

SUSTAINABLE PHOSPHORUS REMOVAL FROM SURFACE WATER

By

AMAR PREM PERSAUD

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To the world

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## LIST OF ABBREVIATIONS

12/12	12 hours on then 12 hours off
AS2	A second batch of Alum Sludge
PLRG	Pollution Load Reduction Goals
SWIM	Surface Water Improvement and Management Act of 1987
(3x)	Something done three times, if 1x means it was done one time, etc.
AS	Alum Sludge
BV	Bed Volume
cm	Centimeter
DI	Deionized
DWS	Dirty Wash Solution
DX	Dowex22
DX (1)	Dowex22 dosed at 1mL/L
DX (4)	Dowex22 dosed at 4 mL/L
FA	Fly Ash
FDEP	Florida Department of Environmental Protection
FITS	Floating Island Treatment System
FS	Ferric Sludge
gpm	Gallon per minute
IEX	ion exchange
IS	Granulated Blast Furnace Iron Slag
L	Liter
LA	Lake Alice
LCM	Low-Cost Materials, a.k.a. industrial by-products

LJ	Lake Jesup
LS	Limestone
N	Normality
M	Molar
mL	Milliliter
MX	MIEX
MX (1)	MIEX Dosed at 1mL/L
MX (4)	MIEX dosed at 4mL/L
OP	Orthophosphate, bioavailable phosphorus or $\text{PO}_4^{3-}$
P	Phosphorus
PAC	Powder Activated Carbon
PX	PhosX
PX (1)	PhosX dosed at 1 mL/L
PX (4)	PhosX dosed at 4 mL/L
PZC	Point of Zero Charge
RC	Recycled Concrete
rpm	Revolutions per minute
SAC	Sanford Avenue Canal
SJRWMD	St. Johns River Water Management District
SS	Basic Oxygen Furnace Steel Slag
TN	Total Nitrogen
TP	Total Phosphorus
UV254	Ultraviolet absorbance at 254 nm
XRD	X-ray diffraction

Abstract of Thesis Presented to the Graduate School  
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By

Amar Prem Persaud

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Phosphorus (P) is often a limiting nutrient in plant productivity. An excess of its bioavailable form, orthophosphate (OP), will cause eutrophication. Natural surface water systems may become overloaded with OP, therefore, it is pertinent to develop a strategy of remediation. Adsorption through upward flowing column has proven to be an effective method of removing OP from surface water. In this research it was found that the use of industrial by-products, also known as low-cost materials (LCMs), as compared to commercially available materials, such as polymeric adsorbents, in the treatment method can become feasible but performance will vary due to changing composition and prepared particle sizes. LCMs tested were, alum sludge, ferric sludge, steel slag, iron slag, recycled concrete, fly ash, and limestone of which alum sludge performed best. It was found that the advantages of using commercially available materials are ease of implementation, consistency of performance, and reusability. Commercially available materials tested were PhosX, MIEX, and Dowex22 of which PhosX performed best. Both alum sludge and PhosX are effective at removing OP from water by adsorption under continuous flow. Implementing fluidized beds to replicate bench-scale column treatment on a larger scale which utilize P-selective materials has

proven to remove OP effectively. Bench-scale studies have helped to successfully predict the removal of OP by the pilot-scale fluidized bed with typically >70% OP removal by both. Materials such as PhosX, a polymeric adsorbent resin, can be regenerated and was found to work as effectively as its virgin version. However, when using a reusable commercially available material, such as PhosX, the by-product of regeneration is a contaminated brine solution. The P in solution can be removed by precipitation and the cleaned brine solution can be used to regenerate another batch of exhausted resin. The technique of considering all aspects of a treatment process, while keeping sustainability in mind, has proven to be useful in developing a highly effective P treatment system.

## CHAPTER 1 INTRODUCTION

Surface waters continue to be overloaded with phosphorus (P) from point and non-point sources, which exist in sediment and surface water runoff. An excessive amount of P and nitrogen in surface waters can cause eutrophication. In this case, P is the limiting nutrient in plant productivity. Therefore, emphasis must be placed on P removal to eliminate eutrophication (Vollenweider et al., 1980).

P mainly occurs in sediment and is released into the water (dissolution) by biogeochemical processes (nutrient cycle). The main form released is  $\text{PO}_4^{3-}$ , also known as orthophosphate (OP), which is immediately available to algae (bioavailable). Diffusion is caused by factors such as temperature, pH, redox and advective forces from flowing water enhancing the exchange of P from sediment to OP in water. These are naturally occurring and cannot be controlled; the act of altering the environment to such a great extent is difficult. Therefore, the bioavailable P, also known as OP, existing should then be the target for removal if eutrophication is to be controlled, as it is impractical to dredge all the P in sediment from waterways or drastically change the water quality characteristics.

Eutrophication can increase the rate of algal production, which consumes dissolved oxygen and blocks the sunlight in the water thus, making it difficult for native plants and marine life to survive. In addition, when algae die it results in a high chemical oxygen demand where an accelerated production causes a larger amount of dead organisms. It was reported by the Florida Department of Environmental Protection (FDEP) that cyanobacterial algae blooms have become a problem in Lake Jesup (FDEP, 2008). These algae blooms can release toxins and increase pH that are harmful

to humans and animal life that are in contact with the water (Jones et al., 2006). Algae blooms are aesthetic issues as well causing foul aromas and discoloration of lakes.

Sources of P pollution include agricultural drainage, municipal and industrial effluents, and urban stormwater runoff. In a specific case, urban stormwater drainage has been cited as the cause of increased levels of total phosphorus (TP) in soil (McCormick and Newman, 2009). This results in the loss of the abundant native macrophyte species and a shift to periphyton communities which have greater impacts on the dissolved oxygen and trophic levels in the Everglades (McCormick and Newman, 2009). In fact, P removal techniques have been developed for agricultural drainage (Dayton and Basta, 2003) and municipal and industrial wastewater effluents (Blaney and Cinar, 2007) to attempt source treatment.

Tributaries often contain OP not only from dissolution but from surface water runoff when located in populated or agricultural zones. For example, Lake Jesup in central Florida receives much of its OP from surface water runoff. During wet years, the average annual watershed loading of TP is 18.7 metric tons P/yr in Lake Jesup (Jia, 2007). This is coming mainly from its tributaries which results in algae blooms. The goal set by the St. John's River Management District (SJRWMD) was to remove 9 metric tons P/yr from the watershed (SJRWMD, 2008). Upon entering the lake, most biological activity occurs because the majority of the surface area of a large lake is directly exposed to sunlight, which is the driving force for photosynthesis. If one were to treat a lake directly, P in sediment and organic P have to be removed. Tributaries are shaded quite often, so less biological activity is likely to happen and a high OP concentration exists, where OP should be the target. Other than the existence of natural organic

matter (NOM) from terrestrial sources, not much plant activity could occur in an area blocked from the sun.

The SJRWMD had embarked on adopting Pollution Load Reduction Goals (PLRG) as reflected in the Florida Administrative Code 62-40 (FAC 62-40) and has instilled the Surface Water Improvement and Management (SWIM) Act of 1987, which involves mainly the achievement of PLRGs (Jia, 2007). A plan like this helps to improve lakes because it, “focuses on reducing the pollution in storm water runoff by reducing excess nutrients and other pollutants which affect water quality” (SFWMD, 2009). Beyond policy, researchers have thought of various techniques to capture P by physical-chemical or biological processes at point sources and non-point sources.

In order to keep the environment in its pristine condition, all water quality characteristics must be considered while removing the P from water sources. By examining real surface water from the Lake Jesup watershed, it is quickly realized that it is important to not only track the removal of P but the water chemistry that will affect its removal and how the removal will in turn affect the water chemistry. Hence, a removal process can become a detriment to the environment if a thorough investigation is not performed. Other constituents in the water can also compete to be removed if they have a similar affinity for removal mechanisms as OP does – for example, NOM, which is a dissolved constituent in the water. NOM can take up space on the surface of an adsorbent that could have been used to remove more OP (Weng and Van Riemsdijk, 2008). Hence, OP can be outcompeted by NOM and other anions in the water.

