acceptor and another type that only uses oxygen. 5) If phosphorus removal is required in the anoxic stage of the process, the nitrification and phosphorus removal should be decoupled or there should be two sludge systems to minimize the exposure of the PAO to oxygen.

As has been stated earlier, PAOs require oxygen or nitrate as a final electron acceptor for final phosphate removal. Ongoing research by Bion Environmental Technologies (BET), (BET, 2011; Morris & Northrop, 2008; Morris & Northrup, 2009), has shown that low oxygen PAO processes are possible. I have had an opportunity to interview James Morris, the CTO officer of Bion Environmental Technologies on two occasions to better understand the process. The company works with large-scale commercial livestock/dairy operations to provide solutions to both wastewater treatment and use of biomass for energy requirements. They are currently working in the Chesapeake Bay area in Pennsylvania as a nutrient trading program is implemented (BET, 2011). The electron environment is very low in concentration and the PAO are referred to through the patent and corporate literature as MEPAO, micro-electron PAO. The dissolved oxygen level is kept low, at less than 2.0 mg/L and the nitrate level is kept below 0.5 mg/L. The low oxygen environment is very similar to the research done by Filipe & Daigger (1999) and the additional process calls for the wastewater stream to be recycled through the system including the anaerobic cells where additional soluble

phosphorus is removed. As stated, “the process favors the growth of PAO denitrifiers” (Morris & Northrup, p. 15). The patented process combines both the use of MEPAO and metal ions from ferric sulphate, ferric chloride, and alum in combination with an organic polymer. The processes for the chemical removal of phosphorus also play an important role; the phosphorus removal efficiencies are in the range of 75% and the particulate phosphorus is permanently removed from the wastewater stream. The actual MEPAO environment is patented; an environment has been developed for the fast reproduction of the MEPAO organisms with a doubling time of less than 30 days and a HRT for the process of 15 to 20 days at a pH of around 7.0. The solids are separated from the MEPAO environment for recovery. The MEPAO biomass will have the particulate phosphorus and the metal ions will have removed the remained of the soluble phosphorus from the wastewater. The concept of using biological nutrient removal and chemical precipitation in tandem is gaining acceptance in the industry. After processing, the wastewater stream is released into a wetland environment or water lagoon and the sediment at the bottom of the wetland/lagoon is dewatered for the recovery of the humus material.

*Biofilm Reactors:* One unique example of a biofilm reactor that successfully removed nutrients and carbon from a pretreated swine slurry was the tubular reactor designed and tested by the University of Valladolid and University of Leon, both of Spain.

The focus of the research was to design a single stage tubular reactor that removed nitrogen, phosphorus, and carbon using transparent PVC tube; bacterial species (microalgae), *Chlorella sorokiniana*; and illuminated lighting for the pretreated swine

slurry. For the purpose of this experiment, the wastewater was centrifuged and the soluble fractions of carbon, and nitrogen and phosphorus were considered, referred to as Centrifuged Swine Slurry (CSS) (de Godos, Gonzalez, Becares, Garcia-Encina & Munoz, 2009). The biofilm reactor removed the phosphorous from the wastewater via assimilation into the algal-bacterial biomass or  $\text{PO}_4$  precipitation. The photobioreactors operated for 3 months under continuous light and 7 day Hydraulic Retention Times (HRT) and increasingly concentrated CSS loading rates. The nutrient concentrations were measured twice weekly and the biomass was characterized by testing the Volatile Suspended Solids (VSS) and the Total Suspended Solids (TSS).

The sustained removal rate of the phosphate was comparable to conventional activated sludge operations and was approximately 80% when compared to inlet concentrations of 120 mg/L. There were a couple of other interesting points that should be noted: 1) the microalgal phosphorus content was 2.1% the specific biofilm and typically, in other applications the percentage is closer to 1.3%. 2) The pH range was 8.5 to 9 during the experiment. It is believed this led to a higher than normal  $\text{PO}_4^{-3}$  precipitation within the algal-bacteria biofilms, and 3) the cross section of the phototubular reactor showed the most active part of the biofilm was the microorganisms exposed to the light and not the organisms directly exposed to the bulk liquid (de Gatos et al., 2009). The initial experiments were performed in a lab setting and the next phase would be in a longer-term outdoor environment.

A second example of a bioreactor that successfully removed phosphorus was designed and tested in Wuhan, China. The reactor was tested in both batch and

continuous mode to characterize the reactor. Similar to the tubular reactor mentioned above because of the PVC tubular reactor design and the use of illuminated lighting. To improve the biofilm growth, inside the PVC pipes were fibers that look like bottle washers that radiate from the center of the PVC pipe. The fiber technology allow for the removal of the algae from the wastewater and the final effluent. The overall removal efficiency for phosphorus was 98% for the batch process and the HRT was only 4 days. The continuous mode results were 95% removal of TP and an average effluent of less 0.5 mg/L. The mechanisms of removal are biofilm assimilation of the phosphorus for growth and some precipitation of the phosphate because of cation concentrations in the influent. It is also important to note that the pH of the water changed from an influent of 8 to 10.8 at the effluent (Wei, Hu, Xiao, Sun & Tao, 2008). This technology was of interest because the there is a possibility of substituting the fibers using in this study with the BioHaven fiber material.

*Membrane Bioreactor:* There are several membrane bioreactors (MBR) that are available commercially. In general suspended media filtration systems, when part of the overall WWTP will have between 1 and 2 % TP in the mixed liquor suspended solids (MLSS) at the end of the process (MPCA, 2006).

The Koch Membrane System uses a hollow fiber technology that is vertically submerged into the pretreated wastewater. The reinforced hollow fibers are packed in bundles, attached together at the bottom of the system; each fiber is approximately 2.6 mm in diameter and several feet tall. The fibers are free to move in a seaweed- like action and the filtrate water passes through the center of the fiber trapping all contaminants to

the outside of the fibers. The results showed that with the proper BOD/P ratio of 10 to 25 (addition of acetate to an earlier anaerobic stage), the membrane technology reduced the phosphorus from an influent concentration of 8.0 mg/L TP to an effluent of 0.4 mg/L TP. The membrane bioreactor also reduced the SRT (solids retention time or sludge age), which is important in managing phosphorus removal, because as the SRT increases, the microbial activity will decrease and the contents of the cell mass will be released back into solution, including the phosphorus tied up in the cell mass. The pilot study demonstrated how the MBR could be used as one component of a larger wastewater treatment system (KMS, 2010; Koch & Von Gottberg, 2009).

This technology caught my attention for a couple of different reasons because it might be applicable to the design and application of constructed wetlands. The plant roots used in constructed wetlands are similar to the submerged hollow fibers. “The submerged plant roots of emergent marsh plants (cattails, bulrushes, and reeds) in constructed wetland systems are hollow vessels that enable the oxygen transport. This in turn enables microbial aerobic decomposition processes and the uptake of pollutants and excess nutrients from the water, however the direct uptake is less than floating and submerged plants” (Sim, Eikaas, Chan & Gan 2010, p. 1515). In a constructed wetland where the plants are rooted and attached to the wetland soil, additional research comparing the MBR fibers and plant phosphorus removal uptakes efficiencies is being undertaken. Another interesting point would be to use the fiber technology of the Floating Islands in a vertically submerged design, essentially replacing the hollow fibers with the BioHaven mat material. The BioHaven mats have been specifically designed to float on the top of

the wetland, but there is possibility of replicating some of the MBR processes if the BioHaven mats were attached to the bottom of the wetlands system and allowed to mimic the seaweed like action of the fibers. The water would flow perpendicular to the fiber materials.

The submerged MBR technology being used for greywater treatment in Australia uses a series of vertical membrane technologies that have a pore sizes between 0.1 and 0.4 microns and can are currently being designed for the smaller household scale and the larger industrial sizes (Allen et al., 2010). These systems are designed to operate at lower energy costs despite the required aeration for biological reactions and minimization of clogging.

At Hiroshima University, Watanabe, Ozaki, Iwashita, Fujii & Iefuji (2008) demonstrated that by breeding two specific wastewater yeasts, *H.fabianii* J640 PFW4 and *H.anomala* J224-1 PAW1, the phosphorus uptake was 2.2 to 3.5 times greater than the parent strains. In the same study, they also demonstrated that the mutant yeasts removed not only the inorganic phosphate but also organic phosphorus compounds. Because the wetlands need to also remove carbon and nitrogen from the water, the ratio of C/P removal was also confirmed to be twice the parent strains. An additional goal was to demonstrate that the sludge produced by the biomass could be harvested for the accumulated polyphosphate granules.

### Chemical

The chemical environment of the constructed wetland plays an important part in the overall removal of nutrients and the final effluent parameters. The water chemistry

and the soil-water interface are very complex and not often looked at in detail when evaluating constructed wetlands. Within the context of the literature review, there is a very brief overview of some of the important concepts. It is well documented in the literature that using chemical additives in the constructed wetlands has been successful in improving the removal of phosphorus and is often cost effective for phosphorus because of the difficulties of removing phosphorus. The chemical additives allow the constructed wetland to be smaller and often provide more consistent results (Kadlec & Wallace, 2009). Often times the chemical additives used are similar to the chemicals used in traditional wastewater treatment as one of the process steps or wetland cells in a hybrid process. The commonly used chemical additives in CWS are referenced to applications in the field that have been successful. The chemical additive is often locally sourced and a waste product of other industrial operations; examples include steel slag, oil shale ash, and alum sludge. Natural materials and composite materials are also used. These materials incorporate various metal ions such as iron, calcium, magnesium, and aluminum and the associated compounds as well as limestone and clay products and finally engineering composite materials and processes that are licensed commercially such as ZEOLITE and lightweight aggregates. These chemical additives are used in a variety of ways and occasionally the phosphorus from these processes is recovered for other applications. The ongoing focus for improved removal of phosphorus in wastewater streams is the reason for continued interest in indentifying chemical additives that will work in a long-term setting. In essence the trade off is: chemical additive vs. much longer

retention times and larger land areas for the constructed wetlands (Cooper, McBarnet, O'Donnell, McMahon, Houston & Brian, 2010).

As a word of caution, the addition of chemical additives to an existing wetland can have long-term negative effects to the overall removal of phosphorus from the system. Kadlec & Wallace (2009) point out that when alum was added to a lightly phosphorus loaded wetland in Michigan after five years of operation, the phosphorus removed improved significantly for the short term, however, the stored labile phosphorus in the sediments re-released to reestablish the equilibrium and the export of phosphorus added 25% to the overall load for the calendar year required to establish a new equilibrium. The wetland systems do not respond instantly to either reduced loads or drastic changes in the overall management of the system. Another important consideration when using the metal ions as chemical additives is polymers are often added to improve the flocculation of the co-precipitate. Another consideration when evaluating chemical precipitates is determining if the precipitate is kinetically stable or is it reversible. The pH of the wetlands system is an important indicator as to the stability and final composition of any precipitate. Solubility coefficients are available for all Al, Mg, Ca, and Fe phosphate combinations (Stumm & Morgan, 1980). The effluent water pH will be higher than 9.0 with the addition of many of the chemical additives such as LECA, blast furnace slag, and needs to be taken into account (Kadlec & Wallace, 2009). As has been pointed out throughout the literature the re-release of phosphorus is possible at either the soil-water interface or in the water if the conditions are right (Pontius, 1990). The trend for chemical additives for phosphorus removal is stand alone cells or chemical

filters that are incorporated into the wetlands. The addition of the chemicals needs to be upstream of the wetland because there are difficulties with providing the chemical contact in the wetland (Kadlec & Wallace, 2009). There are recent articles that suggested mixing the metal salts with the soil in the constructed wetland (Crites & Tchobanoglous, 1998). There is some discussion as to how the chemical additive is applied to the wetlands or lagoon system; either continuous flow application or batch feed process includes an application of liquid poly aluminum applied directly to the wetland. (Crites & Tchobanoglous, 1998)

Calculating the amount of chemical additive required is not as simple as the molar ratios would indicate. However, as a rule the amount of chemical additive will be closer to the molar ratio for higher concentrations of influent phosphorus. However, when removing phosphorus to an effluent concentration of 0.1 mg/L or if the influent concentration is low, the dosage will be higher than the molar requirements because of side reactions (Tchobanoglous et al., 2003). When determining the amount to chemical required, the system as a whole needs to be evaluated, and pH and alkalinity need to be measured as well (WEF, 2006). Another important point that is taken into account for Biological Nutrient Removal (BNR) WWTP is the determination of the required amount of phosphorus needed for all biological processes. Essentially, if too much phosphorus is removed or it is removed at the wrong place in the process stream with chemical additives, the downstream biological processes will not have the required soluble reactive phosphorus (SRP) necessary (WEF, 2006).

The various chemical additives used for phosphorus removal with constructed wetland examples show the success of the additives; in all cases one specific chemical is used. One example of a BNR that caught my attention was the use of both ferric and aluminum chemicals for the removal of phosphorus. In Atlanta Georgia, the Cobb County Water Reclamation Facility (WRF) used ferric chloride at the beginning of the process and alum at the secondary clarifiers. Over several years of monitoring, the effluent phosphorus concentration has been less than 2 mg P/L. In the wastewater, the orthophosphate to total phosphorus ratio was only 0.2 and a typical wastewater would be closer to 0.5. This wastewater also had higher than normal particulate phosphorus concentrations in the TSS. With real-time measurements of the wastewater stream the actual amount of chemical additives are adjusted as needed (WEF, 2006).

Because of the ever changing environment in a constructed wetland, the chemical equilibrium is not at steady state and the equilibrium constant ( $K_{eq}$ ) used in chemistry to determine the final concentrations of the ion species needs to be modified and is typically referred to as the ion activity product (IAP) in water chemistry nomenclature. When looking at the equation under consideration, if the  $IAP > K_{eq}$ , then the reaction will tend to go to the right, if the  $IAP < K_{eq}$ , then the reaction will tend to go the left. As an example, research has shown that the solubility of  $Fe_3(PO_4)_3 \cdot 8H_2O$  (mineral vivianite) is a major control of the Fe and phosphorus concentrations in the water. Essentially, because the waters are rarely supersaturated with respect to the metal ions, the equilibrium constant,  $K_{eq}$  is the upper limit to the dissolved concentrations of the dissolved metals but the lower limits of the IAP are difficult to establish. Secondly, the

crystalline disorder of the precipitates also impacts the final concentrations of the ions (Drever, 1982). The practical implications are that the stoichiometric determinations will not always correlate with the field results.

At the anion - cation- exchange level the water – soil surface will either be negatively or positively charged and a point where the net charge is zero is referred to as the isoelectric point. As an example the naturally occurring Al mineral  $\text{Al}(\text{OH})_3$ , referred to as gibbsite, has an isoelectric point where the Al ion will be neutral at a pH of around 9. However, the zero point of charge (ZPC) is referred to, as the pH where the net charge is zero will be different if anions such as phosphorus are adsorbed to the soil surface. Understanding the isoelectric point is important because it indicates the pH range for anion- cation exchange and the pH range for stable colloidal (i.e. precipitation) suspensions can occur (Drever, 1982). The isoelectric point of phosphates with Al and Fe hydroxides shifts the precipitation to lower pH values (Stumm & Morgan, 1980). The complexity of water chemistry is well understood but within the constructed wetlands industry, there was very little discussion of these concepts except to globally predict how the pH may influence the removal of different nutrients.

An important study, Babatude, Zhao & Kumar (2010b) looked at 39 different materials, 25 industrial by-products and 10 manufactured products as potential P removing substrates and media for a poster session in Italy at the 12<sup>th</sup> IWA International Conference on Wetland Systems for Water Pollution Control. The final report of the data has not been released but “there has been no review of the release of substances from such materials when in used in constructed wetlands and their environmental

implications” (p. 1188). Evaluating a large number of different products and industrial waste products is gaining momentum; an ongoing study looked at 17 different by-products of steel industry (Barca, Gerente, Meyer & Chararenc, 2010). Questions still to be answered include the re-release of phosphorus and/or the release of heavy metals in full-scale systems in operation when using such additives. As researched by Vohla, Koiv, Bavor, Chazarenc & Mander (2010), there has not been enough research at the full-scale constructed wetland size to confirm long term P removal but there are indications that P retention capacity significantly decreases after a 5-year period of application and more studies of full-scale systems is needed.

Another example that is being considered is a sacrificial bed, which can be changed out when it is fully spent. (Cooper et al., 2010; Arias, Brix & Johansen, 2003). These units would be separate filter units containing a replaceable material with the high P-binding capacity (Vohla, Poldvere, Noorvee, Kuusemets & Mander, 2005). These are acceptable alternatives because the phosphorus is either adsorbed onto the substrate and eventually saturated or precipitated; the question of longevity of the sorption capacity and the recycling of the material becomes important.

There are interesting applications under development. A company in the midwest that is working with Floating Islands International is Aquatic Biologist Incorporated (ABI) and they are installing the BioHaven mats. As a proprietary product they have over 80 different combinations of sediment blocks that are essentially combinations of different chemicals that dissolve slowly and improve water quality including phosphorus removal. The blocks are a group of soil-specific, slow dissolving and slow releasing

blocks containing blends of water treatment components and anionic polyacrylamide. The sediment blocks require flowing water conditions and do not contain aluminum or sulphates. As an example, one block will treat between 1 and 1.2 million gallons of water. The literature does not mention the by-products of the chemical reactions but is none the less an interesting concept (ABI, 2011).

Poly Aluminum Chloride: Poly aluminum chloride (PAC) is a class of chemicals that is similar to alum and typically has more Al sites for reaction and precipitation with phosphorus but is not used in environmental restoration projects because it is twice as expensive as alum.

The basic chemical reaction is shown in the section on alum sludge. PAC is the class of chemicals used for drinking water purification and the alum referred to in the next section is the waste product associated with the drinking water purification process. A study in North Carolina (Reddy, Forbes, Hunt & Cyrus, 2010) looked at using PAC in constructed wetlands that had been receiving swine wastewater for over nine years and the purpose of the pilot study was to see if PAC would work to restore the CWS. When the constructed wetland was originally installed, the phosphorus removal rate was 47% but it had slowly decreased over the nine years of operation to a low of 27 % because of heavy loading of the P from the anaerobic lagoons at the start of the process stream.

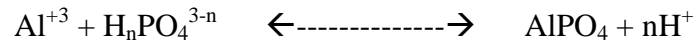
The wastewater from the swine houses was first stored in a two-stage anaerobic lagoon pond and then distributed to the wetland cells. The diluted PAC solution was distributed to the wetland cells by continuous injection. The effluent  $PO_4P$ , TP and Al concentrations were taken and soil concentrations for the: SRP, TP, Fe-Al bound P, Ca-

Mg bound P and residual phosphorus were also measured. At a concentration of 3-6 mg/L of PAC, 100% of the phosphorus was removed from the swine wastewater.

The key consideration with the addition of PAC into the CWS is controlling the pH. The pH of PAC is 2.5 and the pH of the system decreased slightly when a dilute solution was used in the wetland, but for the wetland under study the pH in the water and soil remained in the range of 6 to 8; the system and wastewater were highly buffered. The  $\text{AlPO}_4$  is a solid and basic water chemistry research shows that at a pH of 5.5 the solubility of the solid is at a minimum. In the water environment, the competing reaction will be  $\text{AlOH}_3$  (aluminum hydroxide), also a solid, and it is necessary to add twice as much of the aluminum salt as required by the stoichiometry because of the aluminum hydroxide precipitate. However, the  $\text{AlOH}_3$  also aids in the settling of the  $\text{AlPO}_4$  (Snoeyink & Jenkins, 1980).

An interesting application of poly aluminum chloride is a proprietary product produced by Aquatic Biologists Incorporated (ABI) for reduction in turbidity, TSS and nutrients, including phosphorus. The Bio Boost Phosphorus Cleaner (BBPC) is a concentrated solution of poly aluminum hydrochloride that when added to the water removes phosphorus. The solution contains 23%  $\text{Al}_2\text{O}_3$  and is highly basic so that the pH of the water is not adversely impacted. As an example, 1 gallon of the chemical treats 326,000 gallons of water with phosphorus concentrations of 3 – 6 mg P/L (ABI, 2011). The corporate literature does not mention the Al- P precipitate and requirements for disposal.

Dewatered Alum Sludge: The chemical equation for aluminum and phosphate is:



Looking at the equation, there are a couple of things worth noting, the reaction competes with other reactions in the natural system and is dependent on the alkalinity, pH, and the other elements in the wastewater. Measuring the amount of Al in the wetlands soil is typically an excellent indication of the amount of phosphorus that will be absorbed by the wetland from all the metal ions. As with the other chemical precipitates if the alum is added to the wastewater, the flocs that form are difficult to settle in the wetland so, the addition of alum to the wetlands is often done as a pre-treatment in a separate cell. One example is the addition of the alum from the water treatment facility to the soil; mixing the alum to the soil as a soil amendment will improve the number of adsorption sites for the phosphorus in the wetland (Kadlec & Wallace, 2009). In order to remove 95% of the phosphorus in the wastewater will require a molar ratio of approximately: 2.5 moles of Al/ 1 mole of P (Tchobanoglous et al., 2003). The  $\text{Al}^{+3}$  ion is from the aluminum salts such as aluminum sulphate and the precipitation of the  $\text{AlPO}_4$  falls as the concentration of the phosphate decreases. The removal percentage of phosphorus will be as high as 80 – 90%, when the alum concentration is between 50 – 200 mg/L. The aluminum concentration can adversely impact the microbial activity and the pH of the water will increase based on the buffering capacity of the system but the removal of phosphorus with Al ions will yield good results when the pH is in the range of 6.5 to 7.0. The precipitates can cause a problem because of settling and often times a polymer is added to improve the settling and reduction of the TSS (Lenntech, 2010; Tchobanoglous et al., 2003). As an example, alum is made of the following metal ion

concentrations: 93% Al, 5% Ca, and 2 % Fe (Yang, Zhao, Wang, Guo, Ren, Wang & Wang, 2010).

Several recent studies looked at using dewatered alum sludge for enhancing the removal of phosphorus in the wastewater streams. Dewatered alum sludge is “a by-product of drinking-water treatment processes. It is obtained when aluminum (Al) salts are used as a chemical coagulant. Once alum sludge is dewatered, however, aluminum hydroxides become the dominant constituent, making it possible to reuse the sludge as a valuable raw material in wastewater treatment. The aluminum hydroxide ions enhance adsorption and chemical precipitation processes that remove various pollutants, especially phosphorus, from wastewater” (EPAIE, 2011). Babatunde, Zhao, Kumar & Hu (2010a) at the University College Dublin are lead researchers on the use of alum in wetland applications and have shown that a 2-stage constructed wetland with the addition of Al operated in a tidal flow system successfully removed  $\text{PO}_4 - \text{P}$  on the order of magnitudes greater than constructed wetlands without the added alum sludge in the substrate.

At Xi'an University, the alum sludge was used in a tidal flow constructed wetland with successful results, removing 99.5% of the phosphorus from the wastewater stream by performing two different functions. The alum served as an adsorbent for the phosphorus and as substrate for aerobic biofilm production for the removal of other nutrients (Yang et al., 2010; Zhao, Zhao & Hu, 2010). The system was a four stage in series, vertical subsurface flow constructed wetland (VSFCW), and there was a comparison between raw dewatered alum and air-dried alum sludge, 83% water content

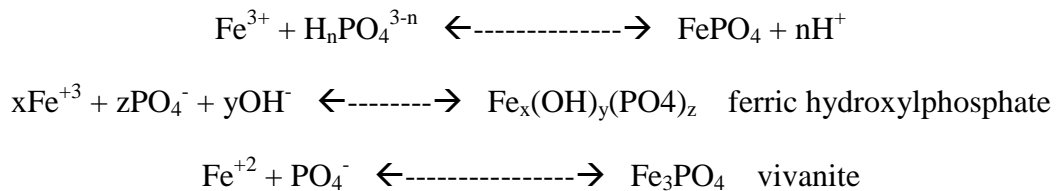
vs. 26% water content respectively. The four stages removed the phosphorus in succession: but “the P removal contributed by an individual stage was highly dependent on the amount of P in the effluent of the previous stage” (Yang et al., 2010, p. 1095). Zhao et al.(2010) in the setup and design of the study designed 3 different scenarios and evaluated the differences in removal efficiencies of not only TP but also soluble reactive phosphorus (SRP), the kinetics of the removal mechanism, the use of tidal flow with recirculation within the system and the final scenario looked at the first cell being anaerobic. First order kinetics was confirmed by showing that the amount of TP removed was linearly related to the HLR of the phosphorus in the influent. The removal of SRP corresponded with the removal rates of TP, in the range of 98% removal. The use of tidal flow and recirculation of the effluent water back to the first cell of the wetland did not improve the removal of phosphorus but did improve the removal of other nutrients. When the first cell of the system was anaerobic, again, the P removal was not impacted but the other nutrient removal rates were markedly better. In all of the different experimental designs, over 90% of the P was removed in the first cell. It is expected that once the first cell is saturated with P, the removal will take place in the next cell in the series. The other important conclusion highlighted was the necessity of removing all suspended solids (SS) from the wastewater before the water enters this configuration of constructed wetland. In this study, the SS was removed with a sand filter.

Alum has also been used to reduce the phosphorus concentration in the water when the primary concern was an algae bloom. The alum inhibited the phosphorus release from the bottom of Lake Eola in Florida. The alum was applied to the surface of

the lake at a concentration of 200 mg/L and resulted in reductions of algae, dissolved orthophosphate, total phosphate and other constituents (Pontius, 1990).

One of the advantages of alum over iron compounds is that aluminum does not undergo reduction –oxidation reactions like iron ( $\text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$ ) in anaerobic conditions; ferric reactions are more sensitive to redox potential changes in the ecosystem and there is an additional concern about the increase in sulphate ions in the effluent streams if ferric sulphate is used (Sherwood & Quall, 2001).

Ferric Compounds: The basic chemical equations for the ferric ion and phosphate are:



There are two considerations when looking at the role that ferric compounds play in removing phosphorus in constructed wetlands: the ferric oxyhydroxides minerals found in the soils and sediments of the wetlands and secondly, the addition of iron compounds to the wetlands to improve the removal efficiency of the phosphorus. Typically, the iron in wetlands is not quantified as to whether it is in a soluble or particulate form. According the Kadlec & Wallace (2009), this is a critical unresolved issue in wetlands research. Research using ferric compounds in constructed wetlands has been studied extensively and the original work showed promise of removing phosphorus to levels as low as 30 µg/L but the challenge is the Fe-P flocs do not settle quickly even at long hydraulic retention times (Kadlec & Wallace, 2009). Determining the amount of

iron required for the phosphorus concentration in the wastewater is in theory a 1:1 molar reaction as is the case also with Al metal ions, but the competing reactions in the water will require bench scale tests using the wastewater in question. As a rule of thumb, removal of 95% of the phosphorus in the water will require a molar ratio of 3.5 Fe to 1 P (Tchobanoglous et al., 2003). As an example, the amount of ferric chloride required to remove 1 gm of phosphorus is 5.24 gm of  $\text{FeCl}_3$  and the amount of ferric sulfate will be 7.36 gm for each gram of phosphorus removed (WEF, 2006).

Other considerations in Fe- P chemistry are the pH, alkalinity, and temperature of the system. The pH at the high and low pH values of a wastewater will also impact the other complex polynuclear species that are formed but at a pH between 6.5 and 7, there will be good phosphorus removal (Tchobanoglous et al., 2003). The solubility of the Fe-P precipitates means the reactions are different than other metal salt – phosphate combinations. Typically, the solubility of metal ion-P complexes will go up with increase in temperature but in the case of  $\text{FePO}_4$ , the opposite is true. For example the solubility constant for  $\text{FePO}_4$  precipitate is  $1.03 \times 10^{-19}$  at 50 °C and  $1.19 \times 10^{-18}$  at 25 °C (Snoeyink & Jenkins, 1980).

*Ferric Reactions with Phosphate from Soil and Sediments:* Ferric oxyhydroxides are reduced by the bacteria in the soils to the form  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$  cations that are then available for reaction with the phosphate anions as pointed out above in the Fe- P chemical equations (Sturman, Stein, Vymazal & Kropfelova, 2008).

It has been shown that the reduction of  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  in the anaerobic environment is one of the mechanisms for re-release of phosphorus in the water and a reduction in the

sorption capacity of the soil in the wetland (Shewood & Quall, 2001; Snoeyink & Jenkins, 1980). The reverse reaction of  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$  (oxidation) takes place in the soil environment when the wetland plants transport oxygen into their roots to support respiration and an aerobic environment (Allen, Hook, Biederman & Stein, 2002). The reaction with phosphorus and  $\text{Fe}^{+2}$  is not fully understood in the BNR systems. The molar concentrations of  $\text{Fe}^{+2}$  would indicate that the ratio would be 3:2; however the experimental results are closer the  $\text{Fe}^{+3} : \text{P}$  ratio of 3.5:1 (WEF, 2006).

Much of the work done to understand the ferric – phosphate interactions in soil and sediments has been done within the confines of the mining industry. Equally as important to the ferric phosphate precipitates is the re-release of phosphorus back into the wastewater stream. Biohydrometallurgy is the study of biofilms used to remove the phosphorus found in metal ores and is based on research that has demonstrated microorganisms remove phosphorus in nutrient limited environments (Delvasto, Ballester, Munoz, Gonzalez, Blazquez, Igual, Valverde & Garcia-Balboa, 2009). Depending on whether the environment is aerobic or anaerobic, there are different microorganisms that are controlling the process. In an aerobic environment, at steady state, the pH decreased slightly and the microbial population reached a stable population in the first three days of the reaction. The reactions of phosphate scavenging show a threshold phosphorus concentration of between 15 – 50 mg/L in the water. An interesting side note of this research showed that the phosphorus was not removed from the ferric compounds in a linear continuous fashion as expected but rather has several rises and falls in the P concentration, indicating that the phosphate is bacterially removed initially

and then re-immobilized and then removed again. This is a dynamic process that is also influenced by the high-phosphate binding capacity of the iron oxides.

As reported in this research and others (Vohla et al., 2010), anaerobic conditions, air limited, favor the release of phosphorus and the decrease in pH as well. When compared with the aerobic study (Delvasto et al., 2010), the phosphorus re-released into the water was actually less in the anaerobic test. In the lab setting, the results for phosphorus release aerobically and anaerobically were 20% and 7.3% respectively. Because the ferric-phosphate precipitate eventually falls to the bottom of the wetland and is in the sediment, the anaerobic conditions are typically, what are seen in CWS, there is more focus on the re-release of phosphorus under these conditions. Depending on the permit requirements for a specific wastewater, a 7.3% re-release may or may not be significant. Additional research has shown that there is a possibility of extraction of the phosphate can be accumulated not only in the “cellular material but also precipitated with the biomineralized secondary ferric oxides because of the higher surface area and reactivity of these oxides” (p.7). The ideal application for CWS requires an understanding of the complex biogeochemistry environment of iron and phosphorus.

*Ferric Reactions with Phosphate and Other Additives:* The ferric ions, often from ferric chloride or ferric sulphate combine to form the ferric phosphate compounds.

The ferric phosphate reacts slowly with the natural alkalinity of the wastewater, so it is important to verify the pH of the effluent and often times lime,  $\text{Ca}(\text{OH})_2$  is added to raise the pH of the water. Lenntech (2010) and Cooper et al., (2010) have done research using  $\text{FeCl}_3$  liquid for removing phosphorus before the wastewater enters the

constructed wetland systems. The study used a hybrid constructed wetland with a HSSF unit followed by a VF wetland to treat high strength runoff from a fertilizer plant. To meet the requirements for the effluent of 0.5 gm/L of PO<sub>4</sub>-P from an influent of 60 mg/L, chemical dosing was required. The ferric chloride was initially added and the floc (ferric-phosphate precipitate) would settle in a holding lagoon preceding the CWS. The primary reason for the holding tank was to minimize the clogging of the reed beds in the CWS.