Due to the fact that sustainability of the process is very important, water treatment processes should have an ambition to adapt a synergistic approach by considering

source of materials, ease of use, and total environmental effects. For example, the use of industrial by-products would be part of a conscious effort to improve the total environment. Industrial processes have waste materials from the production of their specific products. Some of these materials can be used to remove OP by methods such as adsorption or precipitation. The waste products will be considered as low-cost materials (LCMs) from here on, because the only cost associated with the material is shipping. By adapting this approach, their uses are part of a sustainable effort because they will be fully utilized before inevitably disposing of them. Comparing LCMs to commercially available resins that are designed for water treatment (ion exchange (IEX) resins), it is important to establish a benchmark to evaluate the efficacy of using LCMs and the feasibility of using IEX resins. Sustainability, for this project, is therefore defined as a treatment process that would include beneficial reuse of industrial by-products, recycling of materials, handling of by-products of material use, ease of implementation, and a renewable energy source.

The IEX resins have an advantage whereby they are designed for specific contaminants, and can be regenerated and reused. However, in the process, it produces a brine solution containing P. It is important to consider whether the P can be retrieved and marketed, and if the brine solution can be utilized again, to reduce the harmful discharges from facilities equipped to embark on this process. All environmental factors must be carefully considered in designing an effective treatment process.

All of the above considerations describe a variety of synergies that are important in order to design a safe and effective treatment process. In the case of this project, they are applied to the removal process of P from surface water bodies. Hence, a pilot-scale

treatment facility was constructed due to the fact that surface waters are large and non-uniform in water quality. It embodied a floating, solar-powered and sustainable method to remove P with an aim of ensuring that a safe aquatic environment is maintained. This facility will be designated as the Floating Island Treatment System (FITS) upon which a physical-chemical treatment process was designed.

The overall goal of this project is to improve surface water quality by removing P, which will control and prevent eutrophication. The specific objectives are (1) to discuss the properties of LCMs and its P removal mechanisms, (2) to evaluate the effectiveness of LCMs and IEX resins for P removal while screening for P-selective materials, (3) to evaluate OP removal by P-selective materials by comparing laboratory-scale and pilot-scale continuous-flow treatment, and (4) to evaluate disposal and regeneration options for P-selective materials and their byproducts to ensure the process is sustainable.

## CHAPTER 2 LITERATURE REVIEW

Three common mechanisms of removing dissolved constituents from water are ion exchange (IEX), adsorption, and precipitation. Seeking materials that exhibit those mechanisms would be beneficial in order to remove the bioavailable phosphorus or orthophosphate (OP) in water. There are multitudes of materials available on the market for sale that are designed especially for water treatment and the removal of dissolved matter, such as IEX resins (Boyer and Singer, 2008; Blaney and Cinar, 2007). However, in an effort to consider sustainability factors of a treatment process, by reducing its footprint, then it is beneficial to consider the reuse of industrial byproducts. These products are low-cost materials (LCMs) and the process should allow LCMs to be used once more before an inevitable disposal.

Beneficial reuse of LCMs like steel slag, fly ash, and water treatment residuals, such as alum sludge and ferric sludge have been investigated for removal capabilities of OP from wastewater (Johansson, 1999; Mortula and Gagnon, 2007a; Ugurlu and Salman, 1998). Elements such as iron, aluminum, calcium, and magnesium have an affinity for OP and it can be determined which materials are worth investigating based on their composition, such as limestone (Baker et al., 1998) and iron slag. Commercially available materials such as IEX resins and other polymeric adsorbents have also been used for phosphorus (P) removal (Blaney and Cinar, 2007). For example, MIEX which can be applied to water high in natural organic matter (NOM) (Boyer and Singer, 2008), Dowex22, and PhosX (Blaney and Cinar, 2007).

P was removed in the past by using various materials and adopting a number of techniques of experimentation. Jar testing is a popular method to carry out batch

experiments, whereby a large amount of materials can be quickly tested and selected for removal of P (Mortula and Gagnon, 2007a). Another method is the column experiment, where a continuous supply of water is pumped through a media to test for its threshold (Mortula and Gagnon, 2007b). It was determined that adsorption through a column was an effective way of removing P (Baker et al., 1998) especially if a treatment system has to handle an infinite flow of water rather than a fixed volume. Column experiments also provided an ideal environment that allowed adsorption onto metal hydroxide surfaces. It was implied that a continuously flowing system can be applied to receive wastewater from septic tanks from which P could seep into a surface water body (Baker et al., 1998). Pilot studies are important to in order to take laboratory studies to the next level and determine if a hypothesis will work in the real environment.

In previous batch studies, materials such as alum sludge, blast furnace slag and granulated activated carbon performed well, with over 70% removal of P at high initial concentrations of 2.5 mg P/L and more from deionized water. Materials were screened and tested for their capacity through adsorption column experiments (Mortula and Gagnon, 2007b; Baker et al., 1998). Previous column experiments resulted in fly ash yielding removal of 99% of P at initial concentrations ranging from 20 mg P/L to 50 mg P/L (Ugurlu and Salman, 1998). Alum sludge and granulated activated carbon performed well and were relatively inert to water quality characteristics such as pH but can be affected by a change in pH (Mortula and Gagnon, 2007b). However, blast furnace slag yielded the greatest removal of P but raised the pH (Mortula and Gagnon, 2007a). Particle size was deemed an important physical characteristic of materials and drastically reduce the surface area available for adsorption as it gets larger (Mortula and

Gagnon, 2007b); this is also important in the same way for IEX (Boyer and Singer, 2008). Materials that have available calcium usually precipitate P from solutions they are in contact with (Baker et al., 1998).

LCMs were good candidates for OP removal but it must be confirmed if they are formidable opponents to the usage of commercially available resins and if they can be applied to a real treatment process. On numerous occasions, there were more gaps in the studies. For instance, some column studies only used deionized water spiked with OP (Mortula and Gagnon, 2007b; Ugurlu and Salman, 1998) which in fact did not pose a conclusion on how it will work in a real scenario. Current P treatment methods require high concentrations, but when dealing with large natural surface water bodies, the P concentrations are much lower. This must be addressed to contribute meaningfully to the research involved in recovery of the natural environment.

Past studies were also limited, whereby essential water quality characteristics were not fully investigated showing the possibility that the chemistry affected a treatment process and in turn if the treatment process was affected. For example, the usage of alum sludge could release sulfates in the water, which may methylate mercury where it exists forming methylmercury,  $[\text{CH}_3\text{Hg}]^+$  (Benoit, 1997), which results in bioaccumulation and food web magnification.

A comparative study of LCMs and IEX resins is essential to test their P removing capabilities and their effects on organic-rich surface water. Therefore, water from a real source will be beneficial so that all constituents can be observed. It was determined by researchers that competition existed between NOM and P for removal by materials using IEX or adsorption as a mechanism of removal (Guan and Shang, 2006). It is

necessary to prove that these materials are effective in the real environment and can be applied to a large scale treatment system. A comparative study between bench-scale and pilot-scale studies will give insight on this.

Commercially available IEX resins and adsorbents can be regenerated by removing the P from the surface sites by specific regeneration processes, and reapplying them to the treatment system (Blaney and Cinar, 2007; Boyer and Singer, 2008) because they are useful when regenerated with the possibility of multiple regenerations (Apell, 2009). With P dissolved in the dirty wash solution for these materials, it is possible to remove it by precipitation (Sibrell and Montgomery, 2009) so that P is not being released into the environment. Hence, it is crucial to compare all factors involved in a treatment process to evaluate the best approach. This will enable the use of an economical and eco-friendly process for removal of P from natural surface waters.

## CHAPTER 3 MATERIALS AND METHODS

### **Treatment Materials**

Two classes of materials were evaluated in this work: low-cost materials (LCMs) and ion exchange (IEX) resins. All LCMs were analyzed for their composition and physical characteristics. The LCMs evaluated in this work consisted of waste byproducts and natural materials, as described in Table 3-1, and the only associated cost was shipping. The LCMs, alum sludge (AS), steel slag (SS), and iron slag (IS) were crushed with a mortar and pestle and sieved through U.S. Standard sieves 30 and 40, to give a particle size range of 420  $\mu\text{m}$  to 595  $\mu\text{m}$ . Ferric sludge (FS), limestone (LS), and recycled concrete (RC) were dried under ambient laboratory conditions before being crushed as above. A batch of Class F Fly ash (FA), which was received in a powdered form, was used in its original state. These materials were chosen on the basis of studies, which show that Fe and Al oxides have faster adsorption kinetics than those of Ca and Mg (Guan and Shang, 2006). The LCMs were weighed as dry materials ranging from 1 to 16 g for jar tests.

The resins that were investigated are commercial IEX resins and polymeric adsorbents, which are designed for municipal and industrial water treatment. All resins will be considered as IEX resins and are described in Table 3-2. The IEX resins, MIEX (MX), PhosX (PX) and Dowex22 (DX), were used in its original state and stored in deionized (DI) water. They were measured using a graduated cylinder with doses ranging from 1 to 8 mL of wet settled material. The densities of the IEX resins were determined as the mass of dry material per volume of wet settled material. All materials

were evaluated following standard jar tests procedures, as described in the next section.

Materials used for bench-scale continuous-flow column studies were crushed, washed and measured as a wet volume in a graduated cylinder, which represents the bed volume (BV) of water treated.

Materials used for pilot-scale studies were prepared in a similar manner. PX was prepared as described in column studies. AS was crushed and sieved to grain sizes of between 0.5 inches and 0.75 inches, washed, and soaked.

### **Surface Water**

Bench-scale experiments were conducted with surface water obtained from Lake Jesup and one of its tributaries, the Sanford Avenue Canal, based on a project focus directed to the Lake Jesup watershed. Lake Jesup is located near the city of Sanford in central Florida and is part of the St. Johns River system. Lake Jesup is impaired by high concentrations of total phosphorus (TP), total nitrogen (TN), unionized ammonia, and low concentrations of dissolved oxygen (FDEP, 2003). Lake Jesup and its tributaries are also rich in organic material. Figure 3-1A shows a map of Lake Jesup and a detail of the sampling locations where Lake represents Lake Jesup and Canal represents the Sanford Avenue Canal.

All samples were collected by the St. John's River Water Management District (SJRWMD) and delivered to the Department of Environmental Engineering Sciences at the University of Florida. Samples were stored at 4°C upon receipt and were collected on four different dates in 2009. Seasonal differences in water quality and differences in water quality for the two sample locations will be discussed in a subsequent section.

It was later determined that it was more feasible to launch a pilot-scale study in Lake Alice on the University of Florida campus due to its close proximity. Therefore, experiments were also performed on water samples collected from Lake Alice and subsequently, the pilot scale facility was launched there. Lake Alice, located in Gainesville, FL, is an open water/marsh system that receives surface water runoff from the University of Florida campus in addition to a wastewater treatment plant situated to the east of it. It is in the center of the University of Florida campus traversing the western stretch of Museum Road. It is purported to have high levels of TP, orthophosphate (OP), and organic matter making it similar to the conditions found at Lake Jesup. Thus, Lake Alice provided an excellent replacement for the conditions experienced at Lake Jesup. The sample location for bench-scale continuous flow studies was at an outflow canal near Baughman Center. Figure 3-1B exhibits the sampling location for column experiments and location of the Floating Island Treatment System (FITS). All graphs and figures refer to Lake Jessup, Sanford Avenue Canal, and Lake Alice as LJ, SAC, and LA, respectively, and in the case of bench-scale experiments, followed by the month of procurement; for example Sanford Avenue Canal water obtained in April will be presented as SAC April in tables and figures. All water used for bench-scale experiments were obtained during the year of 2009.

### **Jar Testing**

Standard jar tests were conducted using a Phipps and Bird PB-700 jar tester at ambient laboratory temperature (20–22°C) to investigate the materials' P removing abilities. Two liters of Lake Jesup or Sanford Avenue Canal water were added to each jar. Various doses of LCMs or IEX resins were measured and added to each jar.

The following constant mixing speeds were used: 100 rpm for AS, FA, and IEX resins, and 200 rpm for RC, LS, IS, SS, and FS because these materials were denser. All jar tests were conducted for 60 minutes, with samples collected after 5 minutes of mixing (no settling), 30 minutes mixing (no settling), and 60 minutes mixing (with 30 minutes of undisturbed settling). The material doses were tested in duplicate. All results are average values of duplicate samples with error bars showing one standard deviation, unless otherwise noted. Raw water and treated water samples were measured for pH, turbidity, OP, and TP. Samples were also analyzed for inorganic anions, after filtering through a 0.45  $\mu\text{m}$  membrane filter (Boyer and Singer, 2008).

All glass sample containers were soaked overnight in a 6% nitric acid bath, rinsed three times with DI water, and air dried. Jar test paddles and jars were washed with laboratory detergent and DI water, rinsed six times with DI water and air dried. Plastic sample containers used for sampling were not reused.

## **Continuous-Flow Studies**

### **Bench-Scale Experiments**

Following the concept of small-scale laboratory based experiments (Mortula and Gagnon, 2007b), a fixed bed column was setup. The column used had 0.7854 cm inner diameter and a height of 2 cm with 25  $\mu\text{m}$  pore size polyethylene frits on each end. The treatment material was prepared, soaked overnight, and washed of its suspended fine grains. The column was then filled with 1 mL of wet material after which it was topped off with DI water to eliminate bubbles. Tubing was connected to allow for an up-flow direction. If pumped downward, further compaction of the material will occur and other particles will build up, hindering the free flow of water. An upward flow allows the grains to remain somewhat suspended causing an opening of pores between grains, hence

providing additional surface area that were originally covered by grains in contact with each other. The flow rate used was 2 mL/min, preset by using DI water as source water and measuring the outflow in a graduated cylinder. The concept of bed volumes (BV) was applied and in this case, 1 mL flow was equivalent to 1 BV because 1 mL of material was used. Therefore, the treatment flow rate was 2 BV per minute. BV will now represent the volume of any solution used in continuous flow studies, which is derived from the volume of material used.

Before an experiment started, the system was flushed by pumping 120 BV of DI water. Water to be treated was filtered, through a Whattmann GF/A filter (1.6  $\mu\text{m}$  pore size) to control clogging of frits. Two studies were performed: continuous flow and cyclic 12 hours on and 12 hours off (12/12), where 1 hour samples were taken in 125 mL Erlenmeyer flasks every 3 hours and left to flow without sampling for 12 hours or to rest for 12 hours during the night, respectively. A predetermined breakthrough OP concentration (Mortula and Gagnon, 2007b) was determined as 50% removal after which one extra sample was taken at the next sample point to confirm the end of an experiment. Immediate trends in OP changes were observed by measuring with a Hach 850 Colorimeter. The water quality of raw water before and after filtration and all following samples were analyzed for OP, TP, anions, and pH. Each time a new batch of water was received, a continuous-flow column test was performed using the most promising materials, PX and AS, in order to facilitate a reference for comparison.

The column setup was cleaned by scrubbing the interior of columns, and then pumping 50 BV 6% nitric acid and 200 BV of DI water through the entire system.