In Belgium there is ongoing commercial work related to using iron as a substrate additive in the constructed wetlands because of the clogging difficulties with using products like steel slag that contain a percentage of iron in the composition (van Oirschot, 2010). The results better are than 90% removal of phosphorus from the wastewater.

The majority of the recent research in ferric compound additives, the ferric chloride is added in a separate cell and not directly into the wetland. As a part of the Everglades Nutrient Removal Project, lab scale research was done to determine if ferric chloride could be added directly to the everglade marshes with the goal of reducing the P concentrations in the water to below 50 µg P /L. The ferric chloride would be added to the wastewater directly and then as the water traversed through the wetland, the marshes would serve as the settling pond for the precipitate. In addition to the biological processes in the marshes would increase the retention time and allow for lower doses of chemical to be applied (Sherwood & Quall, 2001). To track the phosphorus throughout the series of experiments, isotope P was analyzed in soil and water samples. Taking into account the soils of the Everglades project, the ratio of Fe<sup>+3</sup> to Fe<sup>+2</sup> in the soil sediments was as high as 26 in the samples where the ferric chloride was added; however the re-release of the

phosphorus did not happen as expected. The  $\text{Fe}^{+3}$  remained in the soil for several weeks. The natural soil ratio of  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  was 7. Given the biogeochemical environment of the Everglades, the conclusions after monitoring the soil/water columns for several months indicate that the addition of ferric chloride is a viable option for the long-term storage of phosphorus and the final effluent concentrations will be less than a few  $\mu\text{g P/L}$  and warrants a larger field study. The low solubility of the ferric and phosphorus complex indicates that it formed vivianite, which is a stable mineral.

Zero valent iron (ZVI) when in an aqueous water solution (aerobic or anaerobic conditions) will disassociate and form the  $\text{Fe}^{+2}$  ion, which can then be used for removing phosphate from wastewater streams. Research has been done on the use of this form of iron by Chang & Choi, 2000. This set of laboratory experiments looked at denitrification in the presence of phosphate with ZVI. There are two mechanisms with respect to the phosphate ion that are important: the phosphate ion is adsorbed onto the metal ion surface and secondly the Fe and phosphate precipitate out at a slower rate than the adsorption. Relative to slower wetland processes, the reaction was a very fast process in the lab and more than 99% of the phosphate was removed within 10 minutes but it is important to keep in mind that the pH of the system will impact the final result.

One interesting application of a constructed wetland was the dewatering of ferric sulphate drinking water sludge (Nielsen, & Cooper, 2010). This was an application using the ferric sulphate to see if the plants in a constructed wetland could thrive in a harsher chemical environment. The reed beds not only dewatered the sludge (long residence time of 30 - 55 days) and the phosphorus concentration was quite high, between 8000 and

11,000 mg P/kg dried sludge. The outcome is that despite a somewhat toxic environment of the ferric sulphate and other contaminants, the plants survived were covering the area of the wetland beds overtime.

Oil Shale Ash: At the University of Tartu in Estonia, Vohla et al., (2005) looked at 14 different local materials rich in Ca, Fe, Mg and Al including sands, gravel, LWA and oil shale fly ash and the sediment from the oil shale ash plateau.

The ash and ash sediment are both waste products from burning the oil shale for its energy source. The oil shale ash has a composition of over 40% CaO. For the purpose of this experiment the oil ash, oil ash sediment and crushed ash block were packed in plastic nets. From the batch experiment results it was determined that 1200 kg of the oil shale ash plateau could remove 5 – 6 kg of phosphorus at 96 - 100 % removal of the phosphorus in the water. These results were significantly higher than the other materials used in the study. It was also determined that by using the oil shale ash the hydraulic retention time (HRT) was considerable shorter in the range of 2 days. The follow up experiments recommended further characterize oil shale ash relative to hydraulic conditions and the possibility of constructing a prototype of the filter on a VF constructed wetland system.

Light Weight Aggregates: Lightweight aggregates (LWA) are defined as expanded manufactured clay aggregates with high porosity, high hydraulic conductivity and high concentrations of Ca, Fe and Al (Giaever, 2000).

An example of a commercially available LWA is Filtralite and the composition of the aggregate is documented in the company literature. As an example, there is 62% SiO<sub>2</sub>, 18% Al<sub>2</sub>O<sub>3</sub>, 7% FeO<sub>3</sub>, 4% K<sub>2</sub>O, 3% of MgO and 3% CaO. The porosity of the aggregate is 41% and the voids are 53% of the material (Filtralite, 2011). The high porosity and hydraulic conductivity improves the removal of TP by 80% compared to only 59% for a pretreatment filter and 75% for a sandy wetland in northern Norway. The configuration of the wetland system is complex and the pretreatment filter included LWA. The second stage is a HSSF wetland that contains sand with oxidized iron; the sand was chosen because it is locally available and finally there is a planted HSSF wetland with additional LWA. The three units were also required to eliminate BOD and nitrates and the combined removal efficiency for phosphorus was 98%. (Giaver, 2000) Composite materials like Filtralite are used in constructed wetlands and there is a preference for this process step in the Scandinavian countries.

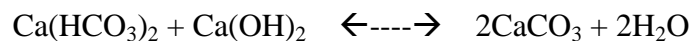
A more recent example of LWA materials being used in Norway was a study completed for the 12<sup>th</sup> IWA International Conference on Wetland Systems for Water Pollution Control in Italy that showed the continued challenges of cold-climate nutrient removal and the importance of maintaining the systems. Phosphorus removal in Norway has been an important focus since the 1980s and currently the Norwegian standard of 1 ppm (1 mg/L) is stricter than the European Community standard of 2 ppm. Communities in Norway are free to set even stricter standards if they choose. Small-scale systems in Norway have historically been a biological/chemical treatment system that required maintenance and ongoing chemical addition. Typically, in Norway, a phosphorus-sorbing

light weight aggregate (LWA) is used in the constructed wetlands; however, the overall cost and maintenance of the CWS is impacted. Jensen, Krogstad, Maehlum, Skjonsberg, Hensel & Jonasson (2010) in conjunction with the Norwegian University of Life Sciences looked closely at the long-term performance of the 21 existing wetland systems in Norway, some of these wetlands had been in operation for up to 10 years and were all considered small systems from single households to 50 PE. The P concentrations in the effluent of these systems increased slowly over time but over 40% exceeded the limit before 10 years of operation; it was suspected that several of the systems had non-ideal hydraulic conditions that led to preferential flow pathways and suboptimal utilization of the sorption capacity of the LWA.

The LWA material used by Vohla et al. (2005) in the study mentioned with oil shale ash determined that the locally sourced (Estonia) and Swedish LWA materials do not perform as well as the Norwegian LWA products.

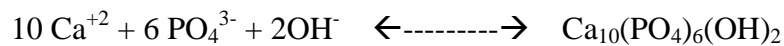
Calcium: Calcium is a biologically active metal that is a nutrient and is important in the carbonate cycle of both natural and constructed wetlands. The amount in calcium in the wetland plants is 0.77% DW and as high as 5 – 7% DW in floating plants and some types of algae (Kadlec & Wallace, 2009). The chemical equations for calcium and phosphorus are:

1) The lime interacts with the water and the natural alkalinity of the water to form calcium carbonate:



The use of lime in traditional WWTP is declining because of the increase in sludge that is produced compared to other metal salts but the calcium carbonate will coagulate other TSS in the wastewater (Tchobanoglous et al., 2003).

2) The calcium carbonate dissolves and reacts with the phosphate ions when the pH is above 10. The precipitate is calcium hydroxylapatite:



The calcium hydroxylapatite is thermally stable but the complexity of the water system requires that at low phosphate concentrations there be a crystal seed to start the precipitation, and the precipitate formed will start out as an amorphous solid that is not stable. It will slowly transform to the stable precipitate. It has also been shown that to improve the removal of phosphorus with the Ca salts, a recycle stream improves the efficiency of the system (Snoeyink & Jenkins, 1980); however, seldom are there recycle loops in constructed wetland systems. The reaction is also dependent on the alkalinity of the wastewater and less so, the concentration of the phosphate in the water. As a rule of thumb, the addition of lime is 1.5 times the alkalinity as  $\text{CaCO}_3$ . The pH of the system is also critical and the Ca-P precipitates at a pH above 10; if below a pH of 10, the competing reaction is with the alkalinity and other metal ions in the wastewater (Crites & Tchobanoglous, 1998). Essentially, the molar amounts required for the Ca-P reaction will need to be verified specifically for the wastewater stream in question. Process steps using high concentrations of  $\text{CaCO}_3$  leaves the water basic and the pH may have to be lower often times with the addition of  $\text{CO}_2$  (Linntech, 2010; Tchobanoglous et al., 2003).

Research shows that calcium products, both natural and manufactured will work effectively to remove phosphorus from a wastewater stream, including various forms of calcium carbonate found in limestone, seashells, and other minerals. Examples of other calcium products include hydrated lime ( $\text{CaOH}_2$ ) and quicklime ( $\text{CaO}$ ). In 2003 at the University of Aarhus, Arias, et al. (2003) looked carefully at the amount of calcite required for phosphorus removal in a constructed wetland and the rate constants for calcite in vertical flow (VF) constructed wetlands. The paper by Arias, et al. (2003) also did any outstanding job of explaining the experimental design used to determine these two characteristics. The key conclusions from the paper are: 1) 30 kg of calcite are required annually for removal of phosphorus per PE; the people equivalent term typically used in Europe for constructed wetland sizing. For the purpose of the experiment, the calcite filters were outside of the actual wetland and there were 3 of them in series. The calcite beds removed 75% of the TP in the municipal wastewater to an effluent concentration of 1.4 mg/L TP. The residence time in the calcite filters was very short, on average 33 minutes, significantly less than the days (approximately 15 days) suggested for phosphorus removal in a CWS without chemical precipitation. It was recommended in the study that the design could be expanded into a full-scale system to improve overall removal of the phosphorus. 2) The pH increased in the calcite filter units because of an increase in the concentration of Ca ions. It was estimated that approximately 17 kg of the calcite dissolved for the total 600 gm of phosphorus that were removed from the system. 3) As has been pointed out in several other papers, the sorption of phosphorus is a dynamic equilibrium process that is reversible, and at the lower mass loading rates the

phosphorus will be re-released in to the wastewater. 4) The rate constant varied throughout the different trials because of difference in the mass loading rate with a range of 0.24 m/d to -0.4 m/d, clearly proving that the removal rate was not 1<sup>st</sup> order kinetics based on an area-based removal concept.

Steel Industry By-Products: Steel slag is waste product of the steel manufacturing process and is composed of varying amounts of Fe, CaO and SiO<sub>2</sub>. There were several articles from the conference in Italy that demonstrated outstanding results with steel slag products. The chemical composition of steel slag includes approximately 10 % iron and 75% CaOH (van Oirschot, 2010).

The chemical mechanism for the blast furnace slag reaction with phosphorus is not completely understood. It is thought that this is a multi-step process where first the phosphorus is adsorbed on to the slag, then the precipitation takes place, and finally the crystallization of the phosphorus with the calcium and iron. The mechanism and use of slag has been proposed because the blast furnace slag is able to regenerate the phosphorus retention capacity after drainage of the water and oxidation (Kadlec & Wallace, 2009). If the industrial by-product is used several times and the phosphorus can be recovered, this is a more economically appealing application.

Barca et al. (2010) looked at steel slag from 17 different production sites in Europe, from two different industry processes: basic oxygen furnace slag (BOF-slag) and electric arc furnace slag (EAF-slag) and determined sorption capacities, pH, kinetics of the process, and removal mechanisms. An excellent paper, it clearly showed the importance of understanding the removal mechanism in the design phase of CWS. The

current work was a pilot study and future projects will be to scale up to a full-sized system. There are three phases to the removal mechanism: reactions where the metal ions dissolve from the slag, formation of metal ion complexes with the P, and finally the precipitation of the metal ion-P complex either by adsorption and /or crystallization on the slag surface. The adsorption capacities of the two different processes were: EAF (0.11 to 0.22 mg P/g EAF slag) and for BOF (0.8 to 2.0 mg P/g BOF slag). Based on these results and additional analytical work, the predominant removal mechanism for EAF slag was adsorption and for the BOF slag, it was both adsorption and precipitation. The BOF slag is more adaptable to high levels of P in the wastewater stream because there are two removal mechanisms happening simultaneously.

Another study in Brazil looked at 3 different configurations of CWS installed after an anaerobic baffled reactor (ABR) to determine if the steel slag addition to HSSF constructed wetlands not only removed more of the phosphorus from the wastewater stream. The study also evaluated other water quality parameters (Cassini, Avelar, Goncalves, Pinotti & Keller, 2010). CW1 was a typical HSSF with sand, gravel, and vegetation, CW2 was a HSSF with steel slag in the substrate with plants and CW3 was an unplanted wetland with steel slag substrate only. These CWS were monitored for 140 days and in the two systems with steel slag substrate, the removal rate of the P was over 99% compared to the control of 42% removal of TP for CW1. Two other water quality parameters were looked at carefully. The pH of the influent was in the range of 7 and with both CW2 and CW3, the pH was as high as 11 – 12 at the effluent requiring an additional step before the water could be discharged to a receiving body. Closely related

to the pH was the increase in  $\text{CaCO}_3$  found dissolved in the water, which CaO is a major component of steel slag.

One interesting application of steel slag as a removal mechanism for phosphorus was used in a hybrid subsurface flow wetland to treat wastewater from a fishery in northern Canada (Snow, Anderson & Wootton, 2010). The phosphorus contamination was from the formulated feed used in the aquaculture fish farm; the phosphorus from the feed is in the form of polyphosphates and the concentration of the TP influent was quite low in the range of 2 – 4 mg/L and the phosphate concentration was in the range of 1 -2 mg/L. These were lightly loaded systems and with the horizontal steel slag filter as a standalone component after the CWS, the removal rates for both the phosphate and the TP were in the range of 80 to 86% for the first year of testing and in the range of 20 – 60% removal over time. While the system was sampled during the winter months, it was determined that reason for the drop in performance was not related to the steel slag filter but rather the wetland upstream because the adsorption of phosphorus in that cell of the system had reached saturation.

Because of the increase in pH and alkalinity, there are ongoing studies on how to incorporate steel slag into constructed wetlands. Wootton, Hussain, Walters, Higgins & Blowes (2010a) is working with a patented substrate that uses 50% steel slag called Phosphex. The product was developed at the University of Waterloo in Canada and almost stoichiometrically removes phosphorus from the wastewater. In small-scale systems, the residence time is less than 1 day (Phosphex, 2011). A pilot study with FWS constructed wetland and a 50% Phosphex 50% gravel media has shown that it removed

the phosphorus on a larger scale and the removal was over 99%. The pH was reduced to an acceptable level by bubbling in carbon dioxide gas but another consideration might be to use ferric chloride.

Reitland, a company in Belgium has worked with steel slag in several constructed wetland configurations and determined that there are clogging problems that need to be addressed if steel by-products can be used successful in the field (van Oirschot, 2010). One of the major concerns they have identified in the design of CWS while using steel slag is where in the constructed wetlands the steel slag additive should be in the soil/sediment. “Adding steel slag in deeper layers might lead to the dissolution of iron under anaerobic conditions and subsequent re-release of bound phosphorus” (p. 1034). They found that the high pH in the water because of the dissolution of CaOH was temporary and did not create long-term problems after the first few months, the pH stabilized at around 7.5. However, they determined that the organic matter in the water reacted with the CaOH and this caused a binding with the sand media that was as much as 20 cm thick; compromising the hydraulic conductivity of the VF system. The crust was broken up and remixed and the removal rates for phosphorus in these systems were back up to 95%. The final design was to put the steel slag into the sediment at a depth of 30 cm so that it was not too deep as to cause problems with re-release of phosphorus but not too shallow as to cause the oxidation of the organic matter and cause clogging and bacterial growth on the iron particles.

Naturally Occurring Minerals: Regionally, there is ongoing research identifying locally sourced natural materials that can be used for the removal of pollutants in wastewater streams.

Not only are these natural materials more environmentally friendly, it is often easier to remove the nutrients, specifically phosphorus from the material for reuse as P in fertilizers and other applications at the end of the process. Following are examples of these materials that are currently being investigated and implemented in various parts of the world. The three papers below show how these naturally offering minerals are refined and used in commercial operations to improve the over nutrient removal performance.

*Apatites:* Apatites are a group of phosphate minerals ( $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ ) that are usually mined for the manufacture of fertilizer. World production of the apatite minerals is over 153 million tons a year (Lenntech, 2010). The X in the chemical composition refers to OH, F or Cl.

Recent research in France has looked at the engineering and design criteria for using apatite in constructed wetlands for the purpose of phosphorus removal (Molle et al., 2010). The composition of the material allows for the adsorption of P and surface precipitation; the precipitate is a more “stable calcium phosphate precipitate” and allows for long term P removal. Molle and colleagues detailed the comparison of apatite to other materials such as calcite, quartz, dolomite, and clay. The experimental design was setup to bypass the shorter-term adsorption of phosphorus onto the surface of the the materials tested and concentrate on the long-term removal mechanisms of sorption into the matrix

of the mineral by looking closely at the kinetics of the system over longer periods. There were several conclusions; some of them specific to the materials tested and others that need to be taken into account when characterizing different constructed wetland processes. The kinetics  $k$  constant decreased over time of operation and it was determined to be because of the biofilm growth on the surface of the minerals after the adsorption sites become saturated. By testing a variety of materials that contained different percentages of apatite it was concluded that a higher apatite content (>90%) allows for the filter area to be smaller and for the lifetime of the product to be extended significantly; doubling the lifetime of the filter before it is completely saturated and needs to be replaced. It is important to note that in a dynamic system there will be some sorption/desorption of P at the surface. It was also recommended that any apatite filter systems be placed late in the wastewater treatment process to avoid clogging and should remain in a system that is saturated with water at all times to reduce hydraulic short-circuiting. The apatite is being used at the end part of the HSSF system and it is assumed that phosphorus collected on the apatite filter will be reused for fertilizer.

*Opoka*: *Opoka* is a naturally occurring silica–calcite mineral found in Poland, Lithuania, Russia and other countries in northeastern Europe. The Warsaw Agricultural University (Brogowski & Renman, 2004) investigated using *Opoka* for  $\text{PO}_4\text{-P}$  removal in wastewater because of its sorption capacity and metal removal properties.

*Opoka* is a well characterized mineral that has high concentrations of  $\text{CaCO}_3$ , a very high porosity (44.5%) and a large surface area ( $64 \text{ m}^2/\text{g}$  of *Opoka*). Currently, the

mineral is mined and treated to high temperatures by a Swedish company to formulate a commercial product called Polonite. The thermal treatment of over 900 °C improves the sorption capacity of the mineral without negatively impacting the overall performance of the material. The results showed that 119.6 gm of PO<sub>4</sub>-P were absorbed for every kg of the opoka. There is ongoing research with opoka, but the pH of the mineral after heating and phosphorus uptake is around 13. Another goal of using this mineral would be reuse for agricultural applications, specifically acidic soils.

*Zeolite:* A hydrolyzed silica with aluminum and other alkali metals that is used in a commercially available wastewater treatment process called ZEOFITO is compared with a typical gravel bed substrate in a traditional wetland.

Rochard, Oldano, & Marengo (2010) compared the use of the mineral zeolite to the gravel bed substrates of traditional wetlands for a winery application in Italy. The mineral zeolite is characterized by its chemical composition and the natural microporosity. The surface area of the proprietary ZEOFITO is 200 – 500 m<sup>2</sup>/g of the material and is composed of up to 90% of the natural zeolite mineral. The results showed that the acidic winery wastewater went from acidic to a pH of 7.0 or greater, and the removal of TP was over 99%. The required treatment area of the ZEOFITO subsurface horizontal flow (HSSF) wetland was 1/3 of a traditional wetland and the hydraulic loading rate (HLR) was twice as fast. A 0.28 m<sup>2</sup>/PE reduction in wetland dimensions proved the benefit of less land required and HLR are possible with a chemical additive. Because of the increased surface area, there are more sites on the zeolite for microbial activity as well as the cation-exchange capacity of the mineral itself. The plants used

were common reeds that adapted to the use of zeolite in the system with no foreseen problems. Within the context of this article, there was no discussion on either the clogging of the material or the lifetime of the zeolite material before it would have to be replaced.

### Other Considerations

Within the context of the literature search, there are other factors that influence the overall performance of the constructed wetlands and need to be taken into consideration when designing a system. This section of the paper briefly describes these other design considerations and then demonstrates the impact with real-world examples. These include hydraulic retention time, hydraulic loading rate, alkalinity, pH, temperature, evapotranspiration and startup parameters. Depending on the specific situation some factors are more important than others, but all of them will potentially impact the performance of the constructed wetlands and are interconnected.

### Hydraulic Retention Time

The hydraulic retention time (HRT) also referred to as  $\tau$  (tau) in the literature is defined as the measure of the average length of time that a soluble compound remains in the constructed wetland system. Typically, HRT has units of time (day or year) and is the volume of the system divided by the flowrate. The HRT and overall hydraulic efficiency are important parameters to evaluate when designing, evaluating and installing constructed wetlands. Designing the HRT for the overall system is not easy and a simple

model is used until more accurate  $k$  constant and rate parameters are known for the specific system (Crites & Tchobanoglous, 1998):

$$\text{HRT} = \ln(C/C_o)/k_{\text{apparent}}$$

where:  $C$  = the effluent concentration (mg/L)

$C_o$  = the influent concentration (mg/L)

$k_{\text{apparent}}$  = the overall rate constant for the constructed wetlands for all constituents; typically based on field observations and empirical data (1/d).

It is important to note that longer retention times are more favorable for all removal mechanisms, with respect to phosphorus removal (Fonder et al., 2010).

At the research level tracer tests are performed, as was done by Dierberg, Juston, DeBusk, Pietro & Gu (2005) in the Everglades Nutrient Removal Project (ENRP).

Unique to ENRP are the very low concentrations of phosphorus in the 100  $\mu\text{g/L}$  TP range for the influent and the effluent concentrations of approximately 20 – 30  $\mu\text{g/L}$  TP. A two dimensional tracer test on the 147 ha free water surface (FWS) showed that 44% of the water bypassed the submerged aquatic vegetation (SAV) with only partial treatment for TP. The actual shorter detention times of the water in the wetland and less interface with the plants contributed to an “environment that reduced the sedimentation rate, direct plant uptake, and the pH, all of which contribute to removal and retention of P in the more quiescent, shallower SAV zones” (p. 23). This research also modeled the wetland for determining the effective HRT, and an equivalent tank in series (TIS). The concept of the TIS allows for comparison of hydraulic performance between systems. The TIS for the 147 ha portion of the larger ENRP was only 1.3 and it had been expected to see a value closer to 3 if there had not been the short circuiting. By using the modeling, it clearly

showed that the system was operating as if it were two different cells, a faster plug-flow pathway of the unvegetated channels and a slower CSTR pathway with the SAV zones and HRT of 2.1 and 7.1 days respectively. These two different areas of the wetland also had different phosphorus removal mechanisms: the short-circuited areas had a reduction in P that was linearly related to the distance from the inlet; the phosphorus removal in the SAV areas followed an exponential decay but there was significantly more dispersion of the tracer in the area of the wetland with SAV. The SAV allowed for more biological uptake of the phosphorus. The deeper channels existed before the wetland was constructed and modifying the system now would be quite difficult. In hindsight, the hydraulic performance of the system should have been evaluated before the wetland was flooded. It was also noted that the SAV vegetation needs to be equally distributed and the inflow of wastewater needs to be uniformly distributed to minimize short-circuiting.

Other studies have shown that for effective phosphorus removal the HRT needs to be in the order of 6 days where as for nitrogen a 2-day HRT is adequate for HSSF (Hunter, Combs & George, 2001). In colder climates, retention times can be as long as 15 days for a consistently successful removal rate, as was shown by Crolla, et al. (2010) in Eastern Ontario, Canada.

The state of Iowa's Conservation Reserve Enhancement Program (CREP) developed 48 treatment wetlands for tile drainage areas in the Des Moines area, the receiving water is the Embarras River in Illinois and found that retention times of 11 to 21 days were required for phosphate removal; while lower values were necessary for nitrate removal (Lowrance, 2010).

Sarmento, Borges, & Matos (2010a) looked at the HRT in relation to specific plants for a vertical flow constructed wetland in Brazil. The four greenhouse wetlands used *Heliconia rostrata*, *Hedychium conronarium*, *Cyprerus sp* and unplanted for control. The plants were compared at different HRT, the *Cyprerus sp* had the best results, removing 54% of the TP from the swine wastewater (SWW), and as reported in most of the literature the longer HRT is required for phosphorus removal relative to the other nutrients.

#### Hydraulic Loading Rate

The hydraulic loading rate is defined as the rate that the wastewater enters the wetlands system. Several studies have demonstrated the importance of determining the hydraulic load rate (HLR) for a specific constructed wetland and the impact that precipitation and stormwater runoff has on the HLR. Using a simple mass balance concept the HLR can be determined and broken out to show the contributions from increased inflows of wastewater and the dilution of the contaminates by rainwater and runoff (Kropfelova et al., 2010). Typically the HLR is measured in cm/day. The mass balance approach also allows for the total amount of load (contaminate) removed to be determined within a specific time frame. It is important to note that HLR and HRT are interrelated and when evaluating constructed wetland systems, there is “probably an optimal level for the HLR at which the P removal is the highest. A similar concept suggests that for selected filter media the optimal P retention occurs at a medium HRT and too long of a HRT induces clogging of the material” (Vohla et al., 2010 p. 1061). A more specific HLR is the phosphorus loading rate (PLR –  $\text{g/m}^2 \cdot \text{day}$ ;  $\text{PLR} = \text{HLR} \times C_i$ ).

Pedrero, Albuquerque, Amado Marcos do Monte & Alarcon (2010) use the PLR concept in Portugal to correlate loading parameters and mass removal rates. It was shown that the PLR and removal efficiencies correlate well to the organic loading rate (OLR) and the solids loading rate (SLR). There was also good correlation between the PLR and the removal rate, pointing to the conclusion that removal efficiency is linearly related to the TP concentrations in the influent wastewater stream. Also confirming the first order kinetic mechanism. Kadlec & Wallace (2009) point out the two most important factors influencing the outlet phosphorus concentrations are the PLR and the inlet concentration,  $C_i$ .

The overall hydraulics of the constructed wetland are an important part in the performance of the wetland and can be studied with tracer tests. Factors to take into consideration are velocity differences of the water caused by patterns of vegetation, wind, waves and vertical velocity profiles. Submerged plants create eddies in the water and mixing profiles within the system (Kadlec, 2006). Kadlec & Wallace (2009) defines the different hydraulic fronts that will impact the overall performance of the wetland. The majority of the work done has been with FWS wetlands but much of it is applicable to HSSF and VF systems. There are three different fronts identified: the water column front, the soil phosphorus front, and the vegetative front. As the water travels from the inlet to the outlet there will be a decreasing profile of the phosphorus in the water along that flow path and near the inlet there will more vegetation and hence more plant decay, flocs, and new soil sediments. The soil phosphorus front takes years to establish and is directly related to the new soils. The flocs formed will move slower than the water but faster than

the soil phosphorus front. The vegetative front also takes years to establish and will change as new species of plants that respond to the nutrient environment enter the wetland.

Johannesson, Tonderski, Wedding & Weisner (2010) looked at seven different agricultural non-point source wetlands in Sweden to determine if there was a correlation between HLR, phosphorus load rate ( $\text{kg/ha} \cdot \text{yr}$ ) and phosphorus retention ( $\text{kg/ha} \cdot \text{yr}$ ). The study period was between 2 and 9 years depending on the specific wetland. The focus points were to identify the phosphate and particulate phosphorus in relation to water flow and different seasons, and determine the phosphorus retention from the agricultural catchments. The overall phosphorus retention ranged from 2 – 40% on an annual basis and the wetland with one of the lowest HLR had the highest removal percentage but was also one of the smallest systems in the study. The wetland systems with the larger HLR had the annual removal percentages in the single digits. The conclusion of the study pointed to a more complex environment than the parameters of the study.

An analysis of four different constructed wetlands looked at the HLR in Nepal as an initial study for the implementation of CWS into the country (Pandey, Krogstad & Jenssen, 2010). There were two VF systems and two HSSF systems in the pilot study; the HLR varied between 20 and 4 cm/day. In all four cases the average removal percentages for TP were in the range of 18 – 48%; the highest removal rate was in the planted VF system and the lowest removal rates were in the unplanted VF system. The lower HLR had somewhat higher removal rates.

### Alkalinity

Alkalinity is defined as the acid neutralizing capacity of the soil and water. In wastewater, alkalinity is typically because of the presence of hydroxides, carbonates, bicarbonate, and elements such as Ca, Mg, Na, K, NH<sub>4</sub>. Typically, wastewaters and groundwater are alkaline (Crites & Tchobanoglous, 1998). One of the recommendations for effluent wastewater streams is that the final alkalinity be in the range of 70 – 80 mg/L as measured by CaCO<sub>3</sub> (Tchobaboglous et al., 2003).

The buffering capacity of the soil (resistance of the soil to changes in pH of the soil solution) in the wetland will have a major impact on the overall amount of phosphorus removed and the overall alkalinity of the CWS. Zake, Kitungulu, Busurwa & Kyewaze (2010) looked closely at a wetland system in Uganda located close to Lake Victoria and found that the wetland Sio had soils with the highest buffering capacity and ability to protect Lake Victoria from pollution; a total of 6 different sites around Lake Victoria were evaluated. Specifically, the following parameters were identified: the amount of clay and organic material in the soil predicts the extent to which the soils are buffered. The Sio wetland had at least 42% clay and 6.75 % organic matter and therefore a higher cation exchange capacity. The rule of thumb for organic matter in the soil should be 3% or greater. The available phosphorus in the six sites was also measured along with other cations and anions over the course of wetting and drying cycles of the wetlands. The lab experiments also mimicked the wetting and drying cycles of the wetlands, the impact on pH and the necessary requirements to sustain the wetland. With most of the wetland sites, the amount of available phosphorus in the soil decreased after a wetting

and drying cycle while the pH stayed the same. A study by Bays et al. (2010) suggests “alternative flood/drainage cycles can accelerate nutrient cycling and transport with the soil, identifying a potential conflict between water quality objectives and hydrological management” (p. 10).

### Evapotranspiration

Evapotranspiration (ET) is a term used to describe water loss in a wetland system. The models used to accurately determine the ET for a CWS are complex and take into account several different components and are a part of the overall energy balance of the system. The two important parameters are water loss due to the atmosphere (evaporation) and the uptake/loss of water because of the plants (transpiration) (Kadlec & Wallace, 2009). The transpiration is a two-part process, the water is pulled upward from the roots to the leaves and stems and evaporates on the leaves and stems of the plants. The water carried up will have the phosphorus concentration of the water at the soil-water interface in the root zone, an average of  $0.6 \text{ g P/m}^2\cdot\text{year}$ . The plants remove phosphorus from the underground storage with this extraction and then when the plants decay, the phosphorus is re-deposited onto the top layer of the sediment as new soil accretion, called phosphorus mining by the plants; it is closely tied to the transpiration of the plant cycle (Kadlec & Wallace, 2009). Without a full discussion of the energy balance of constructed wetlands, it is important to consider the overall mass balance of the various nutrients and the measurement techniques used to determine the overall efficiency of the system. High evaporation or transpiration in the CWS will impact the concentration values of the contaminate in the effluent if measured in gm/L per unit of flow and these higher

concentration numbers are misleading when determining the efficiency of the system.

The reverse situation can occur if there is a significant amount of precipitation, the concentrations would be lower and the efficiency of the system would be better than the actual performance of the system. The precipitation itself will add to the amount of phosphorus in the wetland and the phosphorus concentration in the rain will vary between 10 and 50  $\mu\text{g P/L}$  and the annual total atmospheric phosphorus is between 2 and 80  $\text{mg/m}^2\cdot\text{year}$  (Kadlec & Wallace, 2009). It is important to take into account the actual mass balance load ( $\text{kg/year}$ ) of the system over the course of an annual cycle to accurately determine the amount of contaminant removed from the system.

The units of measurement for evapotranspiration are amount of water evaporated and transpired per unit of time for a short green crop, completely shading the ground, or uniform height and never short of water. Meteorological data is used to determine the potential evapotranspiration (EVP) in  $\text{mm/day}$  (Kropfelova, et al., 2010). Typically, the highest values of evapotranspiration are in the summer months and when the plants are at their highest. During the winter months, the loss is often times evaporation only with no transpiration by the plants.

Evapotranspiration parameters are important considerations for both small and large constructed wetlands. In 2008 and 2009, Kropfelova et al. (2010) looked closely at determining the evapotranspiration values for a constructed wetland in Libnic, Czech Republic. The water budget of the constructed wetland is based on the inflows and the outflows of the wastewater and precipitation. The key conclusions are that evapotranspiration of wetland macrophytes may be much higher than precipitation in

areas of low precipitation and in large wetlands the values are 5 – 7 mm/day but for small wetlands these values can be as high as 13 mm/day. At the study site in Libnic, the expected value of EVP was 4.02 mm/day on a hot day in July 2009 and the actual value of evapotranspiration was 16.2 mm/day; in evaluating the area around the wetland it was concluded that the advective heat from the surrounding agricultural fields were the cause of the discrepancy.

Determining the effects of evapotranspiration on a constructed wetland is typically done by comparing wetlands that are planted and non-planted in a controlled environment. Looked at closely by Matos et al. (2010a) at the University of Vicosa in Brazil, it was determined that “evapotranspiration caused cultured solute concentrations, which may have underestimated the efficiency obtained in the cultivated systems” (p. 1402). Another study by Sarmiento, Borges & Matos (2010b) at the same university compared planted and unplanted CWS in a swine wastewater system (SWW) and determined that evapotranspiration in the planted CWS compared to the unplanted CWS has a fundamental role in accounting for the mass removal of all variables.

Towler, Cahoon & Stein (2005) determined the evapotranspiration crop coefficients for two of the most common plants used in constructed wetlands: *Typha latifolia* and *Scoenoplectus acutus*. This study is important for a couple of reasons relative to the floating islands technology and the Rehberg Ranch Subdivision (RRS), because the lagoons at the RRS are in a dry climate with very little surrounding vegetation and plants have been incorporated into the floating island that is in the middle of one of the lagoon ponds. A similar testing method could be used to determine the

evapotranspiration coefficients for the floating islands and/or the floating islands with plants.

$$ET_c/ET_o = K_c$$

where:  $ET_c$  = the crop evapotranspiration  
 $ET_o$  = the potential evapotranspiration  
 $K_c$  = the dimensionless crop specific coefficient.

The  $ET_c$  was measured in a greenhouse environment at Montana State University and there are few conclusions worth noting: 1) the two plants had  $K_c$  values that were unique and they changed seasonally. 2) The  $K_c$  value is influenced by the ratio of the surface area of the vegetation to the surface area of the open spaces in the wetland.

An example of a wetland that takes advantage of high evapotranspiration is an evapotranspiration –absorption system (ETA). Typically, these systems are in arid climates and the wastewater after pretreatment is applied to a sand bed (approximately 24 to 30 inches deep) from pipes below ground. The sand bed is covered with top soil and plants. The capillary forces of the sand- water interface and the plant roots bring the water to the surface for evaporation and transpiration. Often times the system is unlined and water also percolates below the sand bed. Besides knowing the EV parameters for design, the percolation rate and hydraulic load are required for determining the size of the system (Crites & Tchobanoglous, 1998). This is an example of a system that is low tech and can be used in a single family or small system setting.

Qiu, McComb, Bell & Davis (2004) looked at the impacts of the atmosphere on a wetland in southwestern Australia and how weather conditions impacted the movement of phosphorus in the wetlands system. The natural, freshwater wetland is a shallow

aquatic system and the system was evaluated for changes in the P concentration in the water caused by mixing and circulation changes between the catchment, wind or density driven events, atmospheric inputs, and wind transport from surrounding areas. Two sites were chosen, one at the shoreline and one offshore 200 m. The primary phosphorus removal mechanism is assumed to be the accretion of new sediments and the corresponding re-release of P from the sediments back to the water column. The wetland is often times dry or the top soil sediments are not fully saturated. Besides the precipitation the other atmospheric contribution was the wind moving up to 20% of the particulates in the wetland; while more noticeable at the shoreline testing site than the offshore site. Qiu et al. (2004) reported that the results are comparable to a study done in Oregon, where the atmospheric deposition of both rainfall and wind movements contributed 30% of the P inputs. Essentially the wind moved plant and litter around from the area surrounding the wetland into the wetland. It was also noted that the wind stirred up the sediments of the shallow wetland during the wet season.

### Kinetic Mechanisms

There are two different kinetics models commonly used for determining contaminant levels in wastewater effluent, the modified 1<sup>st</sup> order rate reaction and the Monod kinetics model used in traditional wastewater treatment facilities.

Historically, rate kinetics for wetlands is modeled using a modified 1<sup>st</sup> order rate reaction that was developed by Kadlec and Knight. This kinetics model is well accepted as a relatively simple model that successfully describes the complex phosphorous removal mechanisms. The  $k - C^*$  model determines an areal or volume net uptake of

phosphorus ( $k_V = k_A/\text{depth}$  of the wetland if the wetland depth is constant), and is a two-parameter first order kinetics model based on concentration. The  $C^*$  is defined as the background concentration of the nutrient;  $C^*$  is important in evaluating the removal kinetics of all nutrients (Kadlec & Wallace, 2009; Mena, Fernandez, Villasenor, Rodriguez & de Lucas, 2010; Kadlec, 1997). A second model, used in traditional wastewater treatment and activated sludge process is based on Monod kinetics. Referred to as ASM2 or ASM2d, this model is based on specific growth rate kinetics to describe the growth of both autotrophic and heterotrophic bacteria and is used in WWTP that have biological nutrient removal (BNR) processes for removing phosphorus and nitrogen and COD (Henze, Gujer, Mino, Matsuo, Wentzel, Marais & van Loosdrecht, 1999; Henze, Gujer, Mino & van Loosdrecht, 2000). In the recent literature with respect to phosphorus removal in wetlands kinetics modeling, studies and research continue to evaluate whether or not the original 1<sup>st</sup> rate reaction needs to be modified with elements of the ASM2 Monod model. This has come to the forefront as the constructed wetlands have become more complex (hybrid systems), software packages are commercially available and the increased regulatory requirements to monitor and control the effluent of several nutrients in the same system. The added complexity makes sense as hybrid constructed wetlands are mimicking the BNR processes of a traditional WWTP. Following is a description of both kinetic models and the importance of both to understanding and predicting the outcomes of a constructed wetland.

In phone conversations (November 2010; May 2011) with James Morris, CTO from Bion Environmental Technologies (BET), his experience shows that the removal of

phosphorus in a variety of systems changes kinetic models over the lifetime of the system. While not an exact science as to the timing, the trends are the system will behave within a Monod kinetics operating system for the first year or so; the system will change to the modified 1<sup>st</sup> order kinetics model between years 1 and 5, and then settle at a zero order kinetics model for the remainder of the time it is in operation. This lends itself to the arguments that the kinetics behind these constructed wetlands is complex and not stable; it also demonstrates the need for long-term studies. The vast majority of the studies researched did not look at the long-term operation of the constructed wetlands. Kadlec & Wallace (2009) confirms this when stating that the long-term evaluation of the biological activity takes years to reach a quasi-steady state and most studies do not take this into account.

Modified 1<sup>st</sup> Order Rate Reactions: The  $k-C^*$  model works successfully for the concentration of nutrients and compounds that are characterized by removal mechanisms only. The model has evolved over the years, and there are several variations of the model taking into account temperature and evapotranspiration. It is important to note that after startup, according to Kadlec & Wallace (2009), the  $k$  constant is completely assigned to the accretion and buildup of new soils for the phosphorus removal processes and is best used for the design and monitoring of the wetlands system for long-term average performance (Kadlec & Wallace, 2009).

There are three different variations of the kinetics model: 1) the original model assumed an ideal plug flow reactor. 2) The second model was a first order biomachine

model that took into account the biomass growth and decay, and 3) the three model,  $P-k-C^*$  takes into account the HLR, detention time distribution of the contaminate, and a distribution of the  $k$  values (Kadlec & Wallace, 2009).

There is quite a bit of research showing the  $k$  values for a variety of wetland systems and the median value is 10.0 m/year for phosphorus removal; however, the range is between 1.4 and 60 m/year. Kadlec & Wallace (2009) points out that there is a seasonal dependence; temperature and climate are responsible for some of the variations and intra-annual effects should be taken into account. The rate constant is a net transfer; the difference between the uptake processes and the re-release processes from all components of the system.

The equation for the first model is typically represented by the following equation:

$$(C-C^*)/(C_o-C^*) = e^{-kt}$$

where:  $C$  = the final concentration of the effluent (mg/L)  
 $C_o$  = the initial concentration of the influent (mg/L)  
 $C^*$  = the background concentration in the wetland system (mg/L)  
 $k$  = the rate constant (1/d)

The  $C^*$  component is discussed at length by Kadlec & Wallace (2009). Even with very low phosphorus loading, the  $C^*$  concentration will never be at zero. There are many reasons why: 1) some portion of the organic phosphorus will be highly resistant to uptake, examples include the organophosphate pesticides, and other organic molecules with phosphorus. 2) In the wetland system, nonreactive phosphorus particulates (NRPP), are associated with the TSS concentration in the wetland. 3) The atmospheric and

groundwater contribution will likely uniformly distribute phosphorus throughout the wetland. 4) There is the possibility of hydraulic short-circuiting or bypasses and not all of the wastewater receives the treatment. 5) The phytoplankton suspended in the water contains suspended particulate phosphorus (PP). 6) The biocycling processes returns phosphorus to the water column, 7) effluent TSS concentrations and, 8) for HSSF wetlands the breakthrough of the sorptive capacity of the substrate. Kadlec & Wallace (2009) goes on to say that the modeling for phosphorus removal that predicts a concentration of zero is not appropriate. Along the path of the water through the wetland there will be a plateau where the  $C^*$  concentration can be determined for the wetland and the phosphorus removal is no longer taking place, typically near the outlet of the constructed wetland. Because of the atmospheric and groundwater contributions, phosphorus is also seen in natural wetlands with concentrations in order of 0.10 mg P/L for some areas of the United States. The  $C^*$  is the lower limit on achievable phosphorus concentrations.

In Dublin, Ireland at the UCD Lyons Research Farm, a four stage reed bed filter system was designed and operated for the 2009 calendar year. There were several interesting points: the research-constructed wetlands was operated in three different modes: normal tide flow, tide flow with recirculation, and first stage is anaerobic with water recirculation and tidal flow. The results for SRP and TP were exceptional; over 98 and 96 percent removal respectively. From a kinetics perspective, “the removal of COD, BOD,  $\text{NH}_4\text{-N}$  and TP increase with the loading in straight-line correlations, corresponding with the first-order dynamics with is often used in reed bed design,

showing that the pollutant removal rate is proportional to the influent strength” (Zhao et al., 2010 p. 1159).

The modified 1<sup>st</sup> order kinetics model has been used in Singapore in the investigation of floating vegetation mats with research on three different plant species was carried out at Nanyang Technical University. The goal was to determine which plant species were the most efficient at removing, TN, TP, AN and OP. The removal efficiencies for these contaminants and the  $k$  constant for each of the plants were determined. There are two key conclusions: 1) the overall removal efficiency is greater when the influent values are higher and 2) the  $k$  is similar for both TP and TN removal for each of the different plants. Because of the weather and frequent storm events in Singapore, higher efficiencies and higher  $k$  values are desirable (Chua, Tan, Sim, Borana & Li, 2010). While this analysis was done in a tropical environment; it would be interesting to determine if the  $k$  values for plants in colder environments exhibited some of the same trends.

An excellent article by Molle et al. (2010) looked at kinetic parameters for a constructed wetland using the natural material apatite. The study was referenced earlier with an evaluation of apatite as a natural material available for phosphorus removal by sorption and precipitation. The kinetics experiments showed a couple of important conclusions that need to be taken into account. As stated earlier there are two different mechanisms for the removal of phosphorus regarding apatite: the adsorption of the phosphorus onto the surface of the apatite and the longer-term P retention mechanism of surface precipitation of P to the apatite. Each of these mechanisms had different kinetic

rates of reaction and is documented in the different  $k$  values. The  $k$  values for the adsorption of the P were in the order of  $1 \text{ hr}^{-1}$  for the lab experiments and  $0.29 \text{ hr}^{-1}$  for the scale operations. The  $k$  values for the precipitation of P were between  $0.85 \text{ hr}^{-1}$  and  $0.7 \text{ hr}^{-1}$  for the lab experiments but only  $0.08 \text{ hr}^{-1}$  for the full-scale operation. The  $k$  values are different between the two mechanisms but are profoundly different when comparing the lab studies to the actual working facility. The rate of the reactions decrease with time and needs to be taken over the lifetime of the filter. The surface precipitation rate decreased with the amount of the P saturation over time. The conclusions also made several design recommendations based on these results: the filter should remain water saturated to minimize the hydraulic short circuiting, the subsurface flow wetland only had the apatite filter at the end of the system and high quality mineral with over 90% apatite was required.

The temperature affects the overall performance of the wetland systems and is taken into account in the kinetics model with the following modified Arrhenius equation Kadlec (2006):

$$k = k_{20} \Theta^{T-20}$$

But  $\Theta$  is often assumed to be 1 for phosphorus removal kinetics and there is no correction to the rate constants for phosphorus with respect to temperature. However, Stein, Towler, Hook & Biederman (2007) and Stein, Biederman, Hook & Allen (2006) have shown that for the  $k$  values and  $C^*$  concentration for COD concentrations did vary with differences in temperature. There has been less research on the impact of temperature on the rate reactions and the different components of the rate equation for phosphorus. A few

important conclusions are that the  $k$  constant is different for different plants, and while the  $k$  constant does vary with temperature it is equally as important to take into consideration the  $C^*$  changes relative to temperature. In full-scale operations Stein et al. (2006) speculates that the  $C^*$  is more important than the  $k$  constant for predicting effluent concentrations. While the study did not look at phosphorus removal, it is easy to postulate that the same would be true for phosphorus removal because of the sorption-desorption of the P in the wetlands system, which would be reflected in the background  $C^*$  concentration over the lifetime operation of the CWS.

Other studies have looked at the  $k$  constant changes by determining a value on a monthly basis for wetlands that have seasonal changes. Kadlec & Wallace (2009) also point out that the  $C^*$  concentrations are an important parameter, specifically when sizing the constructed wetlands even if the number is considered small. The model is also applied to the re-release of any contaminant, typically the re-release of nutrients is assumed to be a zero order kinetics reaction. There are two other variations of the modified 1<sup>st</sup> order model that are useful for determining the  $k$  constant of a specific contaminant (Crites & Tchobanoglous, 1998).

$$k = k_{\text{overall}} / (1 + rt)^n$$

where:  $k$  = the rate constant for a specific contaminant (1/d)  
 $k_{\text{overall}}$  = the initial overall rate constant (1/d)  
 $r$  = rate of retardation (1/d)  
 $n$  = exponent for the specific constituent  
 $t$  = time (d)

As examples, the values for  $r$  and  $n$  vary between one and zero. The coefficient of retardation varies with plant density and has an average value of 0.2/d. The  $n$  value is

related to the amount of colloidal, soluble and particulate material is in the wastewater stream (Crites & Tchobanoglous, 1998). A second useful variation looks at the annual average hydraulic load and recommends a  $k_A$  value for phosphorus removal.

$$C_e/C_o = e^{(-k_A/L_W)}$$

where:  $C_e$  = the effluent phosphorus concentration (mg/L)  
 $C_o$  = the influent phosphorus concentration (mg/L)  
 $k_A$  = areal rate constant 1.07 mm/d  
 $L_W$  = the average annual hydraulic loading rate (mm/d)

The equation is frequently used for determining the  $C_e$  in Free Water Surface (FWS) constructed wetlands (Crites & Tchobanoglous, 1998).

The second model was developed by Kadlec (1997), because “the view of a wetland as a homogeneous plug-flow reactor that conducts a first order areal reaction is too narrow for process understanding” (p. 171). The updated model was developed and first tested at the Houghton Lake wetland. The equations for the second model, often referred to as the “biomachine” or “autobiotic” are:

$$q(dC/dy) = -k_N N_{max} \{ (C-C_o) / ((C-C_o)+S) \} = -K_N \{ (C-C_o) / ((C-C_o)+S) \}$$

where:  $K_N$  = the autobiotic rate constant ( $g/m^3 \cdot day$ )  
 $dC/dy$  = the change in concentration  
 $q$  = the flowrate ( $m^3/day$ )  
 $C_o$  = the initial concentration in the influent (g/L)  
 $S$  = the half saturation coefficient for the biological processes ( $g/m^3$ )  
 $N_{max}$  = the lumped biomass parameter ( $g/m^2$ )  
 $k_N$  = rate constant (g/day)  
 $C$  = the effluent concentration in the wetland (g/L).

This model takes into account the sorption, biomass expansion as the biological functions of the wetland reach steady state and the new soil accretions. As stated earlier, the sorption will be the primary removal mechanism during the start up of the wetland, and

the biomass compartment of model includes all live and standing dead vegetation and the sediments from the biomass including the burial of the biomass. Because it is a data-fitting model, all of these terms are in the coefficient,  $N$ . The rate constant  $K_n$  is referred to as the autobiotic rate constant. This equation does look like a Monod equation and at high  $P$  concentrations; the equation is first order (Kadlec, 1997).

The equation for the third model is:

$$(C-C^*)/(C_i-C^*) = 1/\{1+k_A/(Pq)\}^P = 1/\{1+k_V\theta/P\}^P$$

where:  $P$  = the apparent number of tanks in series (TIS)  
 $k_A$  = the modified first order areal rate constant (m/d)  
 $k_V$  = the modified first order volumetric rate constant (m/d)  
 $\theta$  = the hydraulic retention time (day)  
 $q$  = the hydraulic loading rate (m/d)  
 $C_i$  = the initial concentration (mg/L)  
 $C^*$  = the background concentration (mg/L)  
 $C$  = the final concentration of the effluent (mg/L)

One of the primary advantages when compared to the recognized modified first order model is that changes in hydraulic loading rate (HLR) over the course of the lifetime of the wetland can be accommodated where as this is not possible with the original model. The  $P$ - $k$ - $C^*$  model allows for evaluation of the system by determining the effluent concentration at different inlet loading rates (LRI) and allows for easier comparison between wetland systems. The  $P$ - $k$ - $C^*$  model takes into account the importance of the HLR to the overall performance of the wetland. Historically, if two systems are designed the same for comparable parameters but have very different performances, the HLR has been determined to be a key difference between the systems (Kadlec & Wallace, 2009). The  $P$  term and the concept of the tanks in series (TIS) more accurately represents

constructed wetlands in the field, because ideal plug flow is not valid. The higher the TIS number, the better the overall performance of the constructed wetland. Higher values indicate that there are fewer dead-zones and short circuits in the water flow pathways. If the TIS number is below 2, the wetland hydraulics are considered poor; average hydraulics is between 2 and 4, between 4 and 6 is considered fair hydraulics and greater than 6 is considered excellent hydraulics (Kadlec, 2006).

The  $k_V$  rate constant as mentioned earlier is the  $k_A$  value divided by the water depth of the wetland. However, Kadlec & Wallace (2009) point out that a better relationship is:

$$k_V = k_A/h \cdot \varepsilon$$

where:  $\varepsilon$  = the hydraulic efficiency of the wetland (dimensionless)

The primary reason for the hydraulic efficiency term is to account for the water depth of the wetland and the overall hydraulic efficiency of the system. The areal rate constant works well for smaller shallower wetlands but for large systems where there are zones of short-circuiting and zones of deeper water a volumetric rate constant is more accurate. The correction shows that as the wetland gets deeper the  $k_V$  constant gets smaller and the overall  $k - C^*$  model is less accurate without the correction term.

The axial dispersion seen by tracer tests, clearly demonstrates the non-ideal flow and the addition of  $\varepsilon$  to the  $k-C^*$  model accounts for axial dispersion (Crites & Tchobanoglous, 1998). The hydraulic efficiency term also takes into account the concept of retardation in the flow caused by the plant density in the constructed wetland. The parameters used need to average over a long enough period of time to take into

consideration the intrasystem or internal variability when comparing systems. When comparing wetlands, all of the wetlands under consideration need to be past startup, so that sustainable performance is evaluated (Kadlec & Wallace, 2009).

However, for the calculations of nutrients that appear and disappear simultaneously in the same system, the mass balance of these nutrients requires additional computations. Men, et al. (2010) have researched the series of calculations required to understand the process for phosphorus removal and the nitrification and denitrification processes. The additional terms added to the basic  $k-C^*$  model are Monod kinetics terms; Stein et al. (2007) and Stein et al. (2006) have pointed out, determining the  $k$  constants for nitrogen removal between different plant species showed variations in the removal rates for COD. It is predicted, the interrelationships between nutrients would also hold true for phosphorus removal, but in the literature search, I did not find articles that supported this research.

Monod Kinetic Reactions: The Monod kinetics reaction models are specifically used for the biological processes of nutrient and COD removal; the application is more specific than the  $k-C^*$  model. The model is based on the concept that biological communities have a limited ability to respond to increases in chemical availability; the concept is referred to as the saturation terms throughout the model (Kadlec & Wallace, 2009).

The ASM models take into account a large number of variables to determine the biological removal mechanisms in wastewater treatment facilities (Tchobanoglous et al., 2003; Henze et al., 2000; Henze et al., 1999). The ASM2D model was designed to

incorporate phosphorus removal in BNR systems (Henze et al., 2000). ASM2D takes into account several key processes for phosphorus removal: 1) the uptake of inorganic polyphosphates by PAO. 2) There are two different PAO communities, the PAOs that use carbon and the DPAO that use nitrates. 3) The recognition that TSS from the decay of biomass will have a phosphorus concentration that needs to be taken into account. 4) The rate equations for all of these reactions are based on Monod kinetics, where saturation coefficients and switching functions that account for concentration variances and the interconnectedness of different parameters in the wastewater stream. 5) Three different groups of microorganisms exist for aerobic, anoxic and anaerobic hydrolysis. 6) The decay of PAO, the particulate phosphates in the cell storage of the biomass, and the decay of the other internal storage component PHA is happening simultaneously. 7) The biological storage mechanisms of phosphate, 8) the yield of PAO organisms, and 9) the precipitation and rerelease of phosphorus with metal ions, including both the metal ions in the wastewater stream and any additional metal ions added to the process stream.

There are other important components of the ASM2D. Examples include the concentration of the fermentation products in the rate equations, in the anaerobic stages of the process. The alkalinity and soluble fermentation products are examples of switching functions in the Monod rate equations. The pH and temperature are also referenced in the model; it is assumed for optimal performance that the pH is close to neutral. The equation for microbial growth takes into account the yield of the biomass and the requirement for phosphorus is 0.021 compared to 0.105 for nitrogen (Grady & Lim, 1980). Other general trends in the model include: 1) the biological growth rates for

phosphorus accumulating organisms are in the same order of magnitude as other heterotrophic bacteria in the wastewater stream and removal processes (Tchobanoglous et al., 2003). 2) When the saturation constant is large relative to the concentration of the contaminate, or if the concentration of the contaminate is low the model is 1<sup>st</sup> order (Kadlec & Wallace, 2009). 3) Growth rates of the biological organisms are directly proportional to the substrate concentration at low concentrations but are independent of it at high concentrations for all nutrients required for growth, including phosphorus (Grady & Lim, 1980).

Henze et al. (2000) list typical kinetic values used, and in order to model the removal of COD, nitrogen products and phosphorus removal there is over 50 different coefficients required. While ASM2D is significantly more complex than what is used for constructed wetlands design and monitoring, it clearly demonstrates the complexity of all the reactions taking place in biological removal, it also accounts for all of the interconnectedness of the different parameters. In the literature search, none of the articles looked to this much detail when evaluating constructed wetlands systems but because CWS are becoming more complex with the implementation of hybrid combinations, parts of the model will become relevant. It is worth noting that some wetland researchers are not a fan of Monod kinetic models for constructed wetlands because the influent concentrations of the nutrients are low and the equations tend toward 1<sup>st</sup> order rate equations.

Hybrid Kinetic Reactions: The hybrid kinetics models are a combination of the Monod kinetics equations and the modified 1<sup>st</sup> order rate equations. Because of the

complexity of the wetlands systems, the use of these equations is gaining recognition.

The k constant rate equations can be used as a generic rate equation for any process and the Monod kinetics equations have been historically used for biological processes.

As stated earlier, the calculation of compound concentrations that both disappear and appear in the system simultaneously may require additional terms to fully characterize the system. The additional terms (Mena et al. 2010) are Monod kinetics terms that have the switching function and take into account the relative concentrations of other components that impact the overall rate of a specific contaminant. The hybrid kinetic model takes into account the interactions between the different nutrients and as the wastewater moves through the wastewater process, the differences can be taken into account. Kadlec & Bevis (2009) are currently looking at this for the nitrogen contaminates; research with phosphorus is probably not far behind.

### pH

Throughout the articles in the literature search, it has been documented several times that the phosphorus processes in constructed wetlands are dynamic and the pH of the wastewater and sediments of the wetland will impact the overall performance of the system and the removal rates for all nutrients, including phosphorus. Ahn et al. (2010) showed that the release rate of the TP back into the wastewater stream is influenced by the pH of the soil/sediments. At a more acidic pH, the release rate of the TP was higher, in the range of 0.6%; closely related to the dissolved oxygen concentrations and the overall redox potential of the sediments. The phosphorus bound by Al, Fe and other metal ions are the most mobile in these situations or when the dissolved oxygen (DO) was low.

### Reduction/Oxidation Potential

The reduction – oxidation potential in the constructed wetlands environment will also influence the removal efficiencies of all the nutrients. The redox processes are related to the amount of dissolved oxygen in the water and soils; and in turn impact the pH and the phosphorus concentrations in the effluent because of the changes in the metal ion concentrations under an anoxic (low oxygen environment) or anaerobic environment (absence of oxygen). The iron hydroxides in either the natural wetland environment or the constructed wetland environment where iron is added for improved phosphorus removal, is “very” dependent on the redox potential of the overall system. The precipitated ferric phosphate compounds may redissolve as the  $\text{Fe}^{+3}$  is reduced to  $\text{Fe}^{+2}$  (Sherwood & Quall, 2001). The redox processes in the wetland also influence the microbial processes in the wetland (Faulwetter, Gagnon, Sundberg, Chazarenc, Burr, Brisson, Camper & Stein, 2009). The depth of the wetland, the design of the system, and depending on the removal requirements, most often affects redox and the CWS needs to be designed accordingly. A couple of points worth keeping in mind: 1) the redox potential of a CWS with plants is higher than an unplanted CWS because of the increased oxygen that is carried into the soils and sediments by the roots. The amount oxygen is dependent on the plant type and can also vary seasonally. 2) Different designs for CWS are more likely to impact the redox potential and typically, the VF systems are aerobic and allow for good oxygen transfer throughout the wetland. HSSF have both anaerobic and aerobic zones but are considered anoxic; these different zones are dictated by the length and depth of the HSSF constructed wetland. Finally, FWS systems are anoxic but

often there is layer at the interface of the soil/water because of the decay of organic matter that is very low in redox potential.

As pointed out by Stein, Hook, Biederman, Allen & Borden (2003) in laboratory studies, the batch loaded subsurface flow wetlands have increased biofilm utilization and oxygen transfer in cold climates and can in turn lead to higher removal efficiencies for nutrients including phosphorus when compared to continuous flow. Batch systems are similar to vertical flow systems and the primary reason for using batch flow process is to increase the oxygen in the root zones and detritus in the beds of the wetlands (Crites & Tchobanoglous, 1998).

### Temperature

Throughout the literature search, most of the studies and research projects have reported temperature variations. Water temperature modifies the microbial processes during both the uptake of phosphorus and the phosphorus re-release during the decomposition of the detritus. The seasonal differences between cold climate and warm climate wetlands also perform differently because with warm climate systems there is no clear period of dormancy for the plants. Warm climate systems will have periods of less growth but do not experience the complete growth stoppage. Cold climate systems will have two periods of higher phosphorus removal: late fall and early spring. The early spring uptake is easily explained by the growth of new vegetation. The autumn uptake is because of the translocation of the phosphorus from the above ground sources to the below ground sources as was explained earlier in the paper. For cold climate wetlands, it is better to use a monthly  $k$  constant because of the annual variations.

Those parameters in relation to water and atmospheric temperature are commonly studied; however, Kadlec (2009c) has shown through the research of Houghton Lake in Michigan that the temperature profiles throughout the wetlands system are quite complex. The water temperature entering the wetland is not likely to be at the same temperature as the wetland itself, these regions are referred to by Kadlec (2009c) & Kadlec (2009a) as the adaption zone and the balance zone respectively. The added complexity is also because within the vertical stratum of the water there are temperature profiles depending on how shallow or deep the wetland is. The vertical temperature profile can have thermal differences between night and day or throughout the 24-hour period. The thermal profile difference between night and day is called diurnal mixing. Temperature differences in the wetland impact the energy balance of the wetlands system, the soil temperatures and the plant root zone temperatures of system. The Houghton Lake studies looked carefully at the temperature differences and showed that the soil temperatures of the system served as a buffer for the more dramatic changes in water temperature. The temperatures under the floating mat were as much as 10 °C warmer in the summer months than the water at the surface. The heat from the soil in the winter is critical to the operation of the wetland in the winter and in cases where there is snow and ice on top of the water, serves as an insulating layer. Kadlec (2009c) demonstrated that a spatially distributed energy budget in the direction of flow is possible for characterization of the wetland.

It is apparent that temperature differences do impact constructed wetland design and operation but constructed wetlands can be effective in removing nutrients specifically phosphorus in the correct conditions even at extreme temperatures. Stein & Hook (2005)

looked temperature variations and the impact on different plants over the course of a yearlong study as the 24 °C and 4 °C was cycled every 20 days. There were a couple of key conclusions for nutrient removal other than phosphorus. Within the literature search, a parallel test showing the effect temperature on plants and the removal of phosphorus was not found. The results with phosphorus would probably be similar. “Temperature is at best a secondary predictor of constructed wetland performance” (p. 1336). Seasonal dormancy of some plant species allows for the increased oxygen transfer to the root zone of the HSSF wetlands and allowing for aerobic reactions at colder temperatures. From a design point of view for CWS, the plant selection needs to take into account the aerobic processes during the colder seasons and the anaerobic conditions of the wetland when the plants are actually growing during the warmer seasons. As stated earlier, the aerobic/anaerobic environment will heavily influence the re-release of phosphorus into the water stream and the redox conditions are more important than the actual temperature of the system. As Stein & Hook (2005) point out there is little research on a large number of different plants, the aerobic processes in the root zone and the overall influence in low temperature periods.

The literature search looked closely at colder climate CWS because of the floating island in Billings, Montana and the winter conditions of that city but there were few articles worth noting. The following study is included because it draws a couple of key conclusions that I did not see in other articles. Kinsley, Kennedy & Crolla (2010) looked at reed bed filters for the solids in septic tanks in cold climates in Ottawa, Canada. The reed plants provide two different mechanisms of nutrient removal depending on the

season. The two reed bed systems have been operational for three years; during the growing season the plants uptake the nutrients, including phosphorus for plant growth. In the winter when the CWS is partially frozen, the plants help to maintain bed drainage, increase evapotranspiration, and add oxygen to the root zones of the system. The freeze-thaw conditions in the early spring help with the solid- liquid separation because the freezing process extracts water from the flocs and pushes the colloidal material together that settles during the spring thaw. The flocs are the sedimentation of new soils on the bottom of the CWS. The temperature variation of the freeze-thaw also helps to restore the hydraulic conductivity of the CWS and permit annual higher loading rates. The influent concentration of TP was 280 mg/L and the effluent concentration was less than 5 mg/L. Another example of reed beds used for sludge dewatering was a pilot study for a winery in northern Italy (Santoro, 2010). It was successful in more moderate climate and the final sludge was available for land applications.