## Pilot-Scale Experiments

Based on the physical-chemical research presented in this project fluidized beds were installed on a combined treatment system which included biological treatment and deployed into Lake Alice. The biological treatment proved to be useful to replicate the filtration of the raw water as done in the bench-scale column studies, reducing turbidity, and some amount of OP. The fluidized beds replicated on a larger scale the bench-scale column setup keeping the treatment of 2 BV/min as a constant factor. The incorporation of two fluidized beds were implemented in order to use two small chambers rather than one large chamber to reduce the pressure required to pump water through it and head loss. This was convenient because it allowed two materials to be compared at the same time. As shown in Figure 3-2A, the fluidized beds were mounted in a position to receive water from the mesocosm, Figure 3-2B illustrates a cross-section of the fluidized bed.

Each fluidized bed was 6 inches in interior diameter and 24 inches high where sediment shields covered both ends to prevent treatment materials from leaving. They were each packed with 946 mL (0.25 gallons) of either AS or PX. Water from the mesocosm was pumped upward at a rate of 2 BV/min (0.5 gpm) through each fluidized bed with a bilge pump for 10 to 12 hours per day and rested through the night. Grab sampling was done every day at consistent times before and after treatment. Therefore each marker in graphs represents a different day. A predetermined breakthrough of OP removal was set at 50%; thereafter two fresh pre-packed fluidized beds replaced the exhausted fluidized beds to continue treatment and experiments. All graphs presented that refer to the pilot study show absolute values rather than  $C/C_0$  values on the y-axis because significant changes in water quality were observed and it was easier to

visualize the quantity of OP that was being removed by the use of absolute values. All samples were analyzed for OP, TP, Ultraviolet absorption at 254 nm ( $UV_{254}$ ), anions, turbidity, and pH.

## **Sustainability Studies**

### **Regeneration Procedure for PhosX**

PX resins were regenerated by a cleaning and neutralization process. Cleaning solution consisted of 2% NaCl and 4% NaOH as recommended by the manufacturer, whereby 1 g dried chemical in 100 mL DI water represented 1%. A column procedure used in previous studies for cleaning PX was not followed exactly (Blaney and Cinar, 2007) but inspired a modified procedure, in lieu 12 equivalent BV of cleaning solution with used PX were shaken on an Innova 2000 platform shaker at 220 rpm for 30 minutes.

The dirty wash solution (DWS) was decanted and stored in a glass vial for further analysis. 20 mL of DI was added to the PX and shaken at 200 rpm for 10 minutes to remove any remaining contaminants. 100 mL of water was added to the cleaned PhosX which was titrated with a 0.1N HCl solution at 25  $\mu$ L increments until a pH of 7 was sustained for 10 minutes whilst being shaken at 200 rpm. It was ensured that the pH did not go below 5 as the Fe will be stripped from the PX. The solution was decanted and the PX stored in DI. For larger scale regeneration related to the pilot study, the shaker plate was set at 220 rpm, and 8 BV equivalent DI was added after DWS was decanted. 0.1N HCl was added in 1 mL increments.

### **Precipitation Procedure**

The DWS from regenerating PX contained all pollutants that the resin had adsorbed. Therefore, this was an effort to separate the P from the solution. The DWS

may then be reused for regeneration as described later. 1 mL was drawn from the DWS and diluted by 100 (i.e., diluted by 100x) to remain within the range that a Hach-850 Colorimeter can read. This sample was filtered through a 0.45 µm filter and analyzed for OP measured by the Hach meter (Hach OP), UV<sub>254</sub>, and pH.

10 BV of DWS was titrated with 0.1M CaCl<sub>2</sub> solution. Titration involved continuously adding 2 mL of 0.1M CaCl<sub>2</sub> and allowing mixing for 2 to 3 minutes; at each increment, 0.25 mL DWS was withdrawn and diluted to 100x, filtered and analyzed for Hach OP, UV<sub>254</sub>, and pH. When a significant drop (<25%) in OP was observed 0.1 mL increments CaCl<sub>2</sub> were then added following the above titration procedure until the Hach Colorimeter showed <0.05 mg P/L. Results were normalized based on addition and extraction of fluid to and from the DWS: (Normalized value = (Vol. Remaining + Vol. Ca Solution Added – Vol. Withdrawn) x Actual Reading / Starting Vol.). Then, results were multiplied by 100 to show concentrations before dilution. For a larger scale pilot study, the same procedure was followed with a few exceptions due to the larger scale. 1 M CaCl<sub>2</sub> solution was made and was added in increments of 200 mL then 100 mL when a significant drop in OP was noticed. AS should be disposed of after being used according to EPA guidelines for disposal of alum sludge with arsenic content (MacPhee et al., 2001).

### **Reuse of Dirty Wash Solution**

After a DWS is generated, it should be considered reusable before final disposal. Therefore, after a DWS was generated in pilot studies, P was precipitated using the above procedure, filtered through a 0.45 µm filter to remove the precipitate and reused according to the regeneration procedure after all OP was removed. However, it became difficult to remove the precipitate during the final 3 BV of solution; therefore, fresh wash

solution was made to replace the loss. The solution was analyzed for Hach OP, pH, and UV<sub>254</sub> absorbance to ensure all OP was removed and the behavior of NOM was tracked.

### **Analytical Methods**

ACS specified grade or better chemicals were used to prepare all standard aqueous chemicals. Aqueous samples were analyzed as follows. An Accumet AP71 pH meter with a pH/ATC probe was used to measure pH. The pH meter was calibrated before each use with pH 4, 7, and 10 buffer solutions. Turbidity was measured on a Lamotte 2020 instrument that was calibrated daily with a 1 NTU standard. Chloride, sulfate, and nitrate were measured on a Dionex ICS-3000 ion chromatograph equipped with IonPac AG22 guard column and AS22 analytical column. All inorganic anions were measured in duplicate with average values reported. The relative difference between duplicate samples was <1%, and the relative difference between calibration check standards and known concentration was <20% percent. OP was measured using a Hach DR-850 colorimeter using an ascorbic acid method equivalent to U.S. EPA Method 365.2 and was checked periodically for its accuracy by measuring 0.05, 0.1, and 0.2 mg P/L standards. Samples were also sent to the UF/IFAS Analytical Services Laboratory for OP and TP in 20 mL scintillation vials and followed U.S. EPA Method 365.1. The TP samples were acidified to pH <2 with sulfuric acid for preservation after which autoclave digestion using ammonium persulfate and sulfuric acid was performed. The agreement between OP measurements for the Hach DR-850 and Analytical Services Laboratory were approximately 30 to 60%. The Hach DR-850 was used to show immediate trends in P removal. All OP data presented in tables and figures were reported from the Analytical Services Laboratory data, unless otherwise specified.

UV<sub>254</sub>, TOC, and TN were measured according to procedures outlined by Banerjee (2010).

Solid samples were analyzed as follows. The elemental composition of the LCMs was determined by two different methods. Samples were sent to the Analytical Services Laboratory, which follows U.S. EPA Method 200.7 to analyze for plant-available iron, aluminum, and calcium using the Mehlich 3 extraction technique for metals. The LCMs were also digested following USEPA method 3050b using heat plus nitric acid followed by hydrogen peroxide oxidation, and metals were determined by Thermo Jarrell Ash Trace ICP-AES. They were analyzed in triplicate doses following the USEPA 3050B method. All results were compared to data from the digestion of standard reference 2709 soil (NIST, 2002). All data retrieved and reported in this project as greater than 0 mg/kg were above the Thermo Jarrell Ash Trace ICP-AES minimum detection limit, which varied per element.

Point of zero charge (PZC) was determined by typically varying the percentage by weight of sample in the water and duplicate doses were performed. Samples were dried overnight, measured, placed in beakers of nanopure water, and were bubbled with N<sub>2</sub> gas for at least 20 minutes while covering with parafilm. 5 mL of bubbled water was then injected into a narrow neck vial with 0.5 g of material. The samples were agitated to ensure mixing. Head space was then filled with N<sub>2</sub> gas for about 30 seconds after which the sample vials were sealed promptly. Samples were shaken for 24 hrs before pH levels were analyzed. Pore size, pore volume, and surface area were analyzed following procedures used by Bach and Mazyck (2007).