In a more temperate environment, the following study looked at a hybrid CWS that was made up of 3 cells: planted wetland, pond and another planted wetland. The soil substrate was volcanic gravel (pheldespatite). Lopez-Galvan, Barcelo-Quintal, Perez-Zarco, Solis-Correa & Rivas-Hernandez (2010) looked at the differences in phosphorus removal between winter and summer seasons at a CWS in Mexico City. There was a slight difference but in both seasons, the results were good: in winter, the removal of TP was 68% and in summer, the removal of TP was 61%. Overall the winter numbers were more erratic (higher standard deviation) compared to the summer and there were

indications that the volcanic gravel provided a phosphorus buffering for the system as a whole.

### Startup Parameters

Throughout the literature, there were references to the length of time needed for the startup and steady state operation for the CWS within a natural environment. Two things come to mind: 1) There were almost no journal articles that carefully quantified the startup time needed to reach a quasi equilibrium state and 2) I suspect that some of the studies that I have researched reported results before the CWS had actually reached steady state. Maine, Hadad, Sanchez, Caffaratti, Pedro, Di Luca & Mufarrege (2010) came the closest to saying that the root rhizome zone of emergent plants plays an important role the removal of contaminants but that the development of the plants takes between 3 to 5 years. Kadlec & Wallace (2009) point out that the initial period of performance for a FWS wetland will depend heavily on the antecedent phosphorus load in the soils and the vegetative response relative to the phosphorus loading. And the initial establishment of plants requires more phosphorus than what is needed to sustain the plants long term. Clearly seen with the startup of a small new hybrid CWS constructed wetland system in Tunisia; the results showed that the 1<sup>st</sup> month of operation had 82% removal of phosphorus. The assumption is that the major removal mechanism during startup is abiotic adsorption onto the substrate and this will not be sustained long term (Ghrabi, Bousselmi, Masi & Regelsberger, 2010).

There is one study worth mentioning, Mietto, Albano, Bergamin, Frank, Re, Turco, Picone & De Nat (2010) looked specifically at the start up removal performance

of a pilot HSSF wetland to confirm design parameters before the full scale 100 ha constructed wetland was to be built. The purpose of the pilot study was to simulate the water monitoring program for both biological and chemical analysis that would be used for the full scale system, determine the design parameters such as depth of water, HRT, and the efficiency of the startup behavior of the overall design. The two pilot cells had excellent phosphorus removal of 83 and 85% for TP and 82% and 73% for TDP. Within the design of the wetland, deeper zones of water were planned for increased wetland volume and HRT, areas for enhancing the settling of suspended solids, passive aeration of the water and the ability to provide areas for fish and other wildlife. The length of time that these pilot systems have been operation was not stated in the report.

Kadlec (2006) looked at the startup of several large-scale wetlands in the United States and came to several conclusions and recommendations. The Everglades Nutrient Removal Project (ENRP) is an example of a system that was not allowed to discharge immediately at the start of operation because of permit delays; while creating higher than desired P concentrations in the early period of the startup it also allowed for the P to incorporate into the soils of the wetland. When the flow through operations started there was no increased P concentration in the outflow. As another example cited by Kadlec (2006), Houghton Lake, Michigan had nutrient poor peats and absorbed significant amounts of P for over two years as the plants reached maturity and were able to absorb more P. The key point is that the “early performance of the CWS depends to a very large degree in the antecedent soil conditions” (p.372). Controlled startups are important.

Virgili & Sabatino (2010) looked at the startup of a free water surface ecosystem filter for a municipal system in Italy. The system was designed with natural materials, and compact clay channels that are perpendicular to the water flow. The system is being started up in phases, 2/3 will be completed initially, and the plants on the borders of the channels and eventually throughout the wetland will be *Typha latifolia*, *Iris pseudocorus*, and *Carex elata*. There are internal berms to create the channels in the FWS and it is assumed that the plants on the banks of the channels will provide stability even if there is vehicular traffic over top of the large berms. With regard to the phosphorus removal of the system, it was estimated that up to 168 kg/year of P will be removed but the total annual input of phosphorus is 98 kg/year. There are two possibly impacts to the wetland: 1) the lack of phosphorus will be a limiting factor to the plant growth or 2) the saturated sediment in the wetlands will release P as needed by the wetlands ecosystem. Installing the system in phases will allow them to establish the overall efficiency of the wetland, and to design knowing that phosphorus will likely be rating limiting and phosphorus is one of the nutrients required for removal requires balancing of the different parameters.

#### Software Packages

The mathematical model, Activated Sludge Model No. 2D (ASM2D), is used through the world for wastewater management and simulation of the biological processes for COD, and nutrient removal in WWTP. The ASM2D is an extension of ASM1 to include biological removal of phosphorus. It also includes two processes for the chemical removal of phosphorus by metal ions, Fe and Ca, and other metal ions found in the waste water stream. Another important characteristic ASM2D is the separation of the soluble

phosphorus reactions and the particulate phosphorus reactions (Henze et al., 1999).

Wallace & Liner (2010) has looked at the modeling of ASM with respect to constructed wetlands while for traditional WWTP the microbial yield ratio is between 1 and 0.7; the yield ratio for CWS is as low as 0.068. The implication is that CWS would not require large amounts of nutrients to maintain a mature microbial community under steady state conditions. Within the literature search, there were several different software packages evaluated for constructed wetlands design and operation. I did not spend a great deal of time doing additional research on these packages, but it worth mentioning that there are software programs that help with design, cost, and life cycle analysis (LCA). None of the following models is as extensive as the ASM2D. In looking at the floating island technology, there are opportunities for evaluation of the BioHaven and the design of the process along the lines of these software packages.

Life Cycle Analysis: The life cycle analysis (LCA) approach is gaining recognition because it allows for the evaluation of wetland projects on the basis of sustainability.

Knowles & Dotro (2010) evaluated five different bed media for the retention of phosphorus in HSSF wetlands: gravel, steel slag, light expanded clay aggregate (LECA), hematite, and zeolite. Different LCA computer models were used to compare each of the different bed media. The three key parameters of the most interest were: phosphate removal efficiency, sorption capacity of the material, and the sorption to cost ratio. A few interesting conclusions: 1) there is no production payback cost to steel slag because it is waste product of the steel industry. 2) Hematite had by far the best results with a sorption

to cost ratio of 26,000 (g P/\$) but is not an easy mineral to work with because it does not form particles easily and is prone to clogging. 3) Zeolite had the highest removal rates of phosphate at 93%.

Another area of research for this type of modeling is a LCA of a full sized WWTP compared with the LCA of a VFCW (Roux, Boutin, Risch & Heduit, 2010). The study compared both of these options to raw waste discharge to a receiving body of water. System A was an activated sludge facility designed for 800+ PE, System B was a two stage VFCW and System C was a sewer network with direct discharge into the surface water. As well as evaluating the three scenarios, the research paper looked closely at the limitations of the LCA modeling. The only time I saw this in the literature review was in the paper by Roux, et al. (2010) where the Eutrophication Potential (EP) was quantified and the EP for the VFCW was only slightly lower than direct discharge into the receiving water. The major weakness of LCA as pointed out was that water is not considered a resource in the parameter settings, and toxicity of pathogens is not a parameter in the model. The Organization of Economic Cooperation and Development (OECD) have a model for determining the eutrophication of the receiving waters but it is not used extensively (Pontius, 1990).

Principal Component Analysis: The Warsaw University using statistical modeling software, STATISTICA 8, looked at the groundwater chemistry of a peat bog and the surrounding wetland plant communities.

Stelmaszyk, Chormanski, Grygoruk, Kardel & Okruszko (2010) looked at the groundwater quality of the Red Bog Strict Protected Area in northeast Poland and

compared the ground water ionic characteristics to the vegetation. There were 16 measurement points and over a 2-year period and at each point, two measurements were taken, at the peat layer and the mineral layer below the peat stratum. The 16 different data points represented five different plant types in the natural wetland: alder swamp forest, fern birch forest, raised bog pine forest, meadow community and shrub birch. There were 13 anions and cations tested monthly along with pH, alkalinity, and EC. Based on the statistical analysis there were a few important conclusions: 1) There are clear relationships between the water chemistry characteristics and the vegetation type and 2) besides the water chemistry connection, overall water management and water table fluctuations determine the predominant vegetative type within the system.

AQUATOX: AQUATOX “is an ecosystem simulation model that predicts the fate of various pollutants, such as excess nutrients and organic chemicals, and their effects on aquatic ecosystems, including fish, invertebrates, and aquatic plants” (USEPA, 2011).

The University of Florence, Italy used AQUATOX to decide if a portion of the agricultural land around Lake Massaciuccoli in central Italy was converted into a free water surface (FWS) wetland what would be the impact on the water quality of the lake (Giusti, Marsili-Libelli & Mattioli, 2010). AQUATOX was ran with a seven-year time horizon to allow the ecosystem to reach steady state and for the vegetation to reach maturity. Other parameters considered included: nutrient dynamics in both the water and the soil to be submerged, and the vegetation that would naturally emerge over time. As we have seen in other journal articles, the soil environment is complex and the upper layer is modeled to be aerobic and the deeper layers are anaerobic. The AQUATOX rev 3

model allows for the downward flux of the particulate organic material to become sediments in the aerobic layers but then to also be re-released back into the water column when it reaches the anaerobic layer of the soil. Over the period (7 years) selected the AQUATOX model shows that the removal efficiency of phosphorus will be 24%.

ANOVA: One of the more interesting papers relative to phosphorus removal was a paper presented in Italy at the 12<sup>th</sup> IWA conference using the modeling program, ANOVA software.

Di Luca, Mufarrege, Sanchez, Hadad & Maine (2010) used ANOVA, statistical analysis software to help predict if and when phosphorus will be re-released back into the wastewater stream or will it be retained permanently. ANOVA looked at the accumulation and fractionation of phosphorus in the inlet and outlet sediment of a constructed wetland at a metallurgic plant in Argentina. ANOVA is a statistical method based on the analysis of variances and “looks at the observed variance in a particular variable and how it is partitioned into components attributable to different sources of variation” (Statsoft.com, 2011). Twenty six variables were considered and the ones relative to phosphorus are time, depth and P-fractions, P concentration at the inlet and outlet of the constructed wetland, Calcium carbonate concentration, iron oxide concentration, pH, and alkalinity. The analysis available because of the software modeling cleared showed the interconnectivity of the different parameters. Several conclusions that have been written about in other studies and journals were statistically confirmed: 1) the pH and redox condition of the water and the soils impacts the final concentrations of TP and SRP. 2) The redox condition was seasonal and as the pH

decreased, the redox potential increased when the temperature was at the highest and the macrophyte growth was the most active. The active processes at the higher temperatures mineralized the organic matter that was in the sediments lower the pH. The macrophytes growth rate increased the oxygen in the root zones of the plants and this increased the redox potential of the system. Overall, despite being in an acidic environment, the pH of the wetland did increase with time. 3) This wetland was for a metallurgical plant in Argentina and the concentration of Fe-PO<sub>4</sub> was the highest percentage of the TP at 28% at the inlet. 4) In the sediments of the soil, the CaCO<sub>3</sub> – P fraction was the highest and the higher pH helped to explain that. The software results showed that CaCO<sub>3</sub> – P is the main precipitating mechanism of the CWS. 5) The phosphorus fractioning showed that the inorganic forms were the most significant, after the Fe – P fraction, the others were CaCO<sub>3</sub> – P, orgP-acid, orgP – alkalinity and residual fractions in order of significance. 6) The P concentration was higher at the inlet of the wetland when compared to the outlet and decreased with depth at the inlet. 6) At the outlet, the orgP-alk fraction was composed of phytates that are highly resistant to bacterial action. 7) For the system as a whole, it was estimated that 52% of the TP in the system was made up of Fe-P and Ca-P, the two more unstable forms that can re-release with changes in pH, electric conductivity and that they will eventually form in the sediments of the CWS.

STELLA: A modeling and simulation software, STELLA, was used by Jeyakumar & Zhao (2010) to model the removal of removal of phosphorus from a VF constructed wetland. This paper was to be presented at the IWA conference in 2010 and is still in the process of being published.

The reason it is included is because it will be looking more closely than other studies at the partitioning of phosphorus based on a laboratory study of a VF constructed wetland, and use of dewatered alum sludge cake in tidal flow operation. The five different phosphorus parameters are  $RP_p$  (reactive phosphorus in plants),  $RP_{ww}$  (reactive phosphorus in wastewater),  $RP_{as}$  (reactive phosphorus in alum sludge) and the same parameters for SRP, soluble reactive phosphorus. The initial results of the model correspond well with the actual effluent concentrations of phosphorus. The key here is that modeling software and careful analytical analysis of the different phosphorus types is required to full understand the constructed wetlands system.

SubWet 2.0: The United Nations Environmental Programme released a software program (no cost to the user) called SubWet 2.0 in 2009 for the design of subsurface horizontal flow artificial wetlands.

SubWet 2.0 looks at 16 different parameters and has versions of the software for both cold and warm climates (Wootton, Jorgensen, Santiago & Yates, 2010b; UNEP, 2011). Wootten et al. (2010b) has started to use the model and the two initial case studies looked at a site in Tanzania for a warm climate evaluation, and in northern Canada for a cold climate evaluation. First indications are that the model works well in diverse climate scenarios.

### Hybrid Systems

The latest research clearly shows that the trend in constructed wetlands is towards hybrid systems that built to meet the effluent parameters of several pollutants. It is well

established that each of the basic type of wetland system works better for some pollutants than for others. As shown, throughout the literature search most research is looking at hybrid systems specific to the application required. In this section of the paper, additional constructed wetland systems are mentioned because of the excellent results, specifically phosphorus removal or a unique solution using constructed wetlands. It is quickly apparent that the hybrid systems are more complex and they are designed to more closely mimic the traditional wastewater treatment systems.

#### Vertical Baffled Flow Wetland + Horizontal Subsurface Flow Wetland

The design was by Zhai, Xiao, He and Kerstens (2010) at the Chongqing University near the Three Rivers Gorge in China. A key consideration for the project was to design a system with the smallest footprint possible because of land constraints in the area. Land costs would be 40 – 50% the cost of the overall project. There are three stages to the constructed wetland. The Vertical-Baffled Flow Wetland (VFBW) was designed to be a deep anaerobic system that had between 4 to 6 vertical flow steps interconnected in a U shape with gravel media through the 1<sup>st</sup> stage. Between each of the steps there is a guide wall installed. The second stage of the hybrid system was a Horizontal Subsurface Flow Wetland (HSFW) also with 4 -6 sections that were baffled with three walls to form an S shape, resulting in a long ditch like structure. Between every two section of the HSFW, there was a Natural Aeration Ditch (NAD) to increase the dissolved oxygen in the HSFW. There was also an internal circulation (IC) system to pump the effluent back to the VBFW to improve the denitrification process; the IC was not used continually

throughout the year. The plant chosen was Umbrella Palm because of the tropical climate of the region.

The project started as a pilot study on campus and eventually one pilot study and three full-scale systems have been built. A few important considerations: 1) the hydraulic retention time (HRT) is still quite long in the range of 30 – 45 days for the full-scale systems but the longer HRT did improve the overall removal of the phosphorus. 2) The internal circulation also improved the removal rate of the TP but the change was not as significant as with nitrogen. 3) Zhai et al. (2010) proved that the baffle walls and overall hydraulic design of the system made better use of the wetland area and prevented stagnant water zones and, 4) the overall removal rate for TP was between 76 and 84% for the full-scale systems.

#### Horizontal Subsurface Flow Constructed Wetland Upgrade

The performance of a HFCW built in 2001 in Brazil was not meeting the nutrient removal requirements that it was initially designed for because of superficial runoff and clogging of the bed media from excess of organic matter (OM). There was an imbalance in the accumulation and decomposition of OM on the filters (Philippi, Pelissari, Furtado & Sezerino, 2010). In 2009, a VFCW was added in front of the HFCW and the performance of the system improved significantly; the results were outstanding with regard to phosphorus removal. The VFCW removed 83% of the orthophosphate in the system and the key removal mechanisms were adsorption to the new bed media and uptake of phosphorus by the seedlings in the macrophyte plants. However, when the

water moved to the HFCW, the amount of phosphorus in the final effluent increased because of excretion of phosphorus by the cellular biomass and plants. Suspended solids (SS) contain phosphorus and the concentration of the SS almost doubled in the HFCW when compared to the VFCW. There are a couple of important conclusions: 1) the clogging of the HFCW was caused by an excess of biofilm on the bed media and by reducing the organic load in the HFCW with the addition of the VFCW. There was biofilm shearing because of the lower availability of organic matter to microorganisms as seen in the increased SS concentrations. 2) The addition of the VFCW is in its initial startup phase and eventually the adsorption and plant uptake will reach equilibrium but the system had not reached that point. The overall phosphorus removal for the hybrid system is 69% and continued monitoring.

#### Integrated Constructed Wetland

By definition the integrated constructed wetland (ICW) is a series of shallow free water surface constructed wetlands with a variety of emergent plant types. No artificial liners are used in these systems and the systems were treating domestic wastewater. ICW use the same processes as other CWS and natural wetlands for removal of nutrients: microbial, biological, chemical and physical. The purpose was to determine if contaminants in the sediments of two different unlined ICW in the same region of Ireland could be remobilized and reach groundwater due to infiltration (Dong, Kayranli, Scholz, Harrington & Hedmark, 2010). The two ICW evaluated were on a small domestic site of 0.3 ha and an agricultural site of 0.5 ha. Each of the systems were four unlined cells in series and the plants were predominately *P australis* and *A stolonifera*; both had been

treating wastewater for about the same length of time (7 and 8 years). The experimental setup was unique and I did not see it used in other studies; five mesocosm soil columns were setup to replicate the two different ICW under study but they were in a controlled environment with respect to temperature, humidity, light etc. The soil core samples used in the study was taken directly from the wetland cell # 1 of each of the two ICW. The water used in the columns was also taken from the inlet of the ICW. The results showed that the sediment was saturated with phosphorus for both of the ICW and were actually a source of phosphorus in the water. By using core samples from the site, they were also able to show that as the contaminated effluent passes through the system, the suspended matter settles on the soil surface and probably slows down the contamination of the nutrients into the groundwater. It was also considered but not tested, that other biogeochemical processes slow down groundwater contamination: the soil matrix is clogged, insoluble biogas formation in the soil microbes, and biomass accumulation. After completing the laboratory study, Dong, et al. (2010) looked at other ICW in the region and estimated that the sediment accumulation was about 3 cm·year for moderately loaded systems and is a key parameter to be considered when designing an ICW.

This was another comparison study between one new ICW and a mature ICW in Ireland (Hofmann, Scholz, Tumula, Harrington, Dong & Hedmark, 2010). The new ICW at Glaslough removed over 99% of the phosphorus but the mature system at Dunhill (the same region as the study above) only removed 34% of the phosphorus from the influent wastewater. The newer ICW had larger water cells and longer overall retention times, one of the reasons why the results were better. Another important point relative to the sizing

of the ICW is that the population of Dunhill had grown and the ICW was essentially overloaded. Hofmann et al. (2010) also recognized that the sorption of the phosphorus on the sediment had not reached saturation. The key point was to demonstrate that the ICW could operate without an artificial liner making the project much more economical to build; the groundwater was not negatively impacted by the ICW. I think it is important to note that the study did not go into any detail as to the soil composition and to globally assume that all ICW operate well with no groundwater contamination is risky in a long-term setting.

#### Hybrid Constructed Wetland in Cold Climate

At Hokkaido University in northern Japan, Sharma, Inoue, Kato, Ietsugu, Tomita & Nagasawa (2010) looked at a full scale hybrid constructed wetland (VF+ VF+ HSSF) for the removal of nutrients in a high-strength milking parlor waste stream in a very cold climate, where the annual average air temperature of 6.4 °C. It can be as cold as -22.8 °C in the winter and as high as 30.6 °C in the summer. The hybrid system has been operation since 2006 and was unique in the use of Supersol, a porous floating material made from recycled glass. The Supersol is a product designed in connection with the Japanese government that uses crushed glass and foaming materials ([www.trims.co.jp](http://www.trims.co.jp), 2011). Supersol does a couple of things: 1) it serves as an insulating layer on the top of the two vertical flow wetlands that are in series, and 2) traps and settles the suspended solids in the wastewater stream. Another important characteristic of the hybrid system is the use of clinker ash in the sediment bed to improve the removal of phosphorus from the system. Clinker ash is defined as the ash residue from coal fired power facilities. The overall

removal rate of phosphorus was 76% and the best results were during the non-snow melting periods because there was no overflow water in the HSSF wetland. A couple of key points: 1) the paper did not thoroughly study the use of clinker ash and its viability as a filter media for long term phosphorus removal, and 2) a key the design improvement required for the wetland was to ensure that there was no overflow of water during the annual snow melt.

#### Comparative Study of Two Identical Hybrid Wetlands

In Mexico, a comparative study looked at two identical CWS from a design point of view but with different effluent results. Both systems met the discharge requirements set by the Mexican government except for phosphorus. These systems were evaluated for two years and the study does not definitely conclude why the systems are operating differently. It shows the challenges of completely understanding a constructed wetland. Rivas, Barcelo & Moeller (2010) looked at two systems near the Patzcuaro Lake. The municipal water was split between module A and module B; both of which consisted of a septic tank (ST), a horizontal subsurface flow wetland (HFW), a maturation pond (MA), and a horizontal subsurface flow polishing pond (HFPW). The HFPW was designed for the final removal all pathogens. Module A removed 13% of the phosphorus and module B removed 36% of the phosphorus. It is important to note, that the two systems produced similar removal percentages for all other parameters, i.e. nitrogen, COD, BOD, etc. There was no discussion as to why the phosphorus removal percentages were so different.

### Comparison of Single Stage Constructed Wetlands to Multi-Stage Constructed Wetlands

At Nigde University (Tuncsiper, Ayaz, Gunes & Akca, 2010), a systematic comparison was done looking at several different configurations of single stage CWS and then combining these systems into multi-stage CWS. The single stage units evaluated were: FWS with both floating and emergent plants, and HSSF systems. Two different multi-stage systems were also evaluated; the only difference being one of the systems included a recirculation of some the effluent water back to the second cell of the wetland system and rapid drain of the first cell, an unplanted gravel filtration bed (v-GF). One of the operational problems in the design was that the floating plants on the FWS moved along to other cells of the wetlands by the wind. It was concluded that the plants used in these systems removed between 4 and 7% of the phosphorus. The paper did not give final conclusions for each of the systems individually but did make following conclusions: 1) the single cell systems on average removed 40% of the phosphorus. 2) The multi-stage system with no recirculation removed an additional 40% of the remaining phosphorus. 3) Adding the recirculation removed an additional 26% and finally, the rapid drain operation removed approximately an additional 3%. The final analysis is over 70% of the phosphorus was removed from the municipal wastewater system. The value in this study is the experimental methodology used to systematically start with a single stage CWS and add in series more cells and increasingly more operational parameters to understand how the different components improve the final effluent water quality.

### Comparative Study of Different Constructed Wetland Systems

Ahmad & van Bruggen (2010) compared six different systems for both purification efficiency and economics. Domestic wastewater from the village of Carrion, Spain was treated in parallel to six different scenarios of constructed wetlands. The removal percentages of any of these systems averaged between -17% and 38% for TP. This study caught my attention because of the design of the experiment and the analysis for determining the capital cost relative to each nutrient and the maintenance cost based on 1 gm/day removed. Taken into consideration is the cost and availability of the land needed for each of these systems. A few interesting design variations and conclusions: 1) a horizontal surface flow constructed wetland (HSF) was used in one of the six scenarios. The authors did not comment, but it is not typically seen, more often than not horizontal subsurface flow (HSSF) wetlands are used. Based on the data presented, it looks as though it actually added phosphorus back into the wastewater stream. This warrants further investigation. 2) The free floating macrophytes filters (FMF) were supported with pipes and planted with *Typha domingensis* and overall had the lowest removal rates for TP when compared to the other hybrid constructed wetlands configurations, only the anaerobic pond + facultative pond scenario were worse. However, based on capital and operational costs, the FMF was more competitive the other scenarios that included VSSF and HSSF systems. As stated earlier, the FMF systems also require less land than other constructed wetland configurations and when deciding the best option, needs to be taken into consideration. 3) In looking at the data, I think the performance of the FMF systems would be improved with a HLR higher than the operational  $1.9 \text{ m}^3/\text{day}$ .

### Comparison of Hybrid Wetlands to Biological Nutrient Removal Systems

Traditional wastewater treatment plants (WWTP) are using biological nutrient removal (BNR) operations as alternatives to chemical additives for controlling and reducing nutrients in wastewaters. A combination of nitrogen, phosphorus, and/or ammonia is required for removal in these facilities. A brief description of the BNR operations is included because hybrid system wetlands are increasingly required to do the same – remove all nutrients to legal limits and many of the processes and configurations are similar. Conventional thought indicates that the N:P ratio needs to be 7:1 for biological growth in BNR environments but ongoing research shows that this ratio needs to be closer to 14:1 to achieve low effluent phosphorus concentrations. The PAO process accumulates the phosphorus in the cell biomass that is then settled and removed from the wastewater stream. Any phosphorus not soluble to the cell biomass or particulates not collected from the other stages of the process will be in the final effluent. While most BNR remove on average 50% of the influent phosphorus, the goal is typically closer to 80% removal (Morris & Northrup, 2008).

There are biological phosphorus removal (BPR) processes used commercially for large scale WWTP, all have process steps that include first an anaerobic stage and then anoxic and aerobic stages to promote the uptake of phosphorus by the PAO. In general, the processes that include both anaerobic and aerobic stages are referred to as Phoredox. The difference in these commercial systems is the number of stages and whether or not nitrification is included. The systems also often differ as to if return activated sludge (RAS) is included in the process. With respect to recycle and phosphorus removal, often

the recycle stream will be treated with the chemical additives to remove the phosphorus before recycle back into the system or the recycle will occur only when the wastewater strength is higher because of the possibility of removing more phosphorus from the activated sludge. The integrity of the anaerobic zones with a minimum of oxygen and nitrates is required for an optimal BNR process. If the solids retention time (SRT) is too long the process of methanogenesis will occur and the Volatile Fatty Acids (VFA) required for the PAO will be consumed and unavailable for use by the PAO (Tchobanoglous et al., 2003). A partial list of the commercial systems available include A2/O, University of Cape Town, Johannesburg process, and channel systems. There are multiple configurations for these systems, and some of the systems are continuous flow reactors and others are batch, referred to in the literature as sequencing batch reactors (SBR) (WEF, 2006).

One of the most advanced BNR systems is the commercial system called the Bardenpho system by EIMCO Water Technologies. This is the process currently being installed in Bozeman, Montana; a 53 million dollar complex 5-stage system that removes nitrogen, ammonia, and phosphorus. The five stages are fermentation stage, first anoxic stage, nitrification, second anoxic stage, reaeration stage and recycle of the sludge. The wasted sludge with the process also removes phosphorus from the system (EIMCO, 2010). The anoxic stages are for the nitrification processes and have little impact on the removal of phosphorus (WEF, 2006). It is important to note, that the goal of these systems is to remove the nutrients without the use of additional chemicals, but often the one of the final steps in the process is removal of the remaining phosphorus by with

precipitation with lime, as is the case with the PhoStrip process (Tchobanoglous et al., 2003). These large-scale systems also have continuous phosphorus monitoring to assess the concentrations of P and the rates of release of phosphorus from the anaerobic stages and the rate of uptake in the aerobic stages. These controls allow the plant to make changes to the amount of acetate or VFA to ensure the overall process performance (Crites & Tchobanoglous, 1998).

Other examples of hybrid BNR systems have a phosphate stripper tank to chemically remove the phosphorus from the the activated sludge with either ferric compounds or lime; the sludge may or not be returned to the process stream. As is pointed out in WEF (2006), there are no significant benefits to this method unless phosphorus recovery is necessary.

There are several examples of where the measurement techniques and points of concern are different between BNR operations and constructed wetlands but still warrant consideration. In BNR facilities, the TSS is often a contaminant that is regulated in the discharge permit, but there is little discussion of TSS in the constructed wetlands literature. It is worth pointing out that there is a linear relationship between TSS and the amount of phosphorus in the TSS (WEF, 2006). As an example, the soluble phosphorus concentration in the effluent might be as low as 0.1 mg/L, but if the TSS is as high as 10 mg/L the actual TP effluent concentration is closer to 0.5 to 0.6 mg/L. In another example, activated sludge will have around 1% total solids (TS) and of these TS, 2 to 11 % will be phosphorus (Crites & Tchobanoglous, 1998). The phosphorus associated with

TSS is a major consideration for phosphorus removal in BNR is better understood in the WWTP industry than in the CWS systems.

Another example of an important process parameter for BNR is the ratio between the phosphorus and oxidation – reduction potential (ORP). The redox environment of the wetland at the soil- water interface is understood to be an important parameter for the accretion of new soils; however, there is less discussion about the ORP in the wastewater stream itself for CWS. The requirement for PAO to uptake phosphorus requires an anaerobic environment and a low ORP. In the case of a hybrid-constructed wetland, the ORP is of importance to one or more of the cells (WEF, 2006). The majority of the focus has been on the removal of ammonia and the nitrification/denitrification processes historically; whereas, BNR facilities look at the removal of both ammonia and phosphorus and the interactions between the two processes. There is a clearer understanding of where in the process stream the phosphorus will be re-released and how the ammonia removal processes might be interfering with the phosphorus removal. With all of the BNR processes the separation of the different cells between anaerobic, anoxic, and aerobic are in part to minimize this interference (WEF, 2006).

A major consideration in the design of the overall system is the solids retention time (SRT); the longer the SRT, the less biological phosphorus removal there is for a given amount of influent BOD for WWTP facilities. This design parameter does not have an equivalent in constructed wetlands engineering. If the SRT is long or the influent is lightly loaded with phosphorus the overall efficiency is compromised. The final amount of phosphorus removed is proportional to the amount of biological phosphorus storing

bacteria wasted; the phosphorus-storing biomass production is lower so that less phosphorus is removed. At longer SRT, the biological phosphorus bacteria are in a more extended endogenous phase, which will deplete more of their intercellular storage products. If the glycogen is depleted, there is a less efficient acetate uptake and PHB storage will occur in the anaerobic contact zone of the BNR system. (Tchobanoglous et al., 2003).

Several of the papers presented at the recent International Conference on Wetland Systems for Water Pollution Control in 2010 on constructed wetland systems that mimic the biological nutrient processes; the overall designs of these CWS are complex, and involve several wetlands in series or parallel. Kato, Inoue, Ietsugu, Koba, Sasaki, Miyaji, Yokota, Sharma, Kitagawa & Nagasawa (2010) evaluated six hybrid reed bed systems for treating different agricultural wastewater in cold climates in northern Japan. The configuration of the 6 hybrid systems was similar to the biological nutrient removal process with both aerobic and anaerobic stages; each of the systems were between 3 and 5 different reed beds and the average annual air temperature was around 8 °C. The six configurations included HF, VF and Vertical Flow with circulation pumps constructed wetlands.

Without detailing each of the systems there were several important conclusions: 1) in order to overcome clogging of the reed beds in the cold climate, there were several additional engineered components, a safety bypass structure for each bed, floating cover material for the VF, partition and rotational use of the VF bed surface during growing seasons, and self-priming siphon for the VF beds. 2) The materials used in the beds were

pumiceous gravel, pumiceous sand, river gravel, river sand, shale gravel, and clinker ash.

3) With an inflow of wastewater in the range of 7 - 24 m<sup>3</sup>/d and a range of 338 mg/L – 18.5 mg/L TP, the removal percentage was between 70 – 93%. 4) The first bed in each of the six systems removed the most phosphorus but the largest system with five reed beds in series had the highest overall removal rate. 5) All of the systems functioned through the coldest weather without failure; these six examples demonstrated that with high nutrient load and cold climate the constructed wetland systems can achieve good results.

Ecological Treatment System: Lansing & Martin (2006) at Ohio State University demonstrated that a hybrid constructed wetlands system similar to a BNR system with both anaerobic and aerobic stages can be designed and implemented.

The Waterman Ecological Treatment System (WETS) was tested at a dairy farm in Columbus, Ohio for a twenty week period and is shown in Figure 8 below.

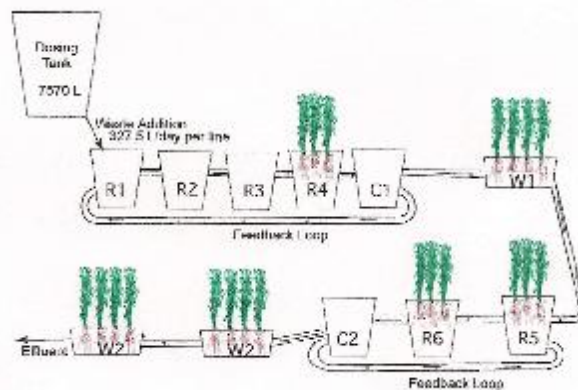


Figure 8: Ecological Wetlands Diagram: R1 anaerobic reactor, R2 anoxic reactor, R3 aerobic reactor, R4 planted aerobic reactor, C1 clarifier, W1 subsurface wetland, R5 and R6 planted aerobic reactors, C2 clarifier, W2 two more subsurface wetlands (Lansing & Martin, 2006).

The ETS system treated 1310 L/day and removed the ammonium-nitrogen, CBOD and phosphorus to acceptable levels. The influent  $\text{PO}_4\text{-P}$  averaged 21.04 mg/L and the effluent was 4.4 mg/L. The planted aerobic reactor has plants supported on racks that allow the roots to be suspended in the water column; the roots provided the area surface area required for the bacterial growth for nitrification, denitrification, and digestion of carbon compounds. The design feature of this experiment caught my attention because; it is essentially, what happens with the plants on the the floating island mats when the roots of the plants are exposed to the water. The plants in R4, R5, and R6 were chosen because of their ability to survive in a nutrient rich environment and included Mexican Papyrus, Umbrella Palm, Black Stern, Purple Stem Taro, Yellow Flag Iris, Canna Lily, March Hibiscus, and Lizard's Tail. The roots were denser in the aerobic reactors than recommended by the USEPA by about 10%. The feedback loops between the clarifiers and the reactors allowed for the selection of microbes with faster settling rates reducing the amount of sludge produced. The subsurface wetlands, W1 and W2 provided for anaerobic zones and surface area for denitrification. In each of these wetlands, there was limestone as a substrate for adsorption sites for additional removal of phosphorus. Water testing through the process showed that the highest percentage of phosphorus removal occurred in the second half of the reactor system. In order to keep the system at a high level of performance, maintenance is required: the clarifiers will need to be keep clog free and the wetlands substrate will have to be periodically recharged. Based on a similar understanding of the BNR processes, it is noted that the anaerobic contact (R1) before (R3) enhances the removal of the phosphorus through the process and the increased

concentration of phosphorus coming into R5 relative to the nitrogen products increased the biological uptake of phosphorus at that point. The recommendations for future consideration are to evaluate the system for short-circuiting within the system since HRT directly affects phosphorus removal, harvesting the biomass and the plants will increase the overall phosphorus removal efficiency and determining the seasonal effects of system performance.

### Floating Mat Systems

Floating mats in the constructed wetlands terminology means one of two different scenarios: natural floating vegetation mats on top of a water surface/constructed wetland, or a manufactured platform that is used to stabilize plants floating on the water surface. There are similarities to the systems and differences. The natural floating vegetation mats found in various parts of the world can be both a problem and/or a benefit to the water body. There is ongoing research for these plants to be harvested for bioenergy, used for indigenous crafts as well better understanding the role they play in wastewater treatment with the uptake of nutrients for growth. Duplicating the benefits of the natural floating mats is a key motivation for the ongoing research and commercialization of the synthetic floating mats. This section of the paper considers both natural and artificial floating vegetation mats, research and applications.

#### Natural Floating Vegetation Mats

Natural floating mats are plants that float onto of the water without support from other structures. There are two different broad categories of these plant systems. Some

plants float as single plants, examples include: duckweed and water hyacinth, water lettuce, and mosquito ferns can occur in any free water surface (FWS) wetland. Typically found in warmer climates, the water hyacinth covered 45% of the Everglades Nutrient Removal Project for the cell that was specifically designed as a FWS (Kadlec, 2006). The other type of floating vegetation is made up of plants that form an actual floating mat, typically cattail, torpedo grass, and meadow grass. This type of natural occurring floating mat is seen in the Houghton Lake wetland in Michigan (Kadlec & Bevis, 2009). There is also increased interest in vegetated mats in a wetlands engineering setting in tropical climates. Managing these types of floating vegetation mats requires several considerations: 1) harvesting these plants is recommended to maintain hydraulic capacity. 2) Sludge management includes both the compost from harvesting and the solids that accumulate in the wetland because of the plant detritus, and other biological sludge 3) Duckweed will kill off the algae in the wetland and a typical detention time is 20 days because they do not transfer oxygen to the water thus creating an anoxic wetland. 4) Duckweed is very sensitive to wind and drifting and requires baffles throughout the wetland to keep the plants in place, and 5) phosphorus removal with water hyacinth is overall limited and erratic, typically pre-treatment or post-treatment is required for phosphorus (Crites & Tchobanoglous, 1998).

The natural floating vegetation mats can also create problems for watersheds and lead to flooding and infrastructure damage if not well managed. The duckweed have very shallow roots (approximately 10 mm long) and grow faster than water hyacinth, doubling every four days. The water hyacinth is very fast growing and will range from 20 to 47

inches above the water line. As little as 10 plants can spread to an area the size of an acre in 8 months (Crites & Tchobanoglous, 1998). As reported in the Philippines with the annual rainy season, this year's water hyacinth growth in the Rio Grande de Mindanao in Cotabato City is a twenty-hectare floating mat that has caused flooding in 37 villages and displaced over 6000 families. The Filipino government is looking at how to use the water hyacinth that is being harvested in an emergency either for livelihood projects or as a biofuel (de Guzman, 2011).

Houghton Lake Floating Mat: The Houghton Lake floating vegetation mat as discussed earlier is a large cattail mat 27 ha. This mat has expanded over the years and the cattails in the floating mat are intruders to this ecosystem.

Kadlec and associates have studied this floating mat extensively and there are several key points worth mentioning. The pre-project planning for the large-scale wetland did not predict either the change in vegetation to the cattails or the formation of the floating mat over time. The vertical layering of the floating vegetation mat sits above the water and the root mat is very tightly woven; the moist dead litter of the plants is on top of the root mat for a total thickness of 20 -25 cm. The mat itself has both living and dead plants mixed throughout and is strong enough to allow foot travel and an ATV supporting 4 people on the surface. Below the root zone is approximately 20 cm of free water before the peat/organic soils. The floating mat is completely organic and floats because of the trapped air in the spaces of the rhizomes and the gases produced in the decomposition process. The floating mat formation mechanisms are several possibilities and include the following: 1) the peat float-up process where the unvegetated organic matter is

“delaminated” from the peat and ongoing germination of the plants continues to occur. 2) The grow- over- process where the rhizomes of the aquatic plants colonize in the water surface that is either unattached or growing from the shore. 3) The mat floating process where the rooted plants and a portion of the substrate separate from the soil medium and float to the surface. 4) The upward retreat of the roots of the plants and detachment from the soils all together. 5) Destabilization of the soils holding the roots because of chemical processes, specifically the peat soils are slightly acidic and the wastewater is slightly alkaline.

The density of the floating mat in Michigan has lead to other changes in the ecosystem. The mat environment is extremely hostile to algae because of the light-limitation under the floating mat. What is less known is whether this improves or hinders the removal of nutrients. There is a microbial environment under the vegetation mat; however, it is assumed to be different than the microbial environment at the free water surface. Without the duckweed, and algae the removal efficiency of phosphorus could be less but might also be compensated for by the fact that the wastewater is exposed to soils on both the upper and lower surfaces, increasing the opportunity for soil processes. The sedimentation under this mat would also be different than other parts of the wetland. The net effect is unknown at this point.

There is speculation as to how and why the floating mat emerged at Houghton Lake, and one theory is that the chemical phenomena at the soil water surface changed the soil structure of the underling peat. The research shows that peat soils will change under alkaline water from a granular soil to gelatinous ooze. The wastewater added is

slightly alkaline compared to the peat. As important is the fact that it receives the nutrients required to sustain and continue to grow from the water and detritus.

In researching, the floating vegetation mats are not specific to constructed wetlands or wastewater treatment. Rydin & Jeglum (2006) have done research showing that floating mats are common features where marshes border lakes in temperate climates similar to Houghton Lake, Michigan and that the plant diversity is greater than just the *Typha latifolia* and *Typha angustifolia* (cattail varieties) found at Houghton Lake. Often there is a brown moss cover, but the systems are actually held together and kept afloat by the rhizomes of *Carex rostrata*, *C. lasiocarpa*, *C. elata*, *Menyanthes trifoliata*, and other species. Sometimes parts of the mat break loose, forming floating rafts. These may be transported by flooding or currents and most plants are capable of establishing a root system once the raft is stranded.

Hydroponic Plants in Asia: Two examples of floating plant systems in Asia, Singapore and Xi'an China show the possibilities in a tropical climate.

A well-designed experiment in Singapore demonstrated the effectiveness of three different plant vegetation mats and successfully quantified the  $k$  rate constant for each of the plants in dry weather flows when the nutrient loads are higher. An outdoor experiment where three 5 m<sup>3</sup> constructed wetlands setup for a one year period using water from three different local rivers (Chua et al., 2010). As well as establishing the  $k$  values for the TN and TP and the 1<sup>st</sup> order kinetics of the system overall, the series of experiments demonstrated that there is a correlation between the  $k$  values and specific plants in the floating vegetation mats. The plant with the highest net removal efficiency

for TP was *Typha angustifolia* with a net reduction in concentration of 35% and the lowest  $k$  value at 0.56/day. It is important to note that because the experiment was done on three different river waters, there are other parameters that may have been different between the three river samples that might have impacted the results, such as pH and alkalinity. The next step of this experiment is to look at larger field applications (Chua et al., 2010).

Xi'an University in China used hydroponic plants as a pretreatment technique in order to reduce the clogging of the constructed wetland that treated municipal wastewater. Ren, Wang, Zhang & Yang (2010) showed that by using the natural floating vegetation mat of *Canna indica*, the suspended solids (SS) and COD are reduced before the water enters the HSSF and VSSF systems. The pilot study tested 3 different depths of the hydroponic ditches (0.1 m, 0.3 m, and 0.6 m) all at the same volume of 0.9. The hydroponic ditches prior to the CWS changed the pH of the water slightly from 7.8 to 8.0 and the pollutant removal performance was better at the shallower depth of 0.1m. It was also shown that the overall performance of the CWS improved with the hydroponic pretreatment system because of reduced clogging and increased dissolved oxygen concentration throughout the system.

#### Manufactured Floating Mats

The floating wetland systems (FTW) are considered to be a constructed wetlands variation that allows for higher treatment level per unit area, a reduction of clogging problems associated with conventional wetlands systems because there are no filters, and the hydroponic plant system will be deeper in the water column. There are several

advantages to this type of system: the deeper pond will accommodate larger and rapid fluctuations in water depth; and the plants are required to get all nutrients from the water column, taking up more nutrients than if some of the required nutrients also were from the sediment at the bottom of the CWS. One of the key parameters to take into account is the contact time between the influent and root zone of the plants, while difficult to accurately measure, it is dependent on the water flow direction and the overall retention time of the system (Hendrickx & Meire, 2010). From a wastewater treatment perspective, the FTW is optimal if designed and operated with both aerobic and anaerobic zones, both zones are important to the removal of phosphorus.

Cubillos, Paredes & Kuschik (2010) compared the floating plant mats (FPM) with HSSF constructed wetlands, both planted and unplanted in a tropical climate. The results did not include phosphorus removal but did look at TSS removal. As there is particulate phosphorus in the TSS of the water, so it is still interesting to see the comparison. The percent removal of the TSS was 96% for the FPM and was 90% for the HSSF.

In the Italian city of Cazzago San Martino, a Floating Wetland System (FWS) was installed in 2009. The photo (Figure 9) below shows the floating platform (tech-ia) before all of the plants were placed on the island. The initial results of this system were presented at the conference in Italy in 2010 (De Stefani, Tocchetto & Borin, 2010). The plants used were typical wetlands plants: cattail, common reed and iris. There were 1800 of the plastic modular elements, and 1400 plants. Initial results for TP removal were only 13.3% but is included because of the floating island elements that are modular and combined as needed for the size of the FWS.



Figure 9: Floating Island Platform: Tech-ia (Tocchetto, 2011)

The floating islands associated with BioHaven of Floating Islands International (FII) have been reported in technical journals, reports to the Montana Board of Research and Commercialization Technology (MBRCT) and marketing brochures. The final report to the MBRCT was in 2010 and reported the importance of the microbial processes occurring on the floating islands, and the relationships to contaminant removal. The concept and application of the floating islands designed and manufactured by FII are well patented for a variety of applications (Cunningham, Camper, Burr, & Stewart, 2010; Kania & Stewart 2010). A key design characteristic is to ensure that the systems will float long term in different weather conditions and with the weight of the substrate and plants that are loaded onto the actual floating island. This is done by designing the floating island to have a gas trapping inset built in the system. Recall that the natural floating islands did this because of the trapped air in the spaces of the rhizomes and the gases

produced in the decomposition process. Also under trademark for the FII is a growth medium, BIOMIX, a mixture of organic materials such as peat and bark. As stated earlier, the majority of the research has been specific to the removal of nitrates, ammonia, and organics. The next phase of study is an in-depth look at phosphorus removal. The final report does show an experimental method that successfully characterized the floating islands relative to the removal of these nutrients and provides a roadmap of how the floating islands could be characterized for phosphorus removal.

There are several important conclusions: 1) determining the microbial communities used for nitrification, denitrification, and consumption of the carbon sources provides an overview for evaluating the phosphorus accumulating organisms (PAO) by analyzing the biofilms and a DNA extraction method that will not only identify the species profile but the extent of the colonies in the FTW. A similar protocol could be used to identify the PAO in the system or evaluate the PAO that thrive in the BioHaven material. 2) Several of the tests ran evaluated the use of aeration and the impact on the removal of the nutrients. The importance of this relative to phosphorus removal is established in the research for constructed wetlands; in anaerobic environments, the soil re-releases the phosphorus back into the wastewater stream. The question to consider is does the mat behave like the soil and re-release bound phosphorus with and without aeration. 3) There is additional work being done on the BioHaven materials; if the material is too buoyant, it can create the problem of less biological treatment by the plants; it has been concluded that the floating island needs to be just below the waterline. 4) There was additional testing of the BioHaven mat materials being wrapped in a porous

nylon bag or other material. The nylon bag type system could be used for holding various chemicals (ie Fe, Al, Ca, etc) to improve the overall removal efficiency of the FTW. 5) The alkalinity and buffering capacity of the system proved to be very important to the overall results and the different materials being tested had different buffering capacities and effluent pH values. The new carpet fiber results had almost twice the buffering capacity when compared to gravel and almost 6 times the buffering capacity of the old matrix. The biofilms or the mat material provided a buffering capacity for the system. These water parameters will be equally as important when evaluating the removal and the mechanisms of removal for the BioHaven mat relative to .phosphorus. 6) Tank tests showed that the phosphate removal happened with the first 24 hours of exposure to the BioHaven material at a rate of 428 mg/d ft<sup>2</sup> with aeration and almost no phosphate was removed without aeration (Stewart et al., 2008). A major goal of this thesis was to design a series of experiments that could further the understanding and hopefully removal efficiency of phosphorus removal using the floating island technology. The experiments that I have suggested are different than the ones used to characterize the ammonia and organic processes but many of the experimental setups would be similar.

### Applications

The research for this section of the thesis focuses on interesting applications. The number of CWS written about agricultural and non-point source wastewater are too numerous to consider all, so only a few representative studies have been included. The focus here is the variety of applications and either the uniqueness of the pollutant

problem or the solution that was used to improve the situation. This includes military applications, industrial, small-scale systems, stormwater, water reuse, developing world challenges and others.

### Agriculture

Not only is agriculture currently the dominant source of pollution to rivers and streams in the US (Lansing & Martin, 2006) it is also the primary reason for the loss of natural wetlands throughout the US; some states in the US have lost more than 85% of their wetlands. The US livestock operations produce more than 1.4 billion tons of organic waste each year (BET, 2011). The Clean Water Act (CWA) does not allow for point source effluent from agricultural operations unless they go through the same rigorous permitting process and treatment that municipalities and industrial applications are required to follow. Agricultural non-point source water pollution is also a major focus of the CWA (USEPA, 2011). In 1985, the Farm Bill passed and changed the policies of the US government to a “no net loss” of wetlands. The USDA set up three different programs to increase wetland areas under the Conservation Reserve Program (CRP), the Wetland Reserve Program (WRP) and a state/federal partnership called the Conservation Reserve Enhancement Program (CREP). As of 2005, over two million hectares of wetland and riparian zones were restored or enhanced (Lowrance, 2010). In the Mississippi River Basin alone, an estimated 2.1 to 5.2 M ha of wetland restoration is required to remove only 20% of the nitrate levels and as of 2006 over 571,000 ha have been restored. With the floodwaters of 2011 along the Mississippi River, there is a renewed interest in the wetlands in the Mississippi watershed and the nine states along the river will contribute

75% of the nitrogen and phosphorus pollution in the river. Of all agricultural products, the largest contributor for phosphorus is livestock manure and many of the farms along the watershed have been built on former wetlands that drain the nutrients before the soils have an opportunity to hold onto some of the nutrients (Kaufman, 2011). There are still questions as to whether wetlands can be used at the watershed level because of the amount of land conversion required.

As another example, phosphorus retention in a restored pine – fen area in Finland were as high as 43% in the peat mix, 25% in the microbial biomass, and 25% in other vegetation, but the land area required for phosphorus removal was over 40% more than what is required for similar removal results for nitrate retention (Bays et al., 2010). The importance of wetlands has been reaffirmed the spring of 2011 with the wide spread flooding along the Mississippi River and its tributaries.

The United States is not alone in realizing the long-term impacts of wetlands being converted to other uses; Budapest University of Technology and Economics (Koncsos, & Derts, 2010) looked at this for the Tisza Valley in Hungary. By looking at key flood events, and the use of the land, as much as 0.3 – 0.45 tonnes/year·km<sup>2</sup> of phosphorus can be absorbed by the wetlands, reservoirs and dyke systems from reaching the surrounding receiving waters. The paper goes on to point out the additional importance of these systems for flood control but that all decisions need to take into account the infrastructure and economic ramifications. The concept of “nutrient farming” is gaining recognition in the United States as an economic approach and by creating a

market incentive for restoring wetlands and reducing the nutrient runoff in Mississippi River Basin (Bays et al., 2010).

Agricultural Irrigation: There is increased pressure to reuse water for a variety of applications; some are for reuse in agricultural applications and others are less essential.

In southern Europe reclaimed water is used for agricultural irrigation (44 %) and urban or environmental applications (37%) (Pedrero et al., 2010). In 2007 – 2009, a 21-month research project was launched to evaluate the performance of HSSF constructed wetland in a rural area of Portugal for the suitability of reclaimed water for irrigation purposes. It is important to note, some of the applications of the reused water are specifically for golf courses and spa resort facilities. Over the course of the 21-month study, the constructed wetland in Vila Fernando was extensively monitored for a variety of contaminants including nutrients, heavy metals, and bacterial activity. Within the HSSF wetland was *Phragmites australis* plants and Filtralite MR 4-8 mm LECA (Lightweight Expanded Clay Aggregate) material. The two primary mechanisms for removal with this LECA are adsorption and chemical precipitation. The average removal efficiency (RE) of the system was 27.4 % for TP but the removal rate for phosphorus should have been in the range of 60 – 90% for the filtralite material. The 2 factors that adversely impacted the performance of the system are the hydraulic loading rate (HLR) and the hydraulic retention time (HRT). As referenced earlier, both of these parameters are important to the design and operation of any constructed wetland. The HLR varied between 2.2 and 56.5 cm/d and the average HLR was as much as 25% higher than the project was designed for because of stormwater. The average effluent TP concentration

of 6.9 mg/L is still too high to be used for an irrigation application; it should be in the range of 3.0 mg/L.

Dairy Application: As a subset of agricultural applications, using CWS for on-site removal of nutrients in dairy applications is typical in a variety of locations around the world.

At Tohoku University in Japan, (Nakano, Chigira, Song, Yano, Normura, Aikawa & Nishimura, 2010) a full-scale constructed wetland successfully removed 89.9% of the Total Phosphorus (TP) during an 8 month study. The wetland experienced increased hydraulic loads because of rainfall and runoff from the paddock and low operational temperatures during the winter months. There are several results worth noting: 1) each of the five stages of the constructed wetland was important to the overall treatment of the wastewater. Stages 1 and 2 were most important for the removal of phosphorus and the later stages were responsible for the removal of the other nutrients and suspended solids (SS). 2) Stages 1 through 4 substrate were covered with a 0.05 m layer of autoclaved lightweight aerated concrete (ALC). Throughout my literature search, this was the only article where ALC substrate was used for a constructed wetland. The experimental design and results did not allow for full discussion of the ALC but it is worth noting that the ALC served to stabilize the pH of the system and absorb the phosphorus. 3) Three different plant strategies used throughout the system: vegetation unsaturated (VU), unvegetation unsaturated (UU) and vegetation half saturated (VH). 4) The temperature difference in the winter months was the major cause of reduction in the removal of phosphorus, even the UU zones of the constructed wetland. 5) The UU system had the

best performance over the 8-month study for the removal of phosphorus. 6) The SS was removed in the final stage of the system, but there was no mention of SS composition.

Queens University of Belfast designed and implemented a complex five earth-lined pond wetlands system for removing BOD and other nutrients, including phosphorus (Forbes, Foy, Mulholland & Brettell, 2010). The watershed area of the facility to CWS ratio was approximately 1:2 and is considered necessary for Dairy Wastewater (DW) based on other studies in Ireland. The annual P loading rate was in the range of 8.7 to 31.8 g P/m<sup>2</sup>·day depending on the time of year. The wetland removed 95% of the influent phosphorus over the course of 4 years and the design and measurement protocol allowed for a thorough characterization of the CWS. The phosphorus was measured as a mass load of kg P/year; allowing for a better understanding of the evapotranspiration of the ponds during the summer months. The total size of the CWS was 12,510 m<sup>2</sup>, each pond was approximately 0.3 m deep for the vegetated areas, and the underground piping between the systems ensured only 1 inlet and 1 outlet for each of the ponds. The plants used, *Phragmites australis*, *Typha latifolia*, *Carex rippraria*, *Iris pseudacrous*, and *Sparganium erectum* were planted throughout in mono blocks and were well established (9 months) before the dairy waste (DW) was introduced into the system. The majority of the phosphorus was removed in Pond 1 but “if the CWS had only 4 ponds (25% less surface area) the effluent would have failed the BOD standard in three years” (p. 360) demonstrates the challenge of design and implementation of any CWS; all concentrations of all pollutants need to meet the regulatory requirements. There were several key conclusions worth mentioning: 1) understanding the potential evapotranspiration (PET)

contribution to the overall performance of the CWS was important because during the months of May to September, there was no discharge to the receiving water. The PET was higher than expected because of the heavily vegetated sides of the ponds that were also sourcing water from the CWS ponds. The retention of the phosphorus was lower in the winter compared to the summer months. 2) The hydraulic retention time (HRT) was around 100 days and was the effective limiting factor to phosphorus retention in the system. 3) With no discharge from the CWS during the summer, months when the receiving body flows were lowest and most vulnerable to the runoff pollution from rainfall, the wetland worked well.

Italian Cheese Production: This application demonstrated a couple of important points, most significantly the operational changes in the production of cheese that produced less phosphorus.

The Research Centre on Animal Production of Italy (Mantovi, Piccinini, Marmiroli & Marmiroli, 2010) looked at two different configurations of SSF constructed wetlands and evaluated the efficiency of two different plant types (cattail and reed) and configurations over a 16-month period. The cheese factory waste under consideration had TP concentrations of 5 to 13 mg/L before treatment. Reed plants (*Phragmites australis*) are typically used in Italy and less is known about the performance of the cattails (*Typha latifolia*). The removal rates for the cattail and reed plants were 75% and 20 % over the course of the study. There were a couple of other important operational changes: 1) using detergents for tank washing that do not contain phosphate lowered the influent concentrations; a common sense operational decision. 2) The phosphorus removal

decreased along the linear length of the wetland indicating that the main process of phosphorus removal was retention of P in the gravel substrate. 3) Plant harvesting, specifically the cattails, more than once during the summer months showed that 10% of the total nutrient load can be removed and the biomass from the cattails could be used for fuel.

Anaerobically Digested Dairy Manure: One of many examples of a hybrid VF wetland is the treatment of anaerobically digested dairy manure (ADDM).

The VF wetland was the second stage of the 2-stage system. The efficiency of the two-stage filtration system was evaluated because ADDM differs from raw manure because altered chemical composition and particle size. The reduction of the orthophosphates in the ADDM was 14% over the course of four different trials. The influent ortho-P values ranged between 103 mg/L to 437 mg/L. Still an area of study and the next phase will include the addition of alkaline phosphatase, an enzyme for removing phosphorus from biologically active species, to the VF wetland to enhance the conversion of organic phosphorus to ortho-phosphates. Orthophosphates in liquid can be recovered as struvite, ammonium magnesium phosphate, a slow release fertilizer. The pilot study (1-week trials) also looked at the efficiency of solid-liquid separation and saw a thickening of 15 to 26% over the course of the different trials (Xia et al., 2010).

Winery and Brewery Applications: Both of these applications require large volumes of water and the amount of nutrients present in the waste stream varies with time as to the actual process step of the operation.

Two agricultural based industries that require unique construct wetland applications are winery effluent and brewery effluent. Several studies internationally have been done to better understand the challenges to these specific industries. Wastewaters from wineries typically have low concentrations of nitrogen and phosphorus relative to the concentrations of COD and TSS. The pH range for this type of wastewater is acidic: 3.5 and 7.0. Any constructed wetland application needs to assimilate large and highly variable flow rates depending on the stage of the wine-making process (vintage, racking, bottling, etc), variable organic loads and the ability to neutralize to low pH (Serrano, Crujeiras, Ruiz & Soto, 2010; Zanieri, Bracali, Bresciani & Masi, 2010). At the University of Coruna in Spain (Serrano et al., 2010), a long term study of three different subsurface horizontal flow (SSHF) construct wetlands using winery wastewater looked at the difference in water depth and how depth influenced the 1<sup>st</sup> order kinetics parameters and overall surface removal rates (SRR). It is well understood that oxygen transfer at the surface of the treatment wetland (oxygen-air interface) is a key factor in determining the overall capacity of the constructed wetland because there are less anaerobic processes in the CWS at the lower depths. A couple of important conclusions after a 50 day startup of the operations: 1) the study showed that the SRR and overall removal efficiency is directly related to the surface loading rate (SLR) and the removal rates are better at lower influent concentrations. 2) An important consideration in designing these systems is understanding the kinetics of the system and it was found that the  $k_A$  values were lower than expected relative to other CWS because of substrate inhibition (this is assumed to be because of an excess of nutrients) but all three CWS values were comparable. 3) The

shallower depth CWS (0.6 m) resulted in more oxygenated effluent but was more sensitive to substrate inhibition. 4) Throughout the study, the effluent water remained acidic with little improvement with time, depth or plants. 5) Most importantly in the broader environmental sense was the evaluation of the amount of methane gas produced and the shallower CWS produced significantly less methane gas (143 to 442 mg/m<sup>2</sup>· d); less anaerobic processes, hence less methanogenic processes.

After the doubling of production at the winery in Siena Italy (Serrano et al., 2010), the wetlands system was redesigned to include four different components, vertical reed bed flow (VRBF), HSSF, FWS, and finally a sand filter. The total HRT was 7.3 days. The VRBF was a filtering bed batch fed system where the sedimentation remained on the bottom of the three parallel basins. The three VRBF lines were intermittently loaded every third day to allow for good oxygen transfer and mineralization of the sediment on the bottom surface of the basins. The overall removal rate of the phosphorus was 60%; the CWS adjusted the pH from acidic values typical of winery wastewater to values that were slightly basic without the addition of any chemicals and the VRBF as the first stage of treatment meant that a primary sedimentation tank was not required. The sludge at the bottom of these basins will need to be removed approximately every 10+ years.

Brewery wastewater remediation is different from winery wastewater for a couple of reasons; the large volume of water used in the manufacturing process and the nutrient loads in the brewery process effluent. In South Africa, a study was done to add a horizontal subsurface wetland as the final step in a brewery wastewater treatment facility

after anaerobic digestion and integrated algal pond systems (IAPS) to further remove nutrient concentrations. Crous & Britz (2010) designed a system to “polish the effluent and serve as a buffer for the fish aquaculture system” where the wastewater is reused. The fish farms are important to the overall project because they provide income for the surrounding community. The HSSF was a four stage serial system and in each stage, the plants were measured for biological productivity. Again, a couple of important conclusions to the study: 1) the influent concentration for phosphorus was in the range of 10 – 50 mg/L and the effluent concentration was in the range of 2 - 4 mg/L. These concentrations meet the water quality standards for South Africa and the water can be reused for hydroponics and aquaculture, such as fish farming. 2) The watercress plants were floated in polystyrene containers and planted at the inlet and outlet of each stage, essentially low tech floating islands; the watercress plants in stages 1 and 2 increased the most in weight (combined increase of 820%). At this point in the HSSF, there are more nutrients available for plant production. This was a successful application of a HSSF and polystyrene containers filled with watercress.

Sugar Factory Stabilization Ponds: A pilot study FWS constructed wetland looked at two different macrophyte species and the treatment of sugar factory effluent in Kenya.

This was a complex study (Bojcevska & Tonderski, 2007) during three different seasons of the year (short rain, dry, and long rain) and two different plants (*Cyperus papyrus* and *Echinochloa pyramidalis*) to determine the relationships relative to the mass removal rate of phosphorus. Sugar factory water has high levels of phosphorus. The evapotranspiration (ET) was taken into account during the different seasons, the removal

efficiency of the two plants and the relationship between TP, total dissolved phosphorus (TDP) and particulate phosphorus (PP) in the wastewater stream. There are several key conclusions: 1) the ET must be accurately established for the specific wetland, and wetlands will have a higher ET if the surrounding area has a lower ET (bare soil vs. vegetation); called the “edge or oasis effect” (p. 73). The shape of the constructed wetland also affects ET and is referred to as the clothesline effect. The TP removal rates actually observed were higher than expected because the water loss had been higher than assumed. 2) The plants did not show major differences in phosphorus uptake but the low removal of TDP suggests that the age of the plants did affect the system performance and the plants should be periodically harvested, especially in tropical environments. 3) When the mass removal calculations were done taking into account the corrected ET data, the proportions of TDP and PP at inflows and outflows indicated that sedimentation was the key process for phosphorus removal. 4) There was a linear relationship between the HLR and the removal rate throughout the experiment. 5) Somewhat surprising the season did not impact the removal rates of TP but did impact the removal of the TDP.

### Industrial

Industrial applications of wastewater treatment are significantly different when compared to municipal or agricultural wastewater systems because the wastewater stream may be composed of specific chemicals where as the municipal system will have nutrients and contaminants that are more predictable in the wastewater stream. The industrial applications are very case specific and are often nutrient-limited; causing the bacteria to grow under different response mechanisms. This is a challenge in a wetland

that receives a high load of COD without the other nutrients. The textile industry is an example where not only does the CWS need to remove the typical compounds it must also remove color. Mezzanotte, Buttiglieri, Canobbio, Occhiuto, Teli, Malpei & Benvenuto (2010) designed three parallel pilot HSSF systems and none of the configurations met the Italian requirements.