XRD method was as follows. Samples were crushed to less than 75  $\mu\text{m}$  then mounted on plexiglas cavity sample holders (Harris and White, 2008). Each sample was scanned from 2-60° 2 $\theta$  at 2° per minute using CuK $\alpha$  radiation (Harris and White, 2008). The instrument used was a computer-controlled x-ray powder diffractometer equipped with stepping motor and graphite crystal monochromator (Harris and White, 2008). Results were reported in graphical form whereby, the dominant existing minerals were estimated.

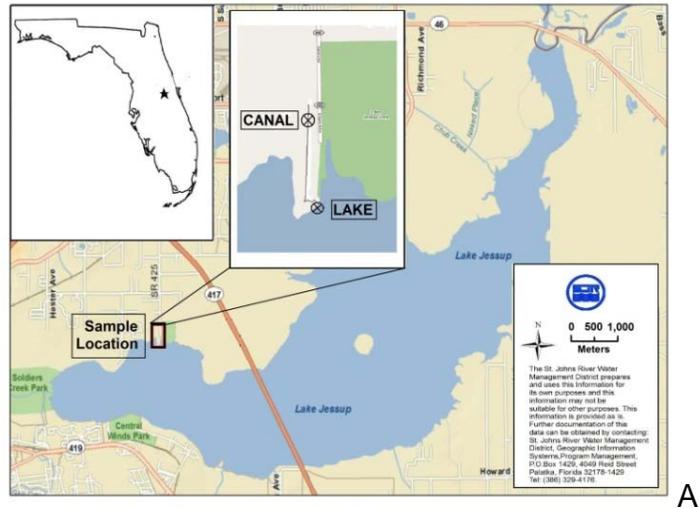
**Table 3-1. Description of Low-Cost Materials Investigated for Phosphorus Removal**

Material	Source	Description
Alum sludge (AS) (Mortula and Gagnon, 2007a)	Peace River Manasota Regional Water Supply Authority, Arcadia, FL	Surface water treatment plant that uses aluminum sulfate to treat water from the Peace River <sup>a</sup> .
Ferric sludge (FS)	David L. Tippin Water Treatment Facility, Tampa, FL	Surface water treatment plant that uses ferric sulfate to treat water from the Hillsborough River.
Granulated blast furnace iron slag (IS)	Civil & Marine Inc., Cape Canaveral, FL	Non-metallic byproduct from iron production.
Basic oxygen furnace steel slag (SS) (Johansson, 1999)	Levy Enterprises, Valparaiso, IN	Byproduct of manufacturing steel from pig iron.
Class F fly ash (Pidou and Avery, 2008)	Boral Materials Technologies, Tampa, FL	Combustion of ground or powdered coal.
Recycled concrete (Pidou and Avery, 2008)	Florida Concrete Recycling Inc, Gainesville, FL	Concrete aggregate collected from demolition sites.
Limestone	Florida Rock Industries Inc., Gainesville, FL	Natural rock mined from various locations.

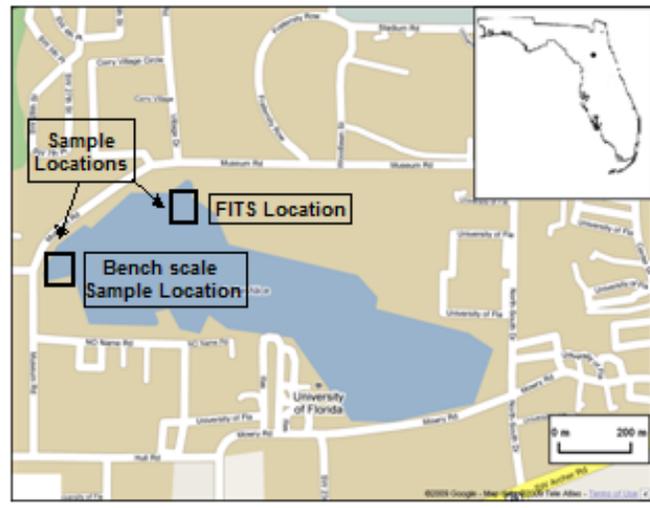
<sup>a</sup> Contain powdered activated carbon, which is used prior to coagulation process.

**Table 3-2. Description of IEX Resins Investigated for Phosphorus Removal**

Material	Manufacturer	Structure and Density, $\rho$ (g/L)	Application
PhosX (PX)	SolmeteX	Macroporous polymer resin impregnated with iron oxide particles; $\rho = 0.343$	Developed specifically for phosphate removal (Blaney and Cinar, 2007)
MIEX (MX)	Orica Watercare	Macroporous, polyacrylic anion exchange resin with strong-base, type II functional groups; $\rho = 0.299$	Used in water treatment for removal of organic material (Boyer and Singer, 2007)
Dowex22 (DX)	Dow Chemical	Macroporous, polystyrene anion exchange resin with strong-base, type II functional groups $\rho = 0.415$	Conventional anion exchange resin; similar to IRA910



A

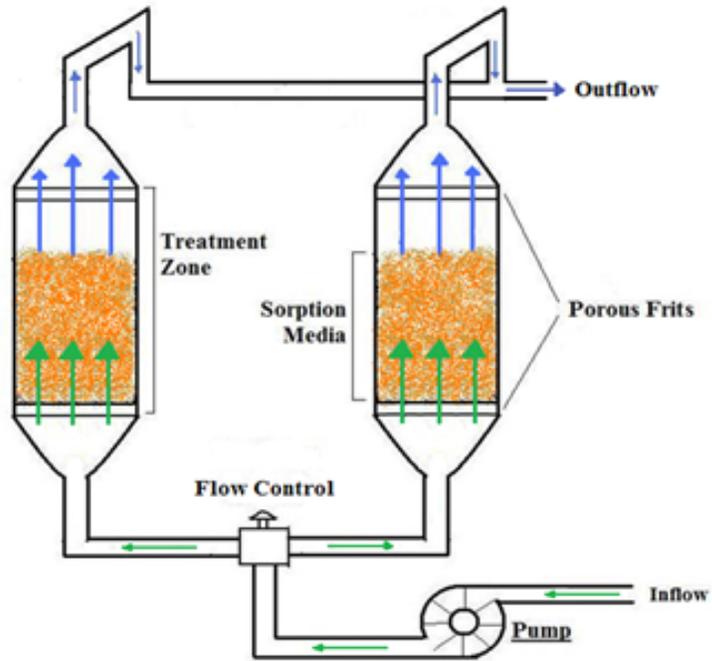


B

Figure 3-1. Sampling locations for A) Lake Jesup and Sanford Avenue Canal, and B) Lake Alice.



A



B

Figure 3-2. Floating Island Treatment System showing A) the fluidized bed, and B) cross-sectional view of fluidized bed system.

## CHAPTER 4 RESULTS AND DISCUSSION

### **Low Cost Materials**

Tables 4-1 and 4-2 list the physical and chemical properties of the low-cost materials (LCMs), which have been used in the bench-scale studies of this project. Results in Table 4-2 were adjusted to 3 significant figures. The composition of materials such as alum sludge (AS) and ferric sludge (FS) varied due to different source treatment methods and the others differed by industrial processes. Each was examined using several parameters in order to explain their removal mechanisms. Some LCMs exhibit metal hydroxide surfaces favorable to adsorption and others with high calcium contents, precipitation occurs (Baker et al., 1998). Aluminum (Al), calcium (Ca) and iron (Fe) have strong affinities for phosphorus (P) and the composition of the tested materials should reflect its efficacy to remove P. It was observed previously that materials higher in Al and Fe hydroxides have faster adsorption kinetics (Sibrell and Montgomery, 2009). AS and FS had high proportions of Al and Fe (see Table 4-2), respectively, and are the precipitates of coagulation processes forming aluminum hydroxide and ferric hydroxide, respectively. Therefore, AS and FS will experience adsorption because of their metal hydroxide surfaces, but recycled concrete (RC) and limestone (LS) will treat by precipitation due to their high calcium content. Further studies were done to determine the surface area of the materials as it helps to compare which may have more adsorption sites. Surface area changes with the pore size distribution if grain size is held constant, because if a material is porous then it has a greater surface area. For example, activated carbon is porous and has a large surface area (Tennant and Mazyck, 2007). The AS obtained was said by the water treatment

plant, as cited in Table 3-1, to have had a large quantity of powder activated carbon and it was observed that the surface area was large compared to other materials. Moreover intra-particle diffusion of P within the pore structure plays a large role in the material's adsorption rate and capacity (Sibrell and Montgomery, 2009). Point of zero charge (PZC) was examined as well. When the pH is below the PZC the surface is positively charged and vice versa for above. The performance of removal will depend on the conditions of the water, such as pH which enhances precipitation when high but hinders adsorption when above its PZC. AS, FS, iron slag (IS), and steel slag (SS) are expected to remove P by adsorption, while RC, LS, and fly ash (FA) are expected to remove P by precipitation. X-ray diffraction (XRD) analysis was performed to help determine the dominant minerals by analyzing the crystal structures. Materials such as SS, RC and LS have many minerals present because they all consist of raw minable materials, such as limestone (contained in RC and LS), and hematite (SS is a by-product from its use in steel alloys). AS and FS did not respond significantly to XRD and this may primarily be due to their formation, which is independent of geologic processes. Table 4-1 shows the specific mineral contents.

### **Bulk-Screening for P-Selective Materials**

#### **Surface Waters**

The two raw waters investigated here showed very different physicochemical properties. While the raw waters were of similar pH values, the greater total organic carbon (TOC) content of Sanford Avenue Canal reflects on the greater ultraviolet absorbance at 254 nm ( $UV_{254}$ ) of the highly colored water. The water quality characteristics for Lake Jesup and Sanford Avenue Canal are summarized in Table 4-3. Both Lake Jesup and Sanford Avenue Canal waters have turbidity on account of high

concentration of algae; more so with Lake Jesup because it is directly exposed to sunlight which drives photosynthesis. Figure 4-1 presents a particular phenomenon occurring related to the nutrient cycle transitioning from the tributary to lake. The orthophosphate (OP) is high in the Sanford Avenue Canal compared to other P species and as the water drains into Lake Jesup the OP is converted to other forms of P which, with turbidity readings in Table 4-3, represents great biological activity. This is due to the fact that tributaries are mainly shaded from the sunlight and the hydraulic flushing rates are high not allowing algae growth, in this case Sanford Avenue Canal has an average flow rate of 11,237 acre-ft/year (Jia, 2007), whereas lakes are open, slow flowing and exposed bodies of water where the sunlight drives photosynthesis. Overall, the Sanford Avenue Canal contributes 2.2 metric ton TP/year (Jia, 2007). P speciation was of particular interest in these water bodies. P speciation was measured by the ratio of OP to total phosphorus (TP) (i.e., OP:TP), where TP includes OP, condensed polyphosphates, organic phosphorus, and phosphorus in biomass. When comparing the OP to TP and natural organic matter (NOM) to TOC contents it can be understood the biological activity occurring in the surface water. For P treatment technologies removal of OP relative to TP was an important aspect as will be discussed in subsequent sections.

Lake Jesup was characterized by a low concentration of OP, low OP:TP, high concentration TOC, and moderate specific ultraviolet absorbance (SUVA), where  $SUVA \text{ L/mg C}\cdot\text{m} = 100 \times (UV_{254} \text{ cm}^{-1} / \text{TOC mg/L})$ . The major seasonal trends for Lake Jesup were an increase in turbidity, decrease in SUVA, increase in TP, and decrease in OP:TP. The seasonal trends suggest increased biological activity within Lake Jesup as

winter progressed to summer. For example, the increase in turbidity reflected increased biomass, the decrease in SUVA was a result of microbial byproducts contributing to the organic matter pool, and the decrease in OP:TP was a result of OP incorporation into biomass. Historic weather data for the Orlando Sanford area (KSFB) showed an increase in temperature progressing through the sampling times and low rainfall (WUnderground, 2009). This may explain the increased concentration of P in the Sanford Avenue Canal via dissolution and evaporation and greater biological activity through the seasons in Lake Jesup. Sanford Avenue Canal was characterized by high concentration of OP, high OP:TP, high TOC concentration, and high SUVA. Overall the tributary water draining into the lake is the main source of nutrient overloading and is rich in TOC and OP.

### **Jar Testing**

**Phosphorus removal.** OP removals of more than 50% were observed for most LCM and ion exchange (IEX) resin treatment experiments on Lake Jesup and Sanford Avenue Canal waters. Sanford Avenue Canal water became the focus of jar test experiments because it had a higher concentration of OP. The mechanisms of IEX and adsorption removes dissolved constituents in the water and the materials achieved the removal of P mainly in the form of OP.

Figure 4-2 represents the rate of OP removal in Sanford Avenue Canal water. It can be seen that the LCMs can be grouped into general categories of removal: good, moderate, and undesirable or no effect. FA, which added P to the water, was an example of undesired effect on the treatment goal. The FA seemed to be a very contaminated material. Although there were slight effects by IS and LS, this can be categorized as having no effect and does not serve as a useful material here, removing

about 5-15% OP. Moderate removal was achieved by SS and FS at about 40% removal. The downward gradient suggests that if given more time they may have the ability to remove more OP. AS and RC had the best performance removing greater than 70% OP. In Figure 4-2 AS showed a steep increase in OP removal (70% removal) in the first 5 minutes to maintain a plateau region up to 60 minutes. In other words, AS reached its peak removal within 5 minutes and had no effect afterwards. RC removed about 20% OP at 5 minutes and then gradually removed OP providing a final removal of about 80% at 60 minutes. All other LCMs exhibit a low OP removal rates from observing the gradients shown in Figure 4-2. Though we can see good performance from AS and moderate performance from FS, kinetically, it ended in the addition of TP; refer to Figure 4-3. An observation during jar testing showed that the grains of AS and FS were breaking down and may have caused release of TP.

The LCMs were sieved to the same particle size, with exception to FA, so not only did the kinetic data suggest that AS had more adsorption sites for P than the other materials, this was confirmed by the surface area studies shown in Table 4-1 previously.

In jar testing IEX resins were represented by their acronyms followed by its dosage in brackets. For example, PhosX dosed at 1 mL/L was represented as PX (1). From Figure 4-1, MIEX (MX) and Dowex22 (DX) resins dosed at both 1 mL/L and 4 mL/L seemed to have a quick removal rate with DX outperforming MX after 60 minutes. PhosX (PX) resin dosed at both 1/mL/L and 4mL/L performed a bit differently in that its initial removal was slow but in the end its capacity proved to be greater exhibiting good removal rates, whereas MX and DX achieved their peak performance in the beginning and leveled off towards the end. PX (4) followed a steady removal rate of OP, of about

30% at 5 minutes to 60% at 30 minutes and 80% at 60 minutes. Note that PX(4) was applied to Lake Jesup water from January spiked with OP providing an initial concentration of 127.6 µg P/L. MX (4) quickly removed more than 45% at 5 minutes and then showed a slow removal rate over time. Although low doses of resin exhibited lower OP removal, PX(1) removed more than 50% OP at 60 minutes and its removal rate was between DX(4) and MX(4) at 60 minutes.

Figure 4-4 helps to deduce that when the bar for  $P_{\text{comparison}}$  is  $>0$  then OP was not the only constituent removed. It can be seen that the IEX resins are not only able to remove OP but other P species can be targeted. This is a major advantage that can supplement the good OP removal. Overall, the IEX resins removal of TP and OP were achieved with PX having the greatest effect on OP and comparable removals by MX and DX. Furthermore, the 4 g/L of LCMs used is comparable in OP removal performance to 4 mL/L of the IEX resins.