Military Application: Installing a constructed wetland in this setting will be challenging because of the sensitivity of the military base and the surrounding community.

A recent study in South Korea along the Tandong Stream used a water quality modeling program (QUAL2K) to design a constructed wetland to meet TP requirement of 0.05 mg/L at the end of the Tandong Stream before entering the Gabcheon River (Seo & Yoon, 2010). In the science town, there are science museums, research facilities and a military base, which is 60 – 90% of the pollution load. The current TP concentrations are in the range of 0.5 – 1.2 mg/L but the standard is 0.05 mg/L. Using the rate equation designed by Kadlec and Knight and referenced throughout the literature on constructed wetlands (Kadlec & Wallace, 2009):

$$A = (Q/k)\ln[(C_e - C^*) / (C_o - C^*)]$$

where: A= required area

$C_e$  = target concentration in mg/L

$C^*$  = background concentration in mg/L

$C_o$  = initial concentration in mg/L

Q = flow rate in m<sup>3</sup>/y

k = rate constant in m/y; assumed to be 12 m/y at 20 °C for P.

The area calculated for the constructed wetland was 80,000 m<sup>2</sup> and because land in the basin area was unavailable, the constructed wetland will be built on the higher land bank areas surrounding the community and military base. It is important to note that the effluent concentrations will not meet permit standards with the constructed wetland alone and the WWTP will need to be upgraded to an advanced system as well. The actual system has not been built but given the land constraints and effluent requirements, it is questionable as to whether it will be completed.

Deicing Runoff Treatment Wetland: Airport applications typically do not have an excess of phosphorus that needs to be removed, but in order for the wetlands system to operate effectively, nutrient requirements must be taken into account.

An interesting wetland treatment system studied by Wallace, Higgins, Liner & Diebold (2007) is the Buffalo International Airport in Buffalo, New York. This wetland was started up in 2009; it was designed with the knowledge that additional nutrients would be needed because of the high carbon load in the deicing chemicals, propylene glycol and ethylene glycol relative to phosphorus, nitrogen and other micronutrients. The second challenge to the wetland is the seasonal nature of the wetland because the deicing chemicals are not used in the summer months. The typical yield for BOD to microbial biomass is in the range of 1.0 to 0.7; the yield corresponds directly to the yield parameter used in the Monod kinetics model. However, the wetland in Buffalo experienced a yield of 0.3 and required a significant addition of phosphorus for the treatment facility to operate without the bacteria formation of polysaccharide slime. The London Heathrow Airport added nutrients at a 10-fold increase to improve the performance after a record

load of deicing fluids because of a severe winter. The performance of the system in London was also improved by the mechanical aeration and increase in the oxygen transfer (Wallace et al., 2007).

### Small Scale Systems

Small scale systems are an important part of the research and implementation of constructed wetlands throughout the world. They are cost effective, used for a variety of applications and allow for water treatment in remote locations. Several papers were presented at the 12<sup>th</sup> International Conference on Wetland Systems in October 2010 and the papers that provided new information, interesting applications relative to phosphorus removal and trends in constructed wetlands are reviewed.

Greenhouse Wetland Technology: The application used in this wetland with organic filters and textile filters for high alpine locations has the potential of being used for larger scale projects with the BioHaven mat material.

Todt, Jenssen & Bulc (2010) demonstrated that using a small scale CWS for the removal of nutrients and particles in a remote location in the Alps was cost effective and required low energy demand on the facility. The end product was reused as fertilizer in the surrounding area. Three different column filters were set up for evaluation: peat (organic filter media), sawdust and a synthetic textile. The organic filter media was compared to a textile with a 10 µm pore openings. The sawdust performed better than the peat at higher loading rates but the organic materials had a higher capacity for retaining small particles. The organic filter material can then be treated in a planted compost bed;

specifically the phosphorus was particulate bound and was retained in the compost soil. The organic materials worked only about 5% better when compared to the textile filter. Overall, the phosphorus in the water was reduced by more than 50%.

Small Agricultural Hotspot in Sweden: Using the Norwegian concept and design of constructed wetlands, a small system was put in place in Sweden outside of Stockholm to treat agricultural runoff by the Swedish University of Agricultural Sciences in 2009 (Kynkaanniemi, Johannesson, Tonderski & Ulen, 2010).

The small wetlands system demonstrates several interesting aspects of the research: the importance of partitioning the phosphorus, and designing a system specific to the application. The area around Stockholm, Lake Bornsjon, has agricultural soils with high percentages of clay that attract the phosphorus from the horse paddocks; however the topsoil samples have aluminum bound P (Al-P) as high as 500 mg P/kg soil, leading to subsurface runoff water concentrations in the range of 6.0 mg P/L. The CWS was designed to “trap” the phosphorus on site before reaching the lake area. The surface area of the wetland was small, only 0.3% of the total catchment area and included a sedimentation basin, and two vegetation filters. An existing culvert was used to collect the subsurface water. Kynkanniemi et al. (2010) evaluated the phosphorus, determining the concentrations of particulate phosphorus (PP), dissolved reactive phosphorus (DRP), and the dry weight of the accumulated sedimentation was analyzed using the Al-bound P extraction methods. The wetland was in operation during snowmelt for the spring of 2009 and the different types of P concentration were tracked over the course of several months.

There were a few conclusions worth noting: 1) the soil in the catchment area is made up of small clay particles and these will bind the P. The clay- P particles settled in the vegetation areas of the CWS. 2) Over the course of monitoring for 27 weeks, the PP retention (g/week· ha wetland area) was highest at the beginning of the snowmelt and later in the year the amount of DP increased as there was no more PP to retain from the runoff. 3) There was also an estimate of the all other phosphorus (OP) as a lumped term, and through continuous monitoring, the OP concentration varied throughout the year. A more complete analysis of OP was not a part of the study.

Small Scale Systems in Denmark: Aarhus University (Arias, Kilian & Brix, 2010) reviewed 160 small-scale constructed wetlands in Denmark of which seven were vertical flow constructed wetlands (VFCW) and came to several conclusions.

The Danish EPA designed construction guidelines for constructed wetlands in 2004 and after several years of operation there are a couple of noteworthy conclusions. The systems are effective at removing organic material and nitrification. However, they are more expensive to construct than originally planned, and the most effective VFCW for phosphorus removal required the retrofit of a phosphorus precipitation unit in order to ensure a constant reliable removal of phosphorus.

Small Scale Systems in Remote Cold Environments: Yates, Wootton, Jorgensen, Santiago & Murphy (2010a and 2010b) along with the University of Waterloo, Canada designed and tested a small scale pilot gravity fed HSSF to review the viability of CWS for remote arctic communities.

The yearly average temperature for the community of Hamlet of Baker Lake is -11.8 °C; average temperature in the summer is between 5 °C and 12 °C. Natural wetland systems have been used historically for the treatment of wastewater in remote Arctic communities and some of these systems have been engineered to enhance the treatment with design modifications to improve residency time. Observations of these natural systems show treatment efficiencies are high in the summer months; as much as 92% removal of phosphorus. Treatment during the winter months is not possible. There are a few design characteristics and conclusions that are specific to cold environments: 1) the piping of the CWS was buried shallowly to minimize late and early season freezing. 2) The plants used are indigenous to the region and natural wetlands (*Carex aquatilis* and *Poa glauca*). 3) The average total phosphorus (TP) removal in the constructed wetland for the summer of 2009 was 5% and during the month of August it was as high as 25% but significantly less than the 92% removal rates seen with the natural systems. 4) Greater pre-treatment prior to the CW will reduce the loading of the nutrients, improving overall efficiency; and 5) temperature is the greatest limiting factor because it influences the mineralization of organic matter and nutrient cycling. Lower areal loading rates and increased residency times are required in the Arctic environment. There was also a comparison between the natural wetlands and the constructed wetlands: natural wetland microbial activity is at its lowest in the summer because of the lack of C and N as available nutrients. In a treated wetland, C and N are not limiting parameters but rather the limiting parameters are temperature and oxygen.

In a more temperate environment, a comparison was done between natural wetlands and constructed wetlands in the Czech Republic and there were similar conclusions, the alkalinity and nutrients was twice as high in the effluent of the constructed wetlands when compared with natural wetlands in the same area of the country (Chmelova et al., 2010). It was felt that increased human and agricultural activities influenced this, however, presented an opportunity for more evaluation of the differences between natural and constructed wetlands and the associated performance of each. As pointed out by Vymazal (2007) constructed wetlands retain more phosphorus when compared to natural wetlands (on average 75 g P/m<sup>2</sup>·year) but the phosphorus loading for constructed wetlands is orders of magnitude higher compared to natural systems.

Single Family Constructed Wetlands: In 2009, the Polish government and the faculty at Gdansk University of Technology jointed studied constructed wetlands for individual households in rural areas with the goal of designing a “ready-to-implement” design.

Three different configurations of constructed wetlands, and nine different households were designed for 4 m<sup>2</sup>/PE (Obarska-Pempkowiak, Gajewska & Wojciechowska, 2010). After primary sedimentation, configuration I was a single bed VF wetland; configuration II was two VF wetlands in series; and configuration III was HF wetland. The final stage for each of the configurations was a settling pond. Each of the investors (farmers) installed their own systems and maintained them throughout the process. There were a couple of important conclusions: high inflow concentrations

caused by poor maintenance or high strength wastewater because of runoff from surrounding fields were the two biggest challenges; if the final settling pond was recontaminated, the benefits of the constructed wetland were negated. The two stage VF constructed wetland performed better than the single stage system. Never the less, there were good results of phosphorus removal (24 to 66%). Follow up research was planned to better understand the mechanisms of removal for these wetlands and improvements to the systems in order to comply with all requirements.

Small Wetland in Switzerland: A small remote constructed wetlands system in Switzerland (Canepel & Romagnolli 2010) was designed as a hybrid system that removed 99% of the total phosphorus.

The CWS was for 66 PE and was monitored for 4 years between the months of June and September. The CWS is preceded by an Imhoff ditch for the settling of sediment and then consists of both a 216 m<sup>2</sup> HSSF and a 225 m<sup>2</sup> FWS. The plants used throughout are “evolving and naturally accepting and selecting the most suitable plants” for high elevations (9000 m in altitude) (p.1229). After the Imhoff ditch the influent concentration of TP is 4.9 mg/L and after the FWS, the 0.01 mg/L TP. The majority of the contaminants were removed by the HSSF but the FWS was included for landscape purposes in the natural park, creating an oxbow-like bend in the river.

Onsite Treatment Facilities in Tanzania: Researchers at the University of Dar es Salaam in Tanzania looked at seven different constructed wetlands currently operating in

the country to better understand the operational challenges and actual performance of each system.

These sites included varied applications: teacher's college, high school, three prisons, small paper mill, and small urban facility (Njau, Mwegoha, Kimwaga & Katima, 2010). All seven systems were HSSF constructed wetlands of varying size and configuration. There were two key conclusions to the project in Tanzania, both predictable. Firstly, systems overall were overcapacity and not well maintained, leading to clogging of the HSSF and eventually blockage, flooding and overland flow problems. Secondly, plant maintenance was more difficult than originally expected because of uprooting of the plants, unwanted weeds in the constructed wetlands and the removal of unhealthy plants was not always consistent. The nutrient removal performance of several of the systems met the effluent requirements for  $\text{NO}_3\text{-N}$  and the higher nutrient concentrations in the effluent allowed for the water to be reused for rice paddy farming at one of the sites. Constructed wetlands are less costly and should be easier to maintain than traditional WWTP but as is seen in several studies of wetlands in developing areas there still needs to be maintenance protocols and training in place to guarantee long-term success.

#### Stormwater Applications

Applications of constructed wetlands for stormwater events is becoming more important; as has been reported throughout this paper. Agricultural runoff is one of the primary causes of degradation in water quality throughout the world and stormwater events from agricultural runoff add considerable nutrients to a receiving water in high

concentrations and short duration events, and often times high water volume events. The average urban stormwater TP concentrations are in the range of 0.26 mg/L, significantly less the agricultural stormwater runoff. The agricultural stormwater runoff TP concentration is in the range of 0.07 to 1.15 mg/L but the higher loading rates do not allow for all of the geobiochemical interactions to take place (Kadlec & Wallace 2009). There is a trend towards treating combined sewer overflow (CSO) systems with stormwater treatment wetlands. Free surface wetlands (FSW) are preferred over subsurface wetlands for event driven systems like storm water applications and are often referred to as stormwater treatment areas (STA). Stormwater wetlands require different design parameters, as each event depends on the flow rate of the event and the time duration of the event. As the flow rate increases, the number of nominal displacements of the water volume in the wetland increases and the phosphorus removal efficiency will drop. For these types of systems the wetlands to watershed area ratio (WWAR) is not good indicator of the phosphorus removal for stormwater events for either urban or agricultural runoff. The WWAR works well as a design model well for constructed wetlands independent of the stormwater events (Kadlec & Wallace, 2009). The original STA design model assumed steady state plug flow and first order nutrient removal; the model was inadequate for design purposes and the dynamic stormwater treatment area model (DMSTA) was implemented and tested extensively with Everglades Nutrient Removal Project (ENRP) (Kadlec, 2006).

A focus on the largest constructed wetland stormwater application in the United States: the Everglades Nutrient Removal Project (ENRP) is necessary to understand the

importance and successes of the ENRP. This is a multi-year, multi faceted project and a brief summary is included. The second paper in this section is a much smaller study but shows the importance of identifying the sources of water pollution and accurately determining the causes before implementing the solution. The trend is for increased design of wetlands that treat stormwater events and there will be increased focus not only on the agricultural applications but also cities and municipalities will design systems that are integrated into the infrastructure of community with planted beltways and smaller scale wetland systems to ensure the effluent water quality.

Everglades Wetland Systems: Established in 1994, this free surface wetlands (FSW) system shows that very large wetland systems are possible. The removal of phosphorus over the operational lifetime of this system is 68 % of the influent from the Everglades Agricultural Area, providing protection for the ecologically sensitive Everglades in southern Florida, USA. These systems are the biggest projects to date for agricultural stormwater treatment systems and the annual average flow is  $4.4 \times 10^6 \text{ m}^3/\text{d}$  (Kadlec & Wallace, 2009; Kadlec, 2006).

This constructed wetlands system is referenced in the literature as both the constructed wetlands itself, Everglades Nutrient Removal Project (ENRP) and the stormwater treatment areas (STA) that the constructed wetland supports. The Everglades Agricultural Area (EAA) is 284,000 ha and the combined STA and ENRP combined are about 10% of the EAA acreage. As with the Houghton Lake wetlands, the *Ecological Engineering Journal* dedicated an entire issue to the Everglades wetlands in 2006. The water conservation areas (WCA) of EAA include not only the STA and ENRP areas but

also reservoirs (3500km<sup>2</sup>), water channels (2400 km), levees and the Everglades National Park. The Everglades ecosystem has historically been very nutrient poor with phosphorus levels in the range of 10 µg P/L. Today most of the EAA runoff from the agricultural activities runs into the WCAs and is impacted by the high P concentrations from stormwater events.

Chimmey & Goforth (2006) described the history of the ENRP for the Ecological Engineering Journal. The ENRP is a 1544 ha unlined prototype treatment wetland built on converted farmland at a cost of over 14 million USD. Because the wetland was built on land previously used for agriculture, the labile P concentrations in the soil were higher than native Florida soil in the surrounding area (Kadlec, 2006). The underlying soil in the ENRP wetland is limestone. As would be expected the discharge permits for this large scale wetland were complex but essentially, there needed to be a 75% reduction in TP load and a long term average TP effluent concentration less than 50 µg P/L. The ENRP began flowing water in 1994 and was a standalone project until 1999 when it was incorporated into one of the STA sites. Because of the P in the agricultural soils, the ENRP was not allowed to discharge water during the startup for 1.5 years (Kadlec & Wallace, 2009). The ENRP wetlands absorbed as much as possible of the P load to the substrate soils. Once the water discharged, it was meeting the regulatory requirements. The goal was a retention capacity of 1.67 g P/m<sup>2</sup>·year, equal to 25 metric tonnes of P/year from EAA runoff and to process between 39-60% of the basin's annual runoff. The ENRP was built in three phases and there were 810,000 seedlings and plant shoots for this system. The planting scheme including allowing the dominant emergent plant

(cattails) populate parts of the wetland and adding various plants known to do well in the Florida environment to create a mixed marsh plant community. Other areas in the wetland were planted with SAV and FAV (Chimmey & Goforth, 2006).

As stated earlier, the major mechanism for removal of phosphorus in the ENRP is accretion of new soils. The new soils are different in structure than the underlying soil and are characterized by the low bulk density. Within the soil environment of the ENRP, there was no consistency in the P concentrations. The rate of accretion for the ENRP was consistent with other wetlands and varied between 0.1 and 2.0 cm/year of new soil with an average of 11.3 gm P/m<sup>2</sup> and the first order settling rates for TP removal were between 12 to 73 m/year (Kadlec, 2006). The ongoing analysis of the P in the ENRP soils shows that sediments are twice as high in P concentration and are comprised of mainly Ca-bound P and organic P.

The six STA are a total of 26,315 ha of constructed wetlands south of Lake Okeechobee with an effective treatment area of 16,190 ha. The purpose of the STA is to remove excess TP from the EAA before it reaches the Everglades Protection Area (EPA). This is a 20 year project that is currently in year 13 and has already cost 1.2 billion USD, and significantly over budget. Since 1994, the STA have received over 12 million ML of influent and retained 1430 metric tons of phosphorus. The effluent flow weighted mean (FWM) phosphorus concentration is in the range of 15 to 94 µg P/L. The importance of these STA systems cannot be underestimated. The design and ongoing operation of these large-scale systems led to the development of several models. These include the Everglades Landscape Model (ELM) that looks at the phosphorus movement

and targets across the entire south Florida ecosystem. As expected, there are hundreds of variables and coefficients. The Wetland Water Quality Model (WWQM) looked specifically at the phosphorus removal in the STA wetlands; but had over 200 coefficients and proved to be too cumbersome for full implementation. The Everglades Phosphorus and Hydrology (EPH) model was simpler and used first order rate equations for the uptake of phosphorus, and the re-release of phosphorus during the dry periods is assumed to be zero order; this model has proved useful for the design and monitoring the STA wetlands. However, the model most useful is the dynamic model for storm water treatment (DMSTA) using long-term rainfall data, detailed water quality information and hydraulic data (Kadlec & Wallace, 2009).

The DMSTA was one of the first wetland models for pulse-driven events and with parameters from the kinetics model ( $k-C^*$ ) and STA modeling; it is able to predict that in periods of time with high phosphorus availability the storage (biota solids) will increase and in time of phosphorus famine the storage of the P will decrease. The  $C^*$  values used for steady-flow rate design are not good descriptors for the pulse constructed wetlands; hence the changes to the DMSTA model for the unsteady state circumstances. The DMSTA accounts for the labile P that returns to the water as well as the P that is permanently stored in the soils. There were three major considerations with the unsteady state model: 1) dynamic events are taken into account when designing wetland treatment systems, 2) the hydraulic flow patterns are not assumed ideal, and 3) the model allows for flexibility in the ecosystem, i.e. the plants used in design and practice. The DMSTA model accounts for the permanent burial of P being directly proportional to the amount of

labile P in storage. The implied labile P was not taken into account in other models. DMSTA model also evaluated different plants communities: emergent aquatic vegetation (EAV), submerged aquatic vegetation (SAV) and periphyton stormwater treatment areas (PSTA). The  $k$  constant values for the DMSTA and specifically the ENRP were calculated for the different plant types. The  $k$  constant for the EAV or PSTA is 24 m/year and the  $k$  constant for the SAV is 74 m/year. There are three different phosphorus pathways that need to be taken into account with this model: biota removal, the surface water phosphorus (soluble phosphorus), and the solid –phase phosphorus (Kadlec, 2006; Kadlec & Wallace, 2009).

In 2003, the research (based on the  $k$  constant data) showed that submerged aquatic vegetation (SAV) lead to improved phosphorus removal when compared with emergent aquatic plants. The six, STA cells are currently being converted to SAV systems. Because these systems are used primarily for agricultural runoff in storm events, the management is different from a system that is continually exposed to water; however, the key lesson learned for these STA in a tropical environment is to not let the STA dry out between rainfall events. The water is kept at a minimum of 15 cm at all of the times and never allowed to be over 137 cm for more than 10 days, requiring frequent field observations (Bays et al., 2010). The SAV plant, *ceratophyllum demersum*, and the attached periphyton complex was researched by Pietro, Chimney & Steinman (2006) to determine the short-term removal rates as well as the environmental conditions such weather, temperature and optical properties of the water. The study area was cell 1 and the plant, commonly called coontail was at almost 100 % coverage of the test area. SAV

plant does not have roots, absorbing all nutrients through its leaves and shoots. The soluble reactive phosphorus (SRP) taken up was measured at different levels to mimic a storm water event. These SAV plants live in the top 30 cm of the water columns and with the optical density/lower light, the plant metabolic activity decreased and the P removal was minimal. It was shown that the SAV plants and not the periphyton used most of the phosphorus; the rate removal constant was between 0.04 and 3.04/hour. The complexity of the system needed to take into account phosphorus removal with respect to solar irradiance, and water temperature. The higher irradiance did not necessarily lead to higher phosphorus removal rates. The SAV plants showed promise for short-term removal of the P which is desired with storm water events and it was felt that the system is P limited and the saturation level of P has not been reached. This study did not look at the long-term nutrient recycle mechanisms for the SAV type. The range of SRP removal was between 26 and 40 % of the influent water phosphorus.

Non-Point Source Evaluation in South Korea: This study in South Korea looked at non-point source water contamination in the Hwa-sung Lake region.

An initial study (Lee, Choi & Oh, 2010) showed the importance of identifying the sources of the water pollution. Historically, it was thought that the major reason for degradation of the water in the Hwa-sung Lake basin was point source contamination from the surrounding municipalities. By looking at the actual nutrient loads during the dry and rainy seasons of the three main tributaries of the lake, it was realized that non-point source contamination was orders of magnitude greater than originally thought. In the past, wastewater management has focused on the point sources only. In theory, this

was a simple evaluation, because there are two distinct periods in the climate. The numbers showed that there was a total of 26.6 kg/day of TP during the dry season from the three primary tributaries and over 950 kg/day during the rainy season. In evaluating the reasons for the large increase in contaminant levels, agricultural activity is important but equally as significant is the increased industrialization of the region and the impermeability of the landscape because of the changes in land use, the runoff from the urban stormwater events was the culprit of the increase in phosphorus load. The tributary with the most urbanization and industrial activity contributed almost 2/3 of the TP contamination. By identifying which of the three tributaries has the largest contribution in non-point source contamination, the next phase of the study will identify strategies for eliminating this with projects that will have the largest impact on the overall water quality.

#### Landfill Leachate

In Thailand, floating pontoons with vetiver grass were tested relative to the removal effectiveness and tolerance for three different landfill leachate strengths (Boonsong & Rittikarn, 2010). Vetiver is a perennial fast growing grass with a deep root system and high biomass production that is native to Thailand. There were two different types of vetiver used for the study and a control pontoon with no vegetation. A total of 27 floating pontoons were evaluated in a 12 week pilot study. Each pontoon was 30 by 30 cm<sup>2</sup> with 25 plants on each pontoon. The removal percentages of phosphorus in all three leachates showed the same trend and the average removal of phosphorus was in the 80% range for the pontoons with the planted vetiver grass. The control pontoon with no plants

showed consistently lower removal rates when compared to the planted pontoons. There was some concern with the survival rate of the vetiver grass in the long term in the landfill leachate and the plants would need to be harvested and new ones planted periodically. This study caught my attention because the experimental setup was excellent and could be used when designing comparison studies with the BioHaven material from Floating Islands.

Scrap iron in landfills creates an underground source of iron. Most of the iron is soluble because of the anaerobic conditions of the landfill leachate and it is important to point out a high concentration of iron will cause clogging in the wetlands (Kadlec & Wallace, 2009). Often there are open water basins with aeration and precipitation of the iron before reaching the constructed wetland. There has also been research that shows the landfill leachate is a low-level source of phosphine gas. The source of the phosphine was the biogenic corrosion of iron and not microbial processes where the phosphate is converted to phosphine. The gaseous concentrations are in the range of  $0.5 \text{ g P/m}^2\text{-year}$  (Kadlec & Wallace, 2009). Ongoing research is looking at the role of phosphine in the overall process. There were no research studies that evaluate the possibility of using this iron-rich wastewater or landfill leachate for the removal of phosphorus.

#### Mine Drainage Waste

The use of constructed wetlands for removing heavy metals from acid mine drainage (AMD) has been applied in the industry for many years. Currently the TVI Resource Development Philippines Inc in the Philippines is considering the installation of a wetland (James, Callora, Inion & Tolentino, 2010). The system currently being

evaluated is an anaerobic down flow system (VF) where the water percolates through organic and limestone substrate. The 90% CaO dissolves and produces alkalinity and the heavy metals are precipitated as hydroxides, sulfates, and carbonates. The other mechanisms of removal include sorption to the soil surface and plant rhizosphere and uptake by the wetland plants: gabi, water hyacinth, bugang reed and vetiver grass. The anaerobic environment will allow for a high rate of removal of the metals in the AMD water and will also require less area for the wetland. The organic load, carbon source, required for the sulfate reducing activity can be either biodegradable (manure) or recalcitrant (forest by-products or sawdust). The natural decomposition of the vegetation will also contribute to the removal of the mine waste water. After the anaerobic operation steps it was recommended that the water pass through an aerobic stage to removal residual metals and create the required balance of COD for the effluent. This CWS is currently being designed at the Canatuan Copper and Zinc Project site in Zamboanga Del Norte, Mindanao, Philippines with a 20 year expected life.

From the discussion of metal-phosphorus chemistry, we know metal ions react with the phosphorus and form a precipitate similar to the limestone. Relative to the BioHaven material, a system could be designed such that the limestone or phosphorus could be attached to the BioHaven mat and as the acid wastewater travels through the wetlands and through the BioHaven mat material a precipitate would form. This is in essence the opposite of attaching metal like products such as alum, PAC or Fe, steel wool etc to the BioHaven mat to remove phosphorus from the wastewater.

### Reuse Water

Reuse water and the technologies supporting the technology will continue to gather momentum as the industry sees annual growth of 25-60% increase in flow rates for countries implementing reuse water strategies. Currently, there are over 3300 reuse water projects either implemented or in progress internationally, over 700 of these are in Europe alone (CIWEM, 2011). The International Water Association (IWA) states that water use efficiency will have to at least double by 2050 at the same time reducing the pollution in the water (Shutes, Revitt & Scholes, 2011). The reuse water management systems are put in place of a variety of reasons including flood control, nutrient management, overall reduced consumption, effluent control and recreational activities. Throughout the literature search, it was apparent that this is an area of future research and applications in the wastewater treatment industry. Constructed wetlands will play a major role in the treatment of wastewater for reuse purposes. Following is a brief description of a few different types of projects gaining recognition.

Singapore is leading the way in Southeast Asia with several different types of constructed wetland projects, with the goal of capturing half to two-thirds of the water in catchment areas. This includes several installations of floating islands as well as more conventional constructed wetland systems (Sims, 2010). The largest of the floating islands systems at Sengkang is 2400 m<sup>2</sup> and made up of 8 different islands. The wetland includes 18 different types of plants for a total of 18,500 individual plants and was completed in November 2010. As of now, the nutrient removal data has not been published but is an ongoing project for the Singaporean government.

In Uganda, greywater towers are being tested at the single-family household level. The greywater towers are columns of soil wrapped in cloth with an inner core of stones and plants grow sideways out of the columns. Greywater is poured into the core of stones from the top to irrigate the plants. This is a very low tech “mini wetland” that can be constructed with local materials, is easy to operate and the plants could be vegetables (Allen, Christian-Smith & Palaniappan, 2010). In this community of Kitgum, after the pilot study additional families also installed the greywater towers.

In Australia, the stormwater effluent from the constructed wetlands (after a 10-day HRT) is pumped into an aquifer for a 12-month period before the water is reused for drinking. The pilot system in place captures 70% of the surface runoff for the community of Salibury and over 30 constructed wetlands were built for the Sidney Olympic Park (Shutes et al., 2011).

## EXPERIMENTAL DESIGN

Based on the literature search, there are a series of tests, I have recommended to better understand and characterize phosphorus removal in constructed wetlands. These experiments are of varying complexity, some are easy and quick to perform and others are more complex with several components required to fully understand the process. For convenience and as an example, the experiments are discussed in the context of the Rehberg Ranch Subdivision and the use of floating islands technology. Realize these experiments could be modified for other wetlands systems and applications. With each of these setups, I have designed the framework for the test, the parameters required for measurement, and the literature sources used for background information. In order to be statistically valid, all tests should be performed in triplicate and the lagoon without a floating island should be used as the control for any of the fieldwork. Any modifications or changes to the process that improve the phosphorus removal cannot negatively impact removal of other contaminants or other water permit considerations. Below is Figure 10 schematic showing the eight experimental ideas divided into three different categories: chemical, biological and field/on-site.

There are three different areas of investigation in this section of the paper. The first looks at the addition of chemical additives to the wastewater stream and the BioHaven mat establish what chemical additives will work and how they can be incorporated into the floating island technology. The second area of research looks at the biological experiments to see if either algae and/or biofilms can be engineered into the BioHaven mat to improve the removal of phosphorus. The third set of experiments is

field work that characterizes the BioHaven mat for basic constructed wetlands parameters and looks at incorporating the floating island technology into a hybrid wetlands system that will improve the uptake of phosphorus with the inclusion of an anaerobic stage before the BioHaven mat to encourage the growth of phosphorus accumulating organisms (PAO). Overall, there are a total of eight different experimental suggestions and possible next steps for continuing the research. It is important to note, that the final determination of what works best to improve the removal of phosphorus with the floating islands technology could be a combination of these different experiments that are optimized for the overall system.

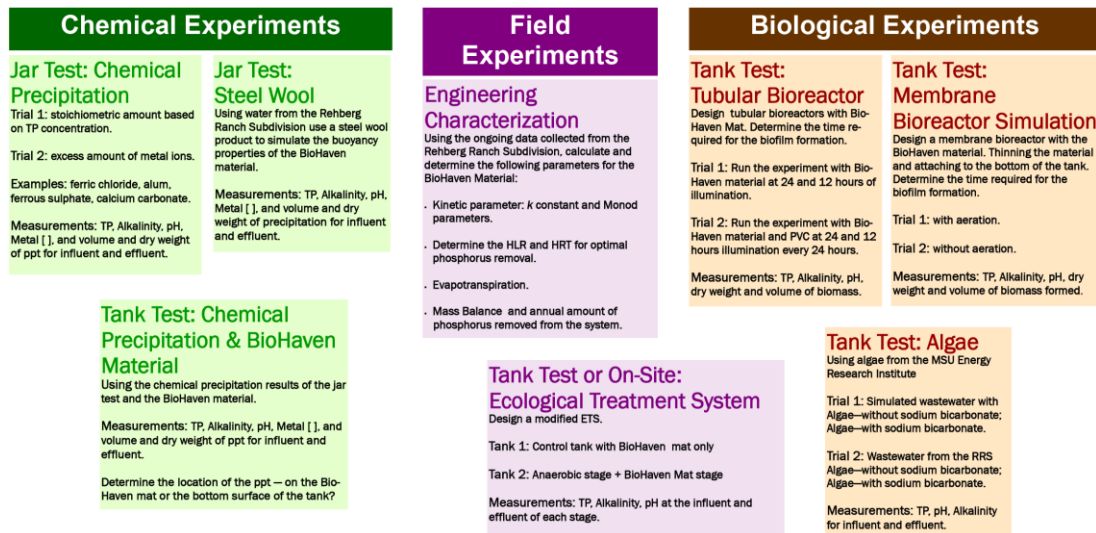


Figure 10: Experimental Design Recommendations

Characterization of Wastewater from Rehberg Ranch  
Subdivision Lagoons for Additional Work with Chemical  
Additives and BioHaven Mat Incorporation

The literature overwhelmingly supports the use of chemical additives to improve the removal efficiencies of phosphorus in wastewater, historically used in traditional wastewater treatment facilities and drinking water facilities. The research shows this is a viable option for constructed wetlands as well. As always, there are tradeoffs: the overall CWS will require more management and possibly cost more because the phosphorus-metal precipitate will have to be managed and there is the additional cost related to the chemicals themselves. As has been recommended in the literature, the use of either waste by-products of nearby industries or natural resources near the constructed wetland are recommended. The advantages to the chemical additives are that the size of the constructed wetland can be minimized; the HRT is shorter and the HLR can be higher. The following three recommendations for further work look at how to begin to incorporate the chemical additives into the BioHaven material used by Floating Islands International for improved phosphorus removal. The recommended wastewater used for these experiments are from the Rehberg Ranch Subdivision and the testing protocols are the standard protocols used for determining TP and phosphate concentrations. These three recommendations are interconnected and the results from the first two determine the parameters for the third. In all three of these experiments, the re-release of phosphorus needs to be taken into consideration. As pointed out in the literature, the solid precipitates will not form in the most stable crystalline structures and the re-release of phosphorus is probable.