**Inorganic water quality.** Abundant growth of algae made the water from Lake Jesup and Sanford Avenue Canal highly turbid which was increased by either the breaking apart of the LCMs during jar testing or precipitation reactions. AS, FS, IS, SS, FA, RC, and LS caused turbidities to increase by approximately 11, 25, 8, 15, 124, 33, and 26 NTU, respectively, at a dose of 4 g/L. The IEX resins resulted in a negligible change in turbidity.

Changes in pH were observed and are represented in Figure 4-5. AS, FS, IS, LS, and the IEX resins maintained the pH at approximately constant conditions. Even though SS showed moderate performance in OP removal it raised the pH to 10. RC was a competitor with AS with respect to OP removal, but RC substantially raised the pH to

almost 10 in the Sanford Avenue Canal water. Also, the calcium in RC formed a precipitate with P which was undesirable due to the need of an additional handling process (Baker et al., 1998).

The anions, chloride and sulfate, are shown in Figure 4-6. The LCMs did not change the chloride concentration; therefore there is no concern of total dissolved solids added to the water. AS and FS increased the level of sulfate as shown in Figure 4-6. This was due to the fact that these were the byproducts of water treatment with aluminum sulfate and ferric sulfate salts and hence had sulfate content. With respect to the IEX resins, MX and DX proved to be true IEX resins, whereby they added chloride to the water and removed sulfate in a stoichiometric ratio (Blaney and Cinar, 2007; Bolto and Dixon, 2002). However, the PX resin behaved more like an adsorbent, which removed many anionic species. Nitrate, in addition to OP, is a problem as it is a nutrient and can contribute to eutrophication. However, because there is a natural nitrogen cycle by which nitrogen gets fixed into plants, nitrogen has not been a focus for this project. Overall, MX, PX, AS, and FS showed the most promise because these materials substantially removed OP and had minimal side-effects on the surface waters treated. These materials were defined as P-selective materials, and were subject to additional testing as described in subsequent sections.

### **Performance of P-Selective Materials**

#### **Surface Waters**

Two raw waters were used in this study from different locations in Florida. One came from the Sanford Avenue Canal and the other was from Lake Alice, Gainesville, Florida. A local source of water was more economical and time efficient to conduct studies due to accessibility. Although the TOC content of Sanford Avenue Canal is

higher than Lake Alice, the OP:TP and SUVA were comparable. Table 4-4 shows the water quality of the sample locations. Because of the highly turbid samples, it was necessary to filter the water through a Whatman GF/A filter to remove any particles that may clog the column setup. Table 4-4 shows a substantial decrease in TP and a slight decrease in OP after filtering. It has been previously determined that the materials were more effective with dissolved constituents in the water; therefore, it is not crucial to keep the particulate P suspended in the water.

Waters used for jar testing allowed an understanding that the major seasonal trends for Sanford Avenue Canal were increases in OP and TP with a net increase in OP:TP, decrease in TOC, and decrease in SUVA as the year progressed through a dry season. Here water batches were obtained from contrasting seasons in the Sanford Avenue Canal, i.e., from dry to wet, but temperatures remained moderately warm (WUnderground, 2009). This resulted in a significant decrease in OP and TP and an increase in TOC from the dry season to the wet season in Florida. This signified dilution of OP whereas the higher concentration of TOC and SUVA suggested stormwater runoff as its source. At the time of collecting samples from Lake Alice it had close resemblance to a batch of water collected from Sanford Avenue Canal in April whereby SUVA and OP:TP were comparable. Based on these dissolved constituents the use of Lake Alice became valid as it was comparable to Sanford Avenue Canal. Lake Alice samples showed increases in TOC and OP during a wet period. Lake Alice is designed to collect stormwater runoff from the University of Florida where rain resulted in more contaminants entering the wetland.

## **Continuously-Flowing Treatment**

**Targeted P species.** OP has been determined as the major targeted P species by the materials used in this project from jar testing experiments. The continuous-flow column results shown in the Tables 4-5 and 4-6 further emphasized that OP was the targeted P specie because TP versus OP removed is similar throughout treatment. To further emphasize this point, OP remaining was subtracted from TP remaining and the result remained constant throughout treatment, showing that other P species were left behind while OP was targeted.

**OP removal.** From the jar testing an idea of which materials work best was derived. The LCMs, AS and FS, and the IEX resins, MX and PX, were tested for their capability to endure continuous treatment. Further screening was done here. Figure 4-7B showed that AS, MX, and PX achieved 80% OP removal in the initial 120 BV of continuous flow. However, MX's capacity greatly degraded shortly after 120 BV indicating that all of its ion exchange sites became utilized quickly. MX had great removal but it seemed to work best for the treatment of fixed volumes of water as observed in jar tests. FS removed 40% OP at the beginning and continued to treat at 30% which was not sufficient for the large volume of water that needed to be treated and the treatment goals set out for the project. Figure 4-7 collectively shows that PX and AS achieved consistent removal of over 50% for larger BVs even under the highly concentrated OP conditions of water used in Figure 4-7A and 4-7C. Overall, the porous P-selective materials, AS and PX, have greater capacities for removing OP from surface water under continuous flow.

**Sulfate effect.** Figure 4-8 shows an important water quality characteristic if mercury (Benoit, 1997) were to be a concern. Sulfate concentration was affected in the

beginning of treatment within the first 1000 BV by both PX and AS. AS increased the sulfate concentration to 231% whereas PX removed 83% of the sulfate in solution. This was reflected in Figure 4-6 as well which predicted such changes in sulfate for the two materials. After 1000 BV the effect diminished indicating that AS had some free sulfate which needed to be washed or released before application. This is important to note so that it does not affect the water quality of surface water bodies.

### **Cyclically-Flowing Treatment**

**Motivation.** It was determined that PX and AS were both porous materials and that porous materials exhibit a greater removal capacity if allowed to rest (Blaney and Cinar, 2007). This is due to internal diffusion, whereby the OP molecules on the surface of the material get time to migrate to the inner pore walls freeing surface area immediately in contact with the flowing water. Another factor that could govern this is desorption of other anions bound to the surface of the materials freeing adsorption sites. The eventual pilot-scale system was envisioned to be powered by solar energy so it was more sensible to have it in operation during the day and off during the night. Therefore, a cyclic 12 hours on and 12 hours off (12/12) was examined.

**OP removal.** It was found that PX and AS yielded over 50% removal consistently as in the continuous flow studies, but after resting overnight an increase in OP removal was observed at the beginning of the next day as compared to the end of the previous day. Figure 4-9 shows that AS and PX were capable of enduring twice as much BVs before exhaustion as compared to PX that was subjected to continuous flow without a break. Lake Alice water was used in this experiment because it had been decided that it was more feasible to launch the FITS in Lake Alice.

## Pilot-Scale Studies

**P removal.** The construction of a pilot-scale facility was found necessary to ensure that the bench-scale experiments can be applied in the real environment. Based on the findings of the 12/12 experiments it has been determined that giving the materials a rest extends their useful life. The FITS was run on solar power conveniently during the day and left to rest overnight, so the material will benefit from this. The results in Figure 4-10 show that the overall treatment of TP by the FITS was effective, yielding greater than 60% by combining the mesocosm and fluidized bed filled with PX for a duration of 9 to 10 days until a 50% breakthrough point was observed. The PX fluidized bed achieved over 70% removal of OP as shown in Figure 4-11 when the mesocosm water was considered as the influent. The PX seems to have 8-10 days of good removal with the flow rate of 2 BV/min in Lake Alice. Subtracting the integral of the removal curves from the integral of the influent curves and dividing by the amount of material used in Figures 4-11A and 4-11B, the PX can remove between 2.0 to 3.5 mg P per mL PX resin depending on the water chemistry flowing at a rate of 2 BV/min. This removal will always depend on the flow rate and competing constituents in the water, such as NOM and sulfate. The difference between the behavior of OP in Figure 4-11A and 4-11B was representative of this. Many environmental conditions occurring day-by-day will affect the system.

AS did not remove P as well as predicted by the column studies. This may be due to a change in composition. A second batch of AS was received from the same source as the first, but at a different time of year. Water passing through a treatment facility is not uniform so the aluminum sulfate to activated carbon proportions used for treatment and sludge content will differ throughout the year. From here on the second batch of AS

was used for the fluidized beds. Table 4-7 gives a comparison of the first batch of AS (AS1) and second AS (AS2). The composition changed slightly.

Another physical factor that can play a role in the reduction of removal was that the grain sizes were much larger, after preparation, than in the bench-scale column studies. Hence, reducing the surface area significantly results in less sites available for adsorption (Mortula and Gagnon, 2007a). It was observed in Figure 4-11 that the AS did achieve some removal of OP and if the grain sizes were smaller it will yield better results. However, to prepare a large batch of AS at a smaller, effective grain size became time consuming and resulted in waste of material.

**Turbidity and pH.** As a note, in the following section, Figure 4-12 and Figure C-5 show that the mesocosm removed a significant amount of turbidity, which was favorable because clogging of the fluidized bed could be an issue with high turbidities. The lake remained between pH 7 to 9 with little changes to other inorganic water quality by the fluidized beds. Much of the TP in Lake Alice was contributed by the level of turbidity in the water, which in this case was directly from biological activity related to algae blooms.

Overall, the bench-scale column studies can be scaled-up to a larger fluidized bed and applied to the real environment. The entire project presented the possibility to accurately predict the behavior of the fluidized beds depending on the material applied and water conditions. The use of water from real surface water systems also helped with understanding how changes in water quality affect performance.

### **Effect of Algal Blooms**

The effects of algal blooms are apparent in a lake. It becomes an aesthetic issue and aquatic life starts to die due to reduced oxygen supply. During the times of algae

blooms the turbidity was higher than prior to algae blooms as shown in Figure C-5. The pH was increased to around 10 as a result of the biological activity, see Figure 4-13. In comparing Figures 4-11 and 4-12 the pH levels track closely with the rising and falling of turbidity. This is a rather common observation as algae blooms impact the pH and turbidity (Foott et al., 2009). However, the adsorption mechanism is affected by changes in pH whereby water with a high pH has a higher concentration of negatively charged  $\text{OH}^-$  ions that will then surround the surface sites and compete with OP which is also negatively charged (Zhu and Jyo, 2005).

Therefore, a rise in pH will have an adverse effect on the removal capability of the treatment materials used because PX and AS act as adsorbents. This effect was shown in Figures 4-14 and 4-15 where there was little to no removal of TP and OP, respectively, by AS and some removal of TP and OP by PX from the beginning of an algae bloom season. Some P was released at the end as the lake water spiked above pH 10.5. Overall, the AS seemed to be more greatly affected by the change in pH than PX.

### **Sustainability Studies**

The attempts to remove P made throughout this project always kept sustainability within arm's reach. The sustainable value of considering a LCM as a media of removal is significant, whereby an extra life could be given to the waste byproduct before its inevitable disposal. But, it has been determined that although LCMs can perform well in small-scale batch or continuous treatment, the existence of commercially available IEX resins can prove to be easier to implement and provide consistently good efficacy for OP removal.

IEX resins are expensive and it would be a shame if after the resin is exhausted it is disposed of. However, IEX resin producers boast the reusability of these materials (Sylvester and Moller, 2004). In order to reuse them they must be regenerated and as PX was the best candidate for implementing in a fluidized bed for the removal of OP, then the regeneration, reapplication, and disposal of byproducts had been experimented with.

### **Regeneration**

Before starting the large pilot-scale regeneration, it must be determined if regeneration is a possible option. Figure 4-16 shows a comparison between the fresh (virgin) PX and once regenerated PX in duplicate, which was done in a bench-scale column experiment. It was found that the materials tracked each other very closely proving that the PX can be regenerated and effectively reapplied to a system. The largest disagreement was a brief 20% difference in removal.

Due to the success of the bench-scale regeneration, it was decided to apply PX regeneration to the FITS. From here it was deemed practical to investigate multiple regeneration cycles. Figure 4-17 proved that PX can be regenerated multiple times. Mesocosm effluent represented influent water here. Regenerations were done three times (3x) and all were in very close agreement with the virgin PX used simultaneously. Over 60% removal was observed at most times until exhaustion in all regeneration cases. Again, having two fluidized beds furnished the convenience of comparing two materials under the same conditions at the same time.

### **Precipitation**

The regeneration process of PX resulted in a dirty caustic brine solution, also known as dirty wash solution (DWS), which was very concentrated in all contaminants

that the PX had originally removed and a pH of 14. For example, the duplicate regenerated PX used in Figure 4-16 resulted in a DWS that contained 49 mg P/L and 14.1  $\text{cm}^{-1}$  of  $\text{UV}_{254}$  absorbing NOM. It is unusual for an environmental engineer to think that such a solution can be disposed of without reducing the hazardous status of the DWS. This defeats the purpose of removing OP and would result in P being re-released to the environment. To prevent this, OP should be removed from the DWS. In this case, the DWS was titrated with a predetermined molarity of calcium solution which resulted in a precipitate. This precipitate from past research was most likely hydroxyapatite and/or, in smaller quantities,  $\text{CaPO}_4$  species because of the high pH conditions that exist (Bowden et al., 2009; Sibrell and Montgomery, 2009). Figure 4-18 shows a variety of DWSs that were treated with the calcium solution significantly reducing the OP in solution; but if too much was used then OP seemed to become released. Jar 1 and Jar 2 existed from two jar tests done on Lake Alice water for the purpose of attaining two batches of used PX resins to produce two extra batches of DWSs to experiment with. Data for the column line was derived from precipitating a DWS of a PX resin used in a column study on Sanford Avenue Canal water from April.  $\text{UV}_{254}$  was measured throughout the precipitation. Initial  $\text{UV}_{254}$  readings varied but were all reduced by 7% to 20% and pH remained around 14. The NOM was not greatly affected but there was some removal maybe due to complexation of the calcium precipitate by the NOM.

### **Reuse of Regeneration Solution**

The cleaned DWS had a long history starting with the preparation of the solution to cleaning it of contaminants. With such labor involved and the hazard it may cause if poured down the drain, it was thought that maybe the cleaned solution can be used again to regenerate the PX resin. After the OP in the DWS was precipitated, the

precipitate was filtered out of solution. Three quarters of the solution was recovered from this process; filtering the remaining quarter became difficult with the resources available. This quarter was replaced with fresh solution. It was found that the cleaned DWS worked once again to clean the PX of its contaminants. After the regeneration process, this PX batch was reapplied to a fluidized bed of the FITS. The DWS regenerated PX performed as well as the virgin PX that it was simultaneously compared to, yielding over 60% removal until exhaustion; see Figure 4-19. Therefore, it is possible to reuse the DWS once, after which a decision can be made to precipitate OP, neutralize, remove NOM and dispose of the safer solution.

Table 4-1. Physical Properties of LCMs

Parameter	AS 1	FS	IS	SS	FA	RC	LS
Al <sup>a</sup> (mg/kg)	2461	9.5	3084	65.4	1271	1054	2.8
Ca <sup>a</sup> (mg/kg)	1142	10810	12460	36290	6910	28080	34240
Fe <sup>a</sup> (mg/kg)	63.6	801.0	78.0	674.0	503.0	527.0	27.1
Pore size <sup>b</sup> (Å)	76.58	69.06	278.98	-	69.27	160.9	-
Surface area <sup>b</sup> (m <sup>2</sup> /g)	227.40	6.67	2.05	-	2.68	3.53	-
Pore Volume <sup>b</sup> (cm <sup>3</sup> /g)	0.440	0.010	0.014	-	0.004	0.014	-
Point of zero