### Jar Test – Chemical Precipitation

In the literature search, several articles evaluated large numbers of different chemical additives to determine which work the most effectively for the removal of phosphorus. The first experiment looks to identify possible chemical additives that will work for the wastewater stream from the Rehberg Ranch Subdivision.

Experiment Purpose: The purpose of the first experiment is to test different chemical additives for removal effectiveness of phosphorus.

It is important to evaluate chemicals that contain Fe, Mg, Ca and Al but at this point, a study of the magnitude of Babatunde, et al. (2010b) which looked at 39 different possibilities is not necessary. The focus should be on ferric chloride, ferric sulphate, calcium carbonate, aluminum chloride, locally mined sources, and waste by-products that are readily available.

Supporting Literature: Following is a partial list of literature sources that support this experiment:

*Water Chemistry* by Snoeyink & Jenkins

*Biological Nutrient Removal Operation in Wastewater Treatment Plants* by WEF.

*Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters* by Stumm & Morgan.

*Use of by-products including water treatment residuals as P-removing substrate in constructed wetland systems: Should any release be a concern?* by Babatunde, Zhao & Kumar.

*Phosphorus* – background information. Lenntech Corporation.

*Wastewater Engineering, Treatment and Reuse*, by Tchobanoglous, Burton & Stensel.

*Water Quality and Treatment: A Handbook of Community Water Supplies* by Pontius, editor.

*The treatment of run-off from a fertilizer plant for nitrification, denitrification, phosphorus removal by use of constructed wetlands: a demonstration study* by Cooper, McBarnet, O'Donnell, McMahon, Houston, and Brian.

Parameters for Measurement: This test can easily be performed in a triplicate jar test format that measures the following parameters:

Initial and final pH

Initial and final TP, phosphate

Initial and final, nitrate, alkalinity and metal ion concentrations

Volume, dry weight and settling time of the precipitate

Questions of Inquiry: The following list of questions provides direction as to the design and the desired results of the experiment:

1) Determine which of the chemical additives are optimal for the overall system parameters. This includes evaluating the pH, nitrate removal and precipitate settling as well as phosphorus removal.

2) Over time, is there a re-release of the phosphorus from the precipitate back to the water?

3) The literature strongly recommended that the material used as chemical additives be either waste by-products from other industries, natural materials, and/or materials near the location of the wetland for operational reasons. Throughout the state of

Montana, there has been a great deal of mining and locally here in southwest Montana one of the products mined is talc. The chemical composition of talc is:  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ . The chemical precipitates with Mg and phosphate are  $\text{Mg}(\text{H}_2\text{PO}_4)_2$ ,  $\text{MgHPO}_4$  and  $\text{Mg}_3(\text{PO}_4)_2$ . Talc is used by the paper and forestry industries in the actual manufacturing processes and as an additive for paper industry wastewater for settling flocs in wastewater treatment operations. Throughout the literature search, there were no articles using talc as one of the chemical additives for phosphorus removal in wetland systems, but given that the mineral is local it would be worth evaluating. Mg is a micronutrient that is necessary for some microorganisms, and is more soluble than calcium, so the precipitation of Mg-P will need to be looked at in the context of the overall wetlands system and the other metal salt concentrations (Kadlec & Wallace, 2009). It is worth noting that the other precipitate with Mg in natural waters is  $\text{MgNH}_4\text{PO}_4$ , commonly called struvite. This is of note because not only does it combine with the phosphate ion but also with nitrate. The pH where the solubility of this compound is at a minimum is 10.7; noted this is a sludge product that is undesirable in traditional WWTP and the precipitate would need to be managed in the constructed wetland (Stumm & Morgan, 1981).

There is ongoing research to use the struvite as fertilizer and/or to recover the phosphorus from the struvite. An added advantage to the precipitate struvite is that ammonium is also removed from the system. It is worth noting that the time required for the crystallization of struvite is longer than other chemical precipitates (WEF, 2006).

Trial Specific Information: There are two trials to this experiment: the stoichiometric recommendations and an excess of chemicals.

Trial 1: Minimum amount of chemical required based on stoichiometric mass balance.

There are a couple of points worth mentioning based on the literature: the stoichiometry is not straightforward and is dependent on the pH and competing reactions, but at the same time, it is important to keep the amount of metal ion salts in the wastewater stream to a minimum. This first trial should be based on the stoichiometric equations specific to the metal ion in question.

Trial 2: Excess of the chemicals.

Based on the results of Trial 1, a series of tests should be designed to quantify the actual amount of chemical required for removal of the phosphate to the concentrations required by the wastewater treatment permit. The literature suggests that this will be between 1.5 to 2 times greater than the stoichiometric values.

Next Steps: The next steps after this test will be related to the third experiment in this set of suggestions. How to incorporate the chemical additives onto the BioHaven mat in tank tests?

#### Small Jar Test – Steel Wool

This second test looks at materials commercially available that could be incorporated into the BioHaven mat, and a first recommendation would be to look at a product like steel wool that is made of iron oxide.

Experiment Purpose: The purpose of this experiment is to identify and test other materials that are similar to the BioHaven mat that are made of metals; the example that comes to mind is steel wool.

Steel wool is very similar to the BioHaven mat with a high porosity. There may be other industrial products that are a fiber like material that would also work and these should be included at this point for comparison.

Supporting Literature: The following is a partial list of literature that supports this experiment:

*RietLand vertical flow wetlands: 16 years of experience in the Netherlands and Belgium* by van Oirschot.

*Steel slag produced in Europe as a potential filter media for phosphorus removal from wastewater* by Barca, Andres, Gerente, Meyer & Chararenc.

*Mobilization of phosphorus from iron ore by the bacterium Burkholderia caribensis FeGL03* by Delvasto, Ballester, Munoz, Gonzalez, Blazquez, Igual, Valverde & Garcia-Balboa.

*The integration of an advanced phosphorus removal technology into an Engineered Wetland System* by Wootton, Hussain, Walters, Higgins & Blowes.

Parameters for Measurement: As with the other suggestions, this test should include a control sample and be conducted in triplicate. The parameters for measurement are:

Initial and final pH

Initial and final TP, and phosphate

Initial and final, nitrate, alkalinity and metal ion concentrations

Volume, dry weight and settling time of the precipitate

Questions of Inquiry: The following list of questions provides direction as to the design and results of the experiment:

1) Will a fiber like material that is made of metal and similar to the BioHaven mat remove phosphorus from the wastewater? Time required?

2) Does the steel wool like material float or will it require additional engineering to be incorporated into the floating island?

3) Where is the metal- $\text{PO}_4$  precipitate? Does it stay attached to the steel wool or does it drop to the bottom of the tank/jar?

4) The Langmuir and Freundlich sorption isotherms help predict the final concentrations and time when adsorption has reached saturation, does either of these hold true for this system?

5) Is the removal of phosphorus with this system improved with or without aeration?

Trial Specific Information: Using the industrial material such as steel wool, the test can be performed in either a jar test or tank test.

Consideration should also be given to establishing the metal ion concentrations that are dissolved in water (not the wastewater stream) before this test is performed.

Knowing the dissolved concentration of the metal ion will help to predict that removal efficiency of the product and the size and quality of the product required for a full-scale application.

Next Steps: The next step will be the third experiment in this set of suggestions.

How to incorporate the steel wool into the BioHaven mat?

It is also important at this point to look at the cost effectiveness of these additives; taking into account the size of this additional material and how frequently it would have to be replaced.

#### Chemical Precipitation and BioHaven Mat – Tank Test

Based on the results of the first two experiments, the chemical additives that removed the most TP without compromising the rest of the removal of the other contaminants nutrients should be evaluated.

Experiment Purpose: The literature search suggests that there is ongoing research with sacrificial beds that can be periodically removed from the floating island when saturated with phosphorus or fabric materials that can be incorporated into the constructed wetlands.

The purpose of these experiments, using a tank test format, is to finalize what chemicals and possibilities there are for incorporating these additives into the BioHaven mat before incorporating these modifications into a pilot test or actual application.

Supporting Literature: Following is a partial list of literature sources that support this experiment.

*Phosphorus removal from municipal wastewater in an experimental two –stage vertical flow constructed wetland system equipped with a calcite filter* by Arias, Brix & Johansen.

Aquatic Biologists Inc. [http:// www.aquaticbiologists.com](http://www.aquaticbiologists.com) (2011).

*Alternative filter media for Phosphorous removal in a horizontal subsurface flow constructed wetland* by Vohla, Poldvere, Noorvee, Kuusemets & Mander.

*Filter materials for phosphorus removal from wastewater in treatment wetlands: A review* by Vohla, Koiv, Bavor, Chazarenc & Mander.

*Greenhouse wetland and technology for blackwater treatment in high alpine locations* by Todt, Jenssen & Bulc.

Parameters for Measurement: The following is a list of recommended parameters for measurement:

Initial and final pH

Initial and final TP, phosphate

Initial and final, nitrate, alkalinity and metal ion concentrations

Volume, dry weight and settling time of the precipitate

Questions of Inquiry: The following list of questions provides direction as to the design of the experiment and the required results to decide if the inclusion of chemical additives is possible with the BioHaven mat:

1) The incorporation of the chemical additives to the floating island either in the form of crushed chemical additives that are encased in a material that is permeable to the water or a material like steel wool will require addition engineering. Does the system float when attached, and can the design be scaled up beyond tank tests to an actual system?

2) What are the disposal requirements for either the spent steel wool or the other chemical encasements? Is there phosphorus that can be recovered for other applications?

3) There are some basic operating parameters to be analyzed, such as does the precipitate remain on the floating island or does it settle to the bottom of the constructed wetland? If the TSS concentrations increase significantly, this needs to be considered. Is the increase in TSS and turbidity a result of the chemical precipitation?

4) Do the sorption isotherms, i.e. Langmuir or Freundlich predict the sorptive capacity of the BioHaven mat as various chemical compounds are attached to the BioHaven mat to improve phosphorus retention? Does it predict the point where the chemical additives have reached capacity and need to be disposed of?

5) It is clear from the literature that a large amount of chemical additive will be required (i.e. 31 kg annually per PE for calcium), and the chemicals will have to be periodically removed from the floating island. There will be additional maintenance to ensure that it continues to work properly. All of this needs to be factored into the design.

6) If possible, the kinetics of the chemical additives should also be evaluated and as the research suggests the kinetics may decrease with time over the life of the filter.

Trial Specific Information: This is a tank test and then a larger small-scale pilot system. This is a trial and error experiment as different materials are tested to see what removes phosphorus with the same performance standards set in the first two experiments and successfully attaches to the BioHaven mat.

Next Steps: The next step along the lines of these experiments is to add the plants to the system with the chemical additives and the BioHaven material. Based on the research showing that reed plants would thrive in an environment when dewatering ferric

based sludge; there are plants capable of living on the BioHaven mat and in an environment with an increased metal ion concentration.

Additional studies have shown that the alum not only removes the phosphorus from the wastewater but is also a substrate for biofilm growth. If this is one of the chemical additive that works successfully with the BioHaven mat, then additional studies should be tested to see if it also enhances the growth of biofilms, allowing for another removal mechanism. Does the biofilm growth enhance the removal of phosphorus or, is this a process that prevents the phosphorus and Al from reacting? Do the biofilms diminish the accessible surface for P adsorption and does this negatively impact the hydraulic efficiency of the system?

Another extension of this experiment would be to work with incorporating the sediment blocks into the floating island technology similar to the work being done by ABI, a franchisee of Floating Islands International. The sediment blocks that dissolve may eliminate the need to remove either the steel wool or the encased chemical precipitate, but there will be sediments at the bottom of the constructed wetland that will require management.

### Biological Experiments

The recommendation for the first two biological experiments is based on an in depth look at the phosphorus accumulating organisms (PAO) and the ongoing research to identify and improve the efficiency of these organisms. The third experimental suggestion is to work with the Montana State University Energy Research Institute, the

Algal Biofuels Group and determine if the work done in increasing the oil production in the algae also improves the removal of phosphorus. All of three of these suggestions involve the BioHaven mat and using the mat as an attachment material for biofilm and algae growth in a collaborative experimental setup.

#### Tubular Reactors – Tank Test

Using the BioHaven mat material as the substrate for biofilm growth and phosphorus removal, requires modifying the BioHaven mat and experimenting with other configurations to see if increased biofilm growth and attachment are possible.

Experiment Purpose: This experimental idea is based on two different papers from the literature search, the design of two tubular biofilm reactors experiments using the BioHaven mat material as the substrate material.

In one of the experiments, the BioHaven material becomes the actual tubular reactor, and for the second experiment, it is the filling inside the clear PVC piping. In both suggestions, the wastewater used could be synthetic and/or water from the Rehberg Ranch Subdivision. Both tubular reactors suggested in this experiment are modifications to the existing BioHaven mat that would need to be setup as tank tests for the initial experimental runs.

Supporting Literature: The following is a partial list of literature that supports this experiment:

*Removing nitrogen and phosphorus from simulated wastewater using algal biofilm technique* by Wei, Hu, Li, Xiao, Sun & Tao.

*Simultaneous nutrients and carbon removal during pretreated swine slurry degradation in a tubular biofilm photobioreactor* by De Godos, Gonzalez, Becares, Garcia-Encina & Munoz.

Parameters for Measurement:

Measure initial and final TP and phosphate

Measure initial and final pH and alkalinity

Measurement the biomass that is formed by dry weight

Measurement of the amount of phosphorus in the biomass

Questions of Inquiry: The following list of questions provides direction as to the design and results of the experiment:

1) Are there other applications, designs or modifications of the BioHaven mat that will promote the growth of biofilms and hence the removal of phosphorus from the wastewater?

2) The experimental setup for both of the papers mentioned was excellent and demonstrated in a lab setting the biological mechanisms for removal of the phosphorus, duplicating these experiments with the BioHaven material will allow for a better understanding of the microbial environment and possibility for biofilm attachment to the BioHaven fibers.

Trial Specific Information: There are two different tubular reactor designs that use the BioHaven mat as the substrate material. My first preference is the suggestion of Trial

1 because it would not require additional materials and the modification can easily be extended to existing floating island systems.

Trial 1: The BioHaven material is hollowed out and made into a tubular reactor. This experimental suggestion is based on the paper by De Godos et al. (2009). The tubular reactor used in this paper was the PVC pipe itself and the wastewater was circulated through the pipes while the system was under illumination. The suggestion for this experiment would be to hollow out the BioHaven mat at equally spaced intervals to allow the water to pass through it. The experimental set up would require adjusting the density of the BioHaven mat to allow for the required illumination and oxygen. The wastewater used in these trials can be either synthetic or water from the Rehberg Ranch Subdivision.

A: 24 hours illumination

B: 12 hours illumination

Trial 2: The BioHaven material is used as the filler in a clear PVC tubular reactor; this experiment is based on a paper by Wei et al. (2008). Wei and his colleagues used a filter material similar to bottle washer fibers with a center rod that allowed for easy removal; the fibers radiated out from the center and were the substrate for biofilm attachment. Instead of using the bottle-washer like fibers, this experiment would use the BioHaven material in the PVC pipe as the substrate for biofilm growth.

A: 24 hours illumination

B: 12 hours illumination

Next Steps: The next steps for this test setup would be to see if these tubular reactors are robust and can operate in an outdoor environment with annually changing illumination and other environmental conditions.

#### Membrane Bioreactor Simulation – Tank Test

Based on the submerged membrane technology (MBR), this is an experimental suggestion that does not take advantage of the buoyancy of the BioHaven mat but rather the fibrous nature of the material. The material is similar to the submerged fibers used in commercially available MBR installations for conventional BNR wastewater treatment facilities.

Experiment Purpose: As constructed wetlands are looking more and more like biological nutrient removal systems in traditional WWTP, the use of something novel like the BioHaven mat in an application that it was not necessarily designed for will allow for more opportunities of use.

By attaching the fibers vertically in the tank and replicating the seaweed like movement with aeration and circulation of the wastewater this should promote the attachment of biofilms to the submerged material and the removal of nutrients. The fibers are essentially like artificial roots and stems of plants.

Supporting Literature: The literature below supports this experimental suggestion and the design requirements necessary to implement this idea.

*Control of microbial processes for enhanced water treatment using floating island treatment systems* by Cunningham, Camper, Burr & Stewart.

*MBR effectively removes phosphorus: controlling phosphorus discharges is a study that demonstrates a method that can improve on current systems* by Koch & Von Gottberg.

*PURON MBR effectively removes phosphorus.* Koch Membrane Systems GmbH.

Parameters for Measurement: The following parameters should be measured in the initial experiments to clarify if this concept is a possibility.

Measure initial and final TP and phosphate

Measure initial and final pH and alkalinity

Measurement the biomass that forms on the BioHaven mat

Measurement of the phosphorus concentrations in the biofilm that forms on the BioHaven mat.

Questions of Inquiry: The following list of questions provides direction as to the design and results of the experiment.

1) The BioHaven mat is denser than the fiber design and materials of the membrane technology that are used commercially. There is a possibility that the material will need to be thinned out before being attached to the bottom of the tank to mimic the movement of the MBR fibers. This will be a trial and error in the tank test to get the best possible results.

2) This experimental suggestion is different than the other suggestions because it requires modifications to the BioHaven that are not part of the floating islands commercial focus, but still worth consideration if it promotes phosphorus removal.

Trial Specific Information: These two trials should be performed in series, with the first trial determining if this is a possible application for the BioHaven mat material in a tank test setting.

Trial 1: This tank test should be designed to pulse-aerate the fibers and create an environment of water movement passing through the BioHaven mat. Quantify the amount of aeration and water flow that maximizes the removal of phosphorus.

Trial 2: This tank test should be designed to more closely resemble the environment of the constructed wetlands with less aeration and water flows similar to most constructed wetland systems.

Next Steps: The next steps or additional work is closely related to the work done by Montana State University and is to look at the identification of the phosphorus accumulating organisms (PAO) found in the bioreactors.

Previous work with Floating Islands International and MSU looked at microbial activity, biofilm and DNA work for nitrifying and denitrifying communities, and this would be an extension of that for the PAO communities found in wastewater treatment and then specifically what grows on the BioHaven mat. This is a major focus of the microbial research for phosphorus removal in both conventional WWTP and constructed wetlands.

#### Phosphorus Removal with Algae

The purpose of this experiment is along the lines of what was looked at by the USEPA in the 1970s to provide for both a method for wastewater treatment and

production of a biofuel. Ongoing research at Montana State University in the MSU Algal Biofuels Group is actively looking at oil production in various algae and has concluded that sodium bicarbonate is a chemical trigger that improves the production of oil in the algae. As established with previous research, algae grow readily in most waste waters. This experimental suggestion is to combine the research being done with the floating islands and the MSU Energy Research Institute.

The Montana State University Transfer Office is actively looking to help market and promote the use of this technology for commercial operations, and this is an example of an industry (wastewater management) that might be able to use this technology in a niche market with dual outcomes of both oil production for biofuels and nutrient removal in the wastewater stream.

Experiment Purpose: The experimental setup and methods used for this experiment would come from the MSU Algal Biofuels Group. Within this group very specific/successful methods of implementation have been optimized and used for the work done to determine the use of bicarbonate in the algae growth process.

As with the work done by the MSU Biofuels Group, this would start as a tank test and with the BioHaven mat material as a part of the experimental setup. The additional steps in this experiment would be to identify if the BioHaven mat helps to promote the removal of phosphorus in this environment.

Supporting Literature: The following partial list of literature that supports this experiment:

*Baking soda dramatically boosts oil production in algae* by Boswell.  
MSU News Service.

*Cultivation of green algae Chlorella sp. in different wastewaters from municipal wastewater treatment plant* by Wang, Min, M., Y.C., Chen. Chen, Liu, Wang & Ruan.

*Effect of depth on the performance of algae-based wastewater treatment ponds* by Isayed & Zimmo.

Environmental Protection Agency, United States (2011). *Clean Water Act*  
<http://cfpub.epa.gov/npdes/cwa.cfm>

Parameters for Measurement: Along with the ongoing parameters for the algae, the following parameters should be measured initially and intermittently throughout the experimental runs:

TP and orthophosphate

Alkalinity and pH

Questions of Inquiry: Several questions are important to this experiment.

- 1) Do the algae when spiked with the sodium bicarbonate remove more phosphorus from the wastewater than algae that is not spiked?
- 2) In a field setting, how is the algae dosed with the sodium carbonate periodically?
- 3) The MSU Algal Biofuels Group is looking at a large number of different algae, and the determination of which algae will remove the most phosphorus for these trials is based on previous work and results.

Trial Specific Information: There are two trials to this experiment, using both simulated wastewater and actual wastewater from the Rehberg Ranch Subdivision.

Trial 1: With simulated wastewater, quantify the removal efficiencies of the phosphorus and phosphate with the different algae species. There are two parts to this trial.

A: Algae without the sodium bicarbonate additive

B: Algae with the sodium bicarbonate additive

Trial 2: Using wastewater from the Rehberg Ranch Subdivision, quantify the removal efficiencies of the phosphorus and phosphate with the different algae species available.

A: Algae without the sodium bicarbonate additive

B: Algae with the sodium bicarbonate additive

Next Steps: Incorporating the algae into a constructed wetlands environment is quite complex and pilot studies would be required to see if this is possible. Currently the Rehberg Ranch Subdivision lagoon ponds freeze during the winter and this would have to take into account; it could be that is use of BioHaven mats and algae is applicable only in non-freezing environments.

If the laboratory tests using the algae that is currently being tested on campus, show an improvement in removal of TP and/or phosphates with either the simulated wastewater or the actual wastewater from the Rehberg Ranch Subdivision. The next step then would be to incorporate the floating islands BioHaven mat into the experimental setup and if the results are reproducible in a lab setting and eventually onsite establishing a protocol for implementation, taking into consideration the climate and environment of the field application. Secondly, the different algae species and this process of adding

sodium bicarbonate could be tried in a variety of constructed wetland settings independent of the floating island technology.

### Field Experiments

The following two recommendations are more extensive than the previously suggested work and require fieldwork and analysis at the Rehberg Ranch Subdivision and the two lagoons, the control with no floating island and the second lagoon with the floating island platoon.

#### Characterization: Kinetics, Evapotranspiration, Total Mass of Phosphorus Removed

The literature search shows continued research and studies calling for a better understanding of the complex biogeochemical systems of any constructed wetlands system. With that in mind, this experiment will characterize the BioHaven mat in an actual setting, Rehberg Ranch Subdivision, and allow for a better understanding of the mechanisms of phosphorus removal and the limitations of the floating island technology.

Experiment Purpose: The recommendation is to use data collected from the last year and half since the installation of the floating islands at Rehberg Ranch to characterize the floating islands BioHaven mat.

The setup for this works well because there is a control lagoon directly next to the lagoon pond where the floating island is installed. There are many different data points that have been collected; this data would allow for the determination of the  $k$  constant for the BioHaven mat with and without plants, the evapotranspiration parameters at the

Rehberg Ranch Subdivision, and the material/mass balance of the phosphorus (kg of phosphorus removed/year) in the system. Based on the research from Kadlec (2009c) and Kadlec & Bevis (2009), the temperature differences in the water below the floating mats and the open water should also be examined because temperature affects the biological processes. As clearly pointed out by Molle et al. (2010), media selection for constructed wetlands is typically done with batch experiments (sorption isotherms and kinetics) because of the simplicity of the tests but dynamic tests in saturated conditions are more useful for determining retention kinetics, but they require long setup and experimental time. This information better quantifies the long-term P removal and essentially bypasses the shorter-term mechanism of sorption.

Supporting Literature: Many of the articles in the literature search supported determination of the kinetics, evapotranspiration and mass balance determinations for phosphorus removal in constructed wetlands. Listed below are a representative few that demonstrated experimental design and techniques that could be used to quantify these parameters for floating islands technology and specifically the Rehberg Ranch Subdivision site.

*Evapotranspiration crop coefficients for cattail and bulrush* by Towler, Cahoon & Stein.

*On fitting  $k-C^*$  first order model to batch loaded sub-surface treatment wetlands* by Stein, Towler, Hook & Biederman.

*Constructed wetland Libnic – Typical example of a constructed wetland used in the Czech Republic for wastewater treatment* by Kropfelova, Vymazal, Chmelova & Sulcova.

*Constructed wetlands systems efficiency in pollutants removal in swine water* by Matos, Freitas & Lo Monaco.

*Kinetics of domestic wastewater nutrients removal by subsurface flow constructed wetlands using different species* by Mena, Fernandez, Villasenor, Rodriquez & de Lucas.

*Nutrient removal from reservoir inflows using floating vegetation mats in Singapore* by Chua, Tan, Sim, Borana & Li.

*Phosphorus removal by use of the apatite in constructed wetlands: Design considerations* by Molle, Martin, Esser, Besault, Morlay & Harouiya.

*An autobiotic wetland phosphorus model* by Kadlec.

Parameters for Measurement: The Rehberg Ranch Subdivision in Billings, Montana has two wastewater treatment lagoons that are next to each other, one of the lagoons has a floating island installed. The floating island has been installed for almost 2 years, unplanted and planted during the course of operation. Currently, the lagoons are owned and operated by the City of Billings; a couple of times each month water from the lagoons is sent for chemical testing, including TP and phosphate.

Using the extensive set of data, statistical analysis software and weather data for the region, the following parameters can be determined: 1) the evapotranspiration constants on a monthly basis for this location. 2) The kinetics  $k$  constant for BioHaven mat material assuming 1<sup>st</sup> order kinetics for the removal of phosphorus on a monthly basis. 3) The mass balance of the phosphorus in the system, and 4) using the concept of 12 month rolling average of TP removal first proposed with the ENRP, run this set of calculations to see if the TP removed meets regulatory standards on an annual basis.

Questions of Inquiry: There are several questions that will dictate the type of statistical programming and analysis required to fully characterize the BioHaven mat material in a floating island constructed wetland setting.

1) What are the evapotranspiration parameters for this location on an annual basis? There is very little vegetation in this location, low humidity and it quite exposed on the top of the Rimrocks in Billings.

2) What is the kinetics  $k$  constant for the BioHaven mat material? The second lagoon does not have a floating island installed and this works perfectly as the control lagoon for this project. As recommended by Kadlec & Wallace (2009), the  $k$  constant should be determined on a monthly basis because of the seasonal changes in the climate.

3) Calculate the mass balance for the phosphorus in this system. At the moment the influent and effluent measurements are taken frequently but because of the evaporation of wastewater, the influent and effluent concentrations can be misleading. The mass balance can be thought of simply as the following equation (Crites & Tchobanoglous, 1998):

$$P_{ECW} = P_{CWP} + P_{RIW},$$

where:  $P_{ECW}$  = the effluent P in the constructed wetland (mg/L)

$P_{CWP}$  = the phosphorus in all of the constructed wetlands processes such as plant decay, re-release, chemical removal, accretion, axial dispersion, etc (mg/L)

$P_{RIW}$  = the residual P in the wetland (mg/L)

Because there are many data points for  $P_{ECW}$  and  $P_{RIW}$ , the  $P_{CWP}$  can be calculated

annually and eventually the important mechanisms in that  $P_{CWP}$  term can be identified.

4) All three of these parameters can be analyzed with and without plants because the floating island was allowed to stabilize before plants were added to the system. Knowing the differences will help in the design of future systems in different locations.

Trial Specific Information: This is a field assignment, but the majority of the data has probably already been collected and needs to be evaluated with an analytical software package using the 1<sup>st</sup> order kinetics equations and phosphorus concentration data collected over the last two years.

In evaluating the plants used on the constructed wetland, it is worth looking at the amount of phosphorus in the dry weight of the plants to determine if additional phosphorus is taken up by the biological activity in a phosphorus rich environment. A second area of interest would be to see if there has been any accretion of new soils on the bottom of the wastewater lagoons.

Next Steps: The experimental setup for this will allow for the complete characterization of other constructed wetlands using the floating islands technology and the correlation of these modeling constants to other installed floating island systems.

These constants are also useful for the design of new systems in determining the size of the system given the wastewater parameters and permit requirements. The kinetics of the constructed wetlands is more complex than the 1<sup>st</sup> order rate reactions and  $k$  constants, and a second level of study would allow for the complete study of all kinetic parameters for the removal mechanisms including: accretion, biomass processing, and sorption.

### Modified Ecological Treatment System

This experiment models the ETS wetlands system that was designed at Ohio State by Lansing & Martin and incorporates the anaerobic, anoxic and aerobic stages into the constructed wetland with the addition of the floating island technology.

Experiment Purpose: The ETS system designed at Ohio State used several constructed wetland elements as a part of a larger system for removing nutrients from a dairy wastewater. The plants in this system were suspended into the water from racks; this is very similar to how the plants are suspended in the water by the floating island technology. The idea behind this experiment is to duplicate the setup used by the ETS but to incorporate the BioHaven mat.

When looking at the ETS, there are several anaerobic, anoxic and aerobic cells incorporated into the experiment. The idea behind this experiment is to add the anaerobic cell before the wetland to improve the environment for the phosphorus accumulating organisms (PAO). The addition of the other cells should be added in a step fashion as required to meet the regulatory requirements. In other words, it might be necessary to have as many cells as the ETS and still be successful.

More than likely the system will require the addition of a carbon source, either acetate or VFA at the anaerobic stage for the PAOs. The amount required will need to be optimized as to not negatively affect the other nutrient removal mechanisms, specifically the COD in the wastewater stream and the required effluent concentrations.

Supporting Literature: The primary article used for this experimental recommendation is the article by Lansing & Martin:

*Use of an ecological treatment system (ETS) for the removal of nutrients from dairy waste* by Lansing & Martin.

Parameters for Measurement: There are several parameters that should be measured at different points in the experimental setup:

Measure initial and final TP and phosphate

Measure initial and final pH and alkalinity

Measure the TP and phosphate concentrations between each of the different stages

Measurement the biomass on the BioHaven mat

Measurement of the amount of phosphorus in the biomass

Questions of Inquiry: There are several questions that need to be answered to know if the addition of these cells will improve the removal of phosphorus with the addition of the BioHaven mat.

1) The ETS system that is discussed in the literature review uses plants suspended on racks in the wastewater stream in several cell locations. This is very similar to the plants that are planted on top of the BioHaven mat in the floating island technology; the roots and stems of the plants are exposed to the wastewater stream.

2) The ETS system was made up of several different cells to remove the ammonia and phosphorus from the wastewater stream, this recommended design looks only at the

phosphorus removal, but additional cells can be added for the removal of the nitrogen contaminants as well.

3) Can the results from the study by Lansing & Martin be duplicated with the floating island technology when compared to the ETS?

Trial Specific Information: This tank test will require a control system, which does not have the anaerobic stage before the floating island technology. The first experimental line will be a tank test sized floating island system and will serve as the control for this experimental setup. The second line will include an anaerobic stage before the floating island cell.

The addition of either acetate or VFA is required for the anaerobic stage of this system and the floating island cells will require additional aeration to ensure an aerobic environment. The source of carbon for this stage can come from a variety of sources, the City of Bozeman will be using sugar-beet waste from the sugar processing facilities in Billings, Montana. This is another example, of using locally sourced products to minimize the cost.

Next Steps: If the addition of the anaerobic stage before the floating islands technology (aerobic stage) improves the overall removal efficiency of the phosphorus from the wastewater, then the experimental setup should be repeated with the addition of an anoxic stage in between the anaerobic stage and aerobic stage.

As stated in the literature, there are denitrifying PAO in the anoxic environment. By separating this experimental design in two phases, the relative contribution of each

stage can be assessed for stage efficiency and overall removal of the phosphorus from the wetlands system.

Secondly, because the lagoons at the Rehberg Ranch location are deeper than typical constructed wetlands, there are anaerobic zones in the system, so the addition of a carbon source such as VFA or acetate to the lower depths of the lagoon, to promote the production of PAO might be possible. This may require modification to the Rehberg Ranch lagoons.

## CONCLUSIONS

After an extensive literature research on the removal of phosphorus with the constructed wetlands technology and an evaluation of the floating islands technology, there are several key conclusions that can be drawn. There are several questions in the goal section of this paper that provide the framework for the conclusions.

- 1) What are the various phosphorus partitioning pathways in a constructed wetland environment? And why is it important to understand these pathways?

Phosphorus enters the constructed wetland in either an organic or inorganic state, and is transformed to different forms of phosphorus during the processing mechanisms. The phosphorus in the water will be either dissolved phosphorus or suspended phosphorus. The major component of the dissolved phosphorus (soluble reactive inorganic phosphorus) is readily available for uptake by all biological processes in the wetland, microbial, algae, or plants during the growth cycles. However, when the plants die and decay, the phosphorus is re-released to the the water and soil system as organic phosphorus. Eventually, decayed plant biomass settles on the bottom surface of the wetland and is incorporated into the soil matrix. The phosphorus in the soil remains reactive until permanently stored at depths beyond the root zone of the plants in the wetland substrate.

Other phosphorus compounds in the wastewater stream react directly with the metal ions in the water and the soil substrate. The phosphorus-metal precipitate in the water will settle on the wetland substrate surface. The phosphorus in contact with the soil, sorbs onto the soil surface and reacts with the metal-salts in the soil matrix. These include

Fe, Ca, Mg, and Al. The phosphorus metal complexes remain active and the phosphorus will re-release to the water under anaerobic conditions or changes in the equilibrium of the wetlands systems. Eventually, the precipitates in the substrate will be incorporated into the soil matrix and permanently removed.

The polyphosphates in the wastewater stream, both dissolved and suspended require additional processing to orthophosphate ions before other processing takes place. This includes the breakdown of polyphosphates by the phosphorus accumulating organisms (PAO) using the polyphosphate as an energy source for growth. The phosphorus is a part of the PAO biomass.

Within the context of this thesis, there was a detailed description of the different phosphorus partitions in both the water and soil environments of the wetland. A clear understanding of these partitions is required because phosphorus is a regulated contaminate for all receiving water bodies. Therefore, while phosphorus in water is regulated, phosphorus in soil is not regulated but is a concern if it re-releases in the water. As stated, the methods for determining the concentrations of phosphorus in the water are defined and universally accepted but this is not the case with the methods for determining the concentrations of phosphorus in the soil. From an engineering point of view, knowing what form and final location of the phosphorus in the wetland dictates the design of the wetlands system.

- 2) What are the major mechanisms (natural and anthropogenic) for aqueous phosphorus removal?

Discussed at length are the four different mechanisms for removal of phosphorus in a constructed wetland environment, accretion, sorption, chemical reaction, and biological activity. Each of these four removal mechanisms plays an important part in the overall removal of phosphorus. Each of these removal mechanisms are interconnected and influence the final effluent concentrations of the wastewater stream as it leaves the constructed wetlands environment.

Accretion and the accumulation of new soils on the bottom of the wetland is the non-saturable removal mechanism that permanently removes phosphorus from the water. Realize that the new soils are made up of the decayed biomass that has incorporated the phosphorus during the growth of the plants, algae and microbes. While the mechanisms of removal between the accretion and biological processes are profoundly different, they are interconnected and a thriving biological community is required for the accretion of new soils. The accumulation of new soils is a slow process at the average rate of 2 cm/year.

The biological processes include the uptake of phosphorus for growth by the plants, algae and microbes. As these living organisms die and decay, they re-release some of the phosphorus back into the water. For this reason, phosphorus removal by all biological activity is less than what is taken up for growth.

Sorption of phosphorus to the substrate surface of the wetland is a saturable mechanism that is very important during the startup of a constructed wetland but typically reaches an equilibrium after about a year. The phosphorus is sorbed onto the top of the substrate and slowly incorporated in the substrate matrix. This happens because of

the chemical properties of the soil and the ability of the metal-ions in the substrate to react chemically and bind the phosphorus in the soil. This mechanism is also closely tied to the accretion of new soils and the ability of the decaying biomass to sorb into the existing substrate. The sorption of phosphorus in the wetland is heavily dependent on the type and chemical makeup of the substrate and is an important design parameter as a result.

The final removal mechanism includes all chemical reactions that permanently remove phosphorus from the water. This includes the chemical reactions at the substrate surface with the metal ions found in most substrates: Fe, Mg, Ca, and Al. Within the context of the paper, there is a detailed discussion of the use of chemical additives to the wetland to improve the removal efficiency of phosphorus. From a research perspective, there are ongoing projects to determine which chemical additives will work best in a constructed wetland. Chemical additives are often required to meet the regulatory requirements but produce precipitates and sludge that needs to be addressed. The use of chemical additives allows the wetland to operate with a smaller land area and with shorter hydraulic retention times, there is a trade off that needs to be taken into account at the design phase of the wetland.

- 3) Why is phosphorus more difficult to permanently remove than carbon and nitrogen based contaminants?

There are several reasons as to why phosphorus removal in constructed wetlands has not had the same successes and improvements in removal efficiencies as carbon and nitrogen based contaminants. The reactions of phosphorus and the biological processing

is on an order of magnitude slower than either the carbon or nitrogen processes. If the hydraulic retention times of the system are long enough, the removal efficiencies are better, but from a design and operation point of view, this is often not possible. Carbon and nitrogen change chemically to products in the wetland system that are more easily removed and managed. As examples, nitrogen based contaminants eventually are transformed to nitrogen gas, the same holds true for the carbon cycles. Phosphorus remains in the wetlands system as the phosphate ion,  $\text{PO}_4^{-3}$ . The phosphate ion is used by the biological processes and reacts with the chemical environment but it is not transformed to a different configuration or different matter state. There is ongoing research to understand the phosphorus interactions between the soil and water environments in constructed wetlands.

- 4) What are the major environmental variables (i.e. alkalinity, pH, ORP, temperature) that affect phosphorus removal?

Within the paper, many different environmental variables affect the final removal efficiencies of phosphorus in the wetland system. These include the hydraulic retention time of the system, the phosphorus loading rate, the alkalinity of the soil and the water, the pH, redox potential, temperature and the wetland surrounding relative to the evapotranspiration of the system. Maintaining a constant HRT and loading rates will ensure that the system continues to operate in a quasi-equilibrium state long term. The wetland should be designed at the start with climate parameters taken into account. Continuous monitoring of the effluent concentrations of TP and orthophosphate are required and I think the first sign of changes in the system will be noticed with pH and

ORP variations. The reasons for the changes in pH or ORP will depend on the wetlands system and could include the following: 1) sorptive capacity of the substrate is depleted, 2) changes in plant population or changes in biological processing for seasonal reasons, and 3) a change from an aerobic to anaerobic environment. There are many other possibilities.

There is ongoing research to better understand the soil-water interface of constructed wetlands and how the pH, ORP and wastewater parameters impact this and the final effluent concentrations. The final effluent concentrations of the constructed wetland depend on the ability of the system to permanently bury the phosphorus in the wetland soils and substrates. The re-release of phosphorus is environmentally driven and the reasons why this happens needs to well understood for both the design and operational of the wetland.

- 5) What bench-scale experiments can be done to assess constructed wetlands removal in an “on-site” context?

From an “on-site” perspective there are two different types of experiments that can be done. The ongoing testing to ensure that continued performance of a wetland are discussed in question four. At a minimum, the effluent concentrations, pH and ORP are all required. From the point of view of determining different applications that will improve the removal mechanisms of phosphorus in constructed wetlands there are three different areas of study: 1) the addition of chemical additives is gaining traction for use in constructed wetlands for the removal of phosphorus. 2) The optimization of biological processes and 3) detailed onsite evaluations will improve the design and performance of

the system. These include a clear understanding of the kinetics and the climate variations specific to the system at hand. Within the context of this thesis, these experiments were designed to improve the removal mechanisms for the floating islands technology but are applicable for a variety of different constructed wetland types.

The use of hybrid systems for the removal of all nutrients are being designed extensively in newly designed and installed systems because of the complex requirements of the wastewater permits and the necessity to meet all standards. The hybrid systems resemble the biological nutrient removal WWTP and are multi-stages systems with anaerobic, anoxic and aerobic cells, typically incorporating different types of constructed wetlands.

In conclusion, the removal of phosphorus from wastewater streams using the technology of constructed wetlands is a multi-prong approach. Table 3 summarizes the different mechanisms and types of constructed wetlands that could be used for large, medium and small systems with different phosphorus loading requirements. This is not a detailed or complete analysis but clearly shows that there are differences in approaches depending on the influent concentrations, the size of the constructed wetland and the effluent requirements.

<b>Size and phosphorus loading of the wetland system</b>	<b>Anticipated primary removal mechanisms</b>	<b>Recommended type of constructed wetland</b>
Small sized systems Lightly loaded at < 10 mg TP/L	Biological removal and accretion of new soils.	Free water surface and floating island technology.
Medium loaded at 10 – 50 TP mg/L	Biological, sorption and accretion of new soils.	Hybrid systems and substrate with sorptive capacities.
Heavily loaded at > 50 TP mg/L	Biological, chemical, sorption and accretion of new soils.	Multi-staged system with an additional cell for the chemical additives.
<b>Medium Sized Systems</b> Lightly loaded at < 10 mg TP/L	Biological removal and accretion of new soils.	Free water surface and floating island technology.
Medium loaded at 10 – 50 TP mg/L	Biological, sorption and accretion of new soils.	Hybrid systems and substrate with sorptive capacities.
Heavily loaded at > 50 TP mg/L	Biological, chemical, sorption and accretion of new soils.	Multi-staged system with an additional cell for the chemical additives.
<b>Large Sized Systems</b> Lightly loaded at < 10 mg TP/L	Biological removal and accretion of new soils.	Free water surface systems.
Medium loaded at 10 – 50 TP mg/L	Biological, sorption and accretion of new soils.	Free water surface systems with long HRT and substrate with sorptive capacities.
Heavily loaded at > 50 mg TP/L	Biological, and accretion of new soils.	Free water surface systems with long HRT. Needs to include algae and plant selection with high biomass production.

Table 3: Summary of Design Recommendations. An overview of constructed wetlands design for systems of different size and phosphorus loading parameters.

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APPENDICES

APPENDIX A

COMMONLY USED ACRONYMS IN  
CONSTRUCTED WETLAND TECHNOLOGY

ABP – Algae-based Ponds  
 ABR – Anaerobic Baffled Reactor  
 AD – Anaerobic Digester  
 ADD – Automatic Dishwasher  
 Detergent  
 ADDM – Anaerobically Digested Dairy  
 Manure  
 ADW – Agricultural Drainage Waters  
 AFDM – Ash Free Dry Mass  
 AHD – Australian Height Datum  
 AL – Acid Ammonium Lactate Solution  
 ALC – Autoclaved Lightweight Aerated  
 Concrete  
 ALD – Anoxic Limestone Drains  
 AMD – Acid Mine Drainage  
 ANA – Anaerobic Pond  
 AS – Active Sediment Layer  
 ASTR – Aquifer Storage Transfer  
 Recovery  
 BAP – Bio-Available Phosphorus  
 BD – Bottom Detritus/Bicarbonate  
 Dithionate  
 BEPR – Biological Excess Phosphorus  
 Removal  
 Bio-P – Biological Phosphorus  
 BMP – Best Management Practices  
 BNR – Biological Nutrient Removal  
 BOD – Biological Oxygen Demand  
 BOF – Basic Oxygen Furnace (slag)  
 BPR – Biological Phosphorus Removal  
 CAFO – Concentrated Animal Feed  
 Operations  
 CBM – Cyanobacterial Mat  
 CBOD – Carbonaceous Biological  
 Oxygen Demand  
 CLC – Cost of Life-Cycle  
 COD – Chemical Oxygen Demand  
 COR – Coefficient of Reliability  
 CRP – Conservation Reserve Program  
 CREP – Conservation Reserve  
 Enhancement Program  
 CWP – Constructed Wetlands Processes  
 CSO – Combined Sewer Overflows  
 Da - Dalton  
 DASC – Dewatered Alum Sludge Cakes  
 DHS – Dissolved Humic Substances  
 DIP – Dissolved Inorganic Phosphorus  
 DMSTA – Dynamic Model for Storm  
 Water Area Events  
 DO – Dissolved Oxygen  
 DOC – Dissolved Organic Carbon  
 DOP – Dissolved Organic Phosphorus  
 DPAO – Denitrifying Phosphorus  
 Accumulating Organisms  
 DRP – Dissolved Reactive Phosphorus  
 DS – Dead Sediments  
 DSSP – Degree of Soil Saturation with  
 Phosphorus  
 DTD – Detention Time Distribution  
 DTP – Dissolved Total Phosphorus  
 DW – dry weight, dairy waste  
 EAA – Everglades Agricultural Area  
 EAF – Electric Arc Furnace Slag  
 EAV – Emergent Aquatic Vegetation  
 EBPR – Enhanced Biological  
 Phosphorus Removal  
 ECP – Equilibrium Phosphate  
 Concentration  
 ECW – Effluent from Constructed  
 Wetlands  
 EDTA - Ethylenediaminetetraacetic  
 Acid:  $C_{10}H_{16}N_2O_8$   
 EL – Exhaustion Lifetime  
 ELM – Everglades Landscape Model  
 ENRP – Everglades Nutrient Removal  
 Project  
 EP - Eutrophication Potential  
 EPA – Environmental Protection  
 Agency/Everglades Protection Area  
 EPAIE – Environmental Protection  
 Agency Ireland  
 EPCo – Equivalent Phosphorus  
 Concentration  
 EPH – Everglades Phosphorus  
 Hydrology Model

EPS – Extracellular Polymeric Substances	HWTS – Hybrid Reed/Willow Treatment System
ET – Evapotranspiration	IAP – Ion Activity Product
ETA – Evapotranspiration Absorption System	IAPS – Integrated Algal Ponds System
ETP/PET – Evapotranspiration Potential	IC – Internal Circulation
EVA – Emergent Aquatic Vegetation	ICW – Integrated Constructed Wetland
EW – Engineered Wetland	IOP – Inorganic Phosphorus
FAC – Facultative Pond	IOTR – Implied Oxygen Transfer Rate
FAV – Floating Aquatic Vegetation	IP – Inorganic Phosphorus
FCP – Filterable Colloidal Phosphorus	IUWM – Integrated Urban Water Management
FFS – Free Floating System	IWA – International Water Association
FII – Floating Islands International	IWTS – Individual Wastewater Treatment Systems
FMF – Free Floating Macrophytes Filter	LCA – Life Cycle Analysis
FOP – Filterable Organic Phosphorus	LCPBT – Life Cycle Payback Time
FPM – Floating Plant Mat	LECA – Light Expanded Clay Aggregate
FRP – Filterable Reactive Phosphorus	LR – Land Requirement
FTW – Floating Treatment Wetland	LRI – Inlet Loading Rate
FWA – Flow –Weighted Mean	LSB – Limestone Leach Beds
FWC – Farm Constructed Wetland	LWA – Light Weight Aggregate
FWS – Free Water Surface Wetland	MAT – Maturation Pond
GAO – Glycogen Accumulating Organisms	MBR – Membrane Bioreactor
GPP – Gross Primary Production	MEAPAO - Micro Electron Acceptor Phosphorus Accumulating Organism
HFAP – Humic/Folic Acid Phosphorus	MLSS – Mixed Liquor Suspended Solids
HFCW – Horizontal Flow Constructed Wetland	MP – Maturation Pond
HFPW – Horizontal Flow Polishing Wetland	MRP – Molybdate Reactive Phosphorus
HFW – Horizontal Flow Wetland	MWTP – Municipal Wastewater Treatment Plant
HLR –Hydraulic Loading Rate	NAD – Natural Aeration Ditch
HPB – Horizontal Flow Planted Bed	NFT – Nutrient Film Technique
HRAP – High Rate Algal Pond	NPK – Nitrogen-Phosphorus-Potassium
HRT – Hydraulic Retention Time	NPP – Net Primary Productivity of Organic Matter
HSF – Horizontal Surface Flow Constructed Wetland	NRPP – Nonreactive Particulate Phosphorus
HSFW – Horizontal Subsurface Flow Wetland	OF – Overflow Land Treatment
HSSF – Horizontal Subsurface Flow Wetland	OLC – Open Limestone Channels
HUPB – Horizontal Flow Unplanted Bed	OLR – Organic Loading Rate
	OM – Organic Matter

OP – Other Phosphorus/Organic Phosphorus	SDD – Standing Dead Detritus
ORP – Oxidation Reduction Potential	SLB – Slag Leach Beds
Ortho P – orthophosphate	SLR – Surface Loading Rate/Solids Loading Rate
OTR – Oxygen Transfer Rate	SOD – Sediment Oxygen Demand
PAC – Poly Aluminum Chloride	SOP – Suspended Organic Phosphorus
PAO – Phosphorus Accumulating Organisms	SSF – Subsurface Flow Wetland
PD - Dissolved Phosphorus in Filtrate	SSFW- Subsurface Flow Wetlands
PE – People Equivalent	SSHF – Subsurface Horizontal Flow Wetland
PHA – Polyhydroxyalkanoates	SR – Slow Rate Land Treatment
PHB – Poly $\beta$ - hydrobutyrate PO <sub>4</sub> -P	SRB – Sulfate Reducing Bacteria
PLR – Phosphorus Loading Rate	SRP – Soluble Reactive Phosphorus
P/O – Phosphorus Oxygen Ratio	SRPS – Soluble Reactive Phosphorus in Soils
Poly – P – Polyphosphate	SRR – Surface Removal Rate
POR – Period of Operational Record	SRT – Solids Retention Time
PP – Particulate Phosphorus or Pyrophosphate	STA – Storm Treatment Area
PPAO – Polyphosphate Accumulating Organisms	SSP – Soil Stored Phosphorus
PPS – Particulate Phosphorus in Soil	SuDS/SUDS – Sustainable Drainage Systems
PPW – Particulate Phosphorus in Water	SWW – Swine Wastewater
PS – Phosphorus Sorption	TAHP – Total Acid Hydrolyzable Phosphorus
PSTA – Periphyton Storm Water Treatment Areas	TBP – Total Biomass Phosphorus
RAPS - Reducing and Alkalinity Producing System	TCA – Tricarbonate Acid Cycle
RAS – Return Activated Sludge	TCP – Total Colloidal Phosphorus
RBZ – Riparian Buffer Zone	TDP – Total Dissolved Phosphorus
RE – Removal Efficiency	TFP - Total Filterable Phosphorus
RGR – Relative Growth Rate	TIS- Tanks in Series
RI – Rapid Infiltration Land Treatment	TMDL – Total Maximum Daily Limit
RIW – Residual in Influent Wastewater	TMP - Trimetaphosphate
RPS – Reactive Phosphorus Suspended	TOP – Total Organic Phosphorus
RTD – Residence Time Distributions	TP – Total Phosphorus or Tripolyphosphate
SAPS – Successive Alkalinity Producing System	TP <sub>acc</sub> – Total Phosphorus Accumulations
SAHP – Suspended Acid Hydrolyzed Phosphorus	TPAS – Total Phosphorus in Active Sediment
SAV – Submerged Aquatic Vegetation	TPBD – Total Phosphorus in Bottom Detritus
SBR – Sequencing Batch Reactor	TPDS – Total Phosphorus in Deep Sediment
SCDB – Sodium Citrate Dithionite Bicarboxylate	

TP <sub>mac</sub> – Total Phosphorus in Macrophytes	VFCW – Vertical Flow Constructed Wetland
TP <sub>phyt</sub> – Total Phosphorus in Periphyton	v-GF – Vertical Gravel Filtration
TP <sub>res</sub> – Total Phosphorus Re-suspended	VPB – Vertical Flow Planted Bed
TP <sub>ret</sub> – Total Phosphorus Retention	VU – Vegetation Under Unsaturated Condition
TRP – Total Reactive Phosphorus	VUPB – Vertical Flow Unplanted Bed
TSCF – Transpiration Stream Concentration Factor	VRBF – Vertical Reed Bed Filter
TSP - Total Suspended Phosphorus	VSFCW – Vertical Subsurface Flow Constructed Wetland
TSS – Total Suspended Solids	VSS – Volatile Suspended Solids
TSSP – Total Soil Surface Phosphorus	WBZ- Wooded Buffer Zones
TWDB – Treatment Wetlands Database	WRF – Water Reclamation Facility
UU – Unvegetation Under Saturated Condition	WCA – Water Conservation Area
USEPA – United States Environmental Protection Agency	WRF – Water Reclamation Facility
UZTC – Ultimate Zone of Total Containment	WRP –Wetland Reserve Program
VH – Vegetation Under Half Saturated Condition	WSUD – Water Sensitive Urban Design
VBFW – Vertical-Baffled Flow Wetland	WWQM – Wetland Water Quality Model
VF – Vertical Flow Wetland	WWAR – Wetland to watershed Area Ratio
VFA – Volatile Fatty Acids	WWTP – Wastewater Treatment Plan
	ZPC – Zero Point of Charge
	ZTC – Zone of Total Containment

APPENDIX B

COMMONLY USED PLANTS IN CONSTRUCTED WETLANDS

<b>Table 4. Commonly Used Plants in Constructed Wetlands</b>	
<b>Scientific Plant Name</b>	<b>Common Plant Name</b>
<i>Agapanthus africanus</i>	Lily of the Nile
<i>Alnus rugosa</i>	Speckled Alder
<i>Alternanthera philoxeroides</i>	Alligator Weed
<i>Anthurium andreaeanum</i>	Flamingo Flower
<i>Azolla microphylla</i>	Mexican Mosquito Fern
<i>Bacopa monnieri</i>	Water Hyssop
<i>Banksia integrifolia</i>	Coast Banksia
<i>Baumea articulata</i>	Jointed Twig Rush
<i>Betula pumila</i>	Bog Birch
<i>Bolboschoenus fluviatilis</i>	River Bulrush
<i>Brassica campestris</i>	Field Mustard or Turnip Mustard
<i>Brassica rapa</i>	Autumn poem or Canola
<i>Canna generalis</i>	Canna Lily
<i>Canna indica</i>	Indian Shot
<i>Carex aquatilis</i>	Water Sedge or Leafy Tussock Sedge
<i>Carex elata</i>	Tufted Sedge
<i>Carex lasiocarpa</i>	Slender Sedge or Woollyfruit Sedge
<i>Carex riparia</i>	Great Pond Sedge
<i>Carex rostrata</i>	Beaked Sedge
<i>Carthamus tinctorius</i>	Safflower
<i>Centella/Hydrocotyle asiatica</i>	Pennywort
<i>Ceratophyllum demersum</i>	Coontail
<i>Chamaedaphnae calyulata</i>	Leatherleaf
<i>Cladium jamaicense</i>	Sawgrass
<i>Colocasia esculenta</i>	Black Stern Taro or Gabi
<i>Colocasia violacea</i>	Purple Stem Taro
<i>Coix lacryma-jobi</i>	Adlay or Job's Tears
<i>Crotalaria juncea</i>	Sun Hemp
<i>Cynodon dactylan</i>	Tifton or Bermuda Grass
<i>Cyperus alternifolius</i>	Umbrella Palm
<i>Cyperus giganteus</i>	Mexican Papyrus
<i>Cyperus haspans</i>	Dwarf Papyrus
<i>Cyperus involucratus</i>	Umbrella Sedge
<i>Cyperus papyrus</i>	Papyrus Sedge or Paper Reed
<i>Dactylis glomerata</i>	Orchard Grass
<i>Echinochloa pyramidalis</i>	Antelope Grass
<i>Eichhornia crassipes</i>	Water Hyacinth
<i>Elodea canadensis</i>	Waterweed
<i>Eleocharis dulcis/interstincta</i>	Spike Rush
<i>Eucalyptus</i>	Eucalyptus Tree

<i>Festuca arundinacea</i>	Tall Fescue or Rough Fescue
<i>Glyceria maxima</i>	Meadowgrass
<i>Hedychium conronarium</i>	Butterfly Ginger
<i>Heliconia rostrata</i>	Lobster Claw
<i>Hemmerocallis dumotieri</i>	Day Lily
<i>Hibiscus cannabinus</i>	Kenaf
<i>Hibiscus moscheutos</i>	March Hibiscus
<i>Hordeum vulgare</i>	Barley
<i>Ipomoea aquatica</i>	Swamp Morning Glory
<i>Ipomoea pes caprae</i>	Sea Morning Glory
<i>Iris pseudocorus</i>	Yellow Flag Iris
<i>Juncus effusus</i>	Common Rush
<i>Lemma minor</i>	Duckweed
<i>Lepironia articulata</i>	Tube Sedge
<i>Lolium multiflorum</i>	Italian Ryegrass
<i>Matthiola incana</i>	Hoary Stock or Tenweeks Stock
<i>Menyanthes trifoliata</i>	Bogbean
<i>Myriophyllum implicatum</i>	Water Milfoil
<i>Najas</i>	Naiads – Bushy Pond weeds
<i>Najas guadalupensis</i>	Water Nymph or Guppy Grass
<i>Nasturtium aquatium</i>	Watercress
<i>Oryza sativa</i>	Rice
<i>Panicum hemitomon</i>	Maidencane
<i>Panicum repens</i>	Torpedo Grass
<i>Pandanus amaryllifolia</i>	Pandan
<i>Paspalum repens</i>	Water Paspalum
<i>Pistia stratiotes</i>	Water Lettuce
<i>Phragmites australis</i>	Reed or Bugang Reed
<i>Phragmites karka</i>	Common Reed in Southeast Asia
<i>Poa glauca</i>	Glaucus Bluegrass or White Bluegrass
<i>Polygonum barbatum</i>	Smart Weed
<i>Pontederia cardata</i>	Pickrel Weed
<i>Populus tremuloides</i>	Trembling Aspen
<i>Potamogeton illinoensis</i>	Illinois Pondweed
<i>Sagittaria lancifolia</i>	Bulltongue or Lanceleaf Arrowhead
<i>Sagittaria latifolia</i>	Broadleaf Arrowhead
<i>Salix alba</i>	White Willow
<i>Salix caprea</i>	Goat Willow
<i>Salix fragilis</i>	Crack Willow
<i>Salix purpurea</i>	Purple Willow
<i>Salix rubens</i>	Hybrid Crack Willow
<i>Salix triandra</i>	Black Maul or Almond Willow

<i>Salix viminalis</i>	Basket Willow
<i>Salvinia minima</i>	Water Spangles
<i>Saururus cernuus</i>	Lizard's Tail
<i>Schoenoplectus validus</i>	River Club Rush
<i>Scirpus mucronatus</i>	Narrowleaf Cattail or Bulrush
<i>Scoenoplectus acutus</i>	Hard Stem Bulrush
<i>Sorghum vulgare</i>	Sorghum
<i>Sparganium erectum</i>	Bur Reed
<i>Strelitzia reginae</i>	Bird of Paradise or Crane Flower
<i>Tages electra</i>	African Marigold
<i>Thalia geniculata/Thalia dealbata</i>	Thalia
<i>Triticum aestivum</i>	Wheat
<i>Typha angustifolia</i>	Narrowleaf Cattail
<i>Typha domingensis</i>	Southern Cattail or Cumbungi
<i>Typha latifolia</i>	Cattail
<i>Typha orientalis</i>	Japanese Cattail
<i>Vetiveria zizanioides</i>	Vetiver Grass
<i>Zantedeschia aethiopica</i>	Easter Lily or Lily of the Nile
<i>Zizania latifolia</i>	Water Bamboo or Manchurian Wild Rice
<i>Zizaniopsis bonarienses</i>	Giant Grass

APPENDIX C

CONSTRUCTED WETLANDS TERMINOLOGY

Aquatic **mesocosms**, or experimental water enclosures, are designed to provide a limited body of water with close to natural conditions, in which environmental factors can be realistically manipulated.

**Allochthonous:** Geological material that has been transported and then accumulates elsewhere is allochthonous, and sediment carried by a river is allogenic.

**Autochthonous:** indigenous, formed or originated in the place where found.

**Benthic:** Relating to the bottom of a sea or lake or to the organisms that live there.

**Biogeochemistry** is the scientific discipline that involves the study of the chemical, physical, geological, and biological processes and reactions that govern the composition of the natural environment. The field focuses on chemical cycles which are either driven by or have an impact on biological activity. Particular emphasis is placed on the study of carbon, nitrogen, sulfur, and phosphorus cycles.

**Bioturbation:** The stirring or mixing of sediment or soil by organisms, especially by burrowing or boring.

**Blackwater:** wastewater generated from household uses like toilets, and kitchens and other water sources that have come in contact with sewage. This is the water that is processed at the WWTP.

**Co-precipitation:** the addition of chemicals to form precipitates that are then removed.

**Cyanobacteria** mat is a layer of *Cyanobacteria* resting on the mud at the bottom of a salt marsh pond. *Cyanobacteria* that form mats range from individual Cyanobacterial cells forming a soft, gelatinous mat to long filaments that can form very tough, thick hard mats.

**Greywater:** wastewater generated from household uses like bathing and washing clothes. Typically lower levels of contamination and higher potential for reuse.

**Helophyte:** any perennial marsh plant that bears its overwintering buds in the mud below the surface.

**Hydric soils:** soil that is saturated with water for all of part of a year. Saturated soils become anaerobic as water stimulates the growth of micro-organisms, which use up the oxygen in the spaces between the soil particles.

**Macrophytes** are aquatic plants, growing in or near water that are emergent, submergent, or floating.

**Necromass** The mass of dead plant material lying as litter on the ground surface.

**Periphyton** is a complex mixture of algae, cyanobacteria, heterotrophic microbes, and detritus that is attached to submerged surfaces in most aquatic ecosystems.

**Phytodepuration** – is a purification technique characterized by biological treatments, in which plants growing in water-saturated soil develop a key role for direct action of the bacteria. With phytodepuration systems, pollutants are removed through a process of chemical, physical, and biological processes. This term is used in papers and journals that are published in Europe.

**Phytofiltration:** the process of using metal hyperaccumulator plants in a saturated environment to treat contaminated water.

**Phytopurification** is an integrated natural water purification system based on the combined effect of various biotic (aquatic vegetation and larger plants, either rooted plants such as reeds or floating plants such as duckweed and water hyacinth as well as bacterial microflora) and abiotic (soil or subsoil; physical phenomena such as sedimentation and adsorption; microhabitat - temperature, oxygenation, pH, and other conditions) components that are found in natural wetlands.

**Postprecipitation:** chemicals are added to form precipitates in separate sedimentation facilities.

**Senescence** or **biological aging** is the change in the biology of an organism as it ages after its maturity. This refers to the decay of plants in constructed wetlands during the autumn and winter months.

**Stochastic Effect:** Injurious effect of a substance occurring by chance (generally without a threshold level of dose), whose probability is proportional to the dose but whose severity is independent of it. In the case of constructed wetlands, this includes events like: rain, drought, biological influences from animals, fish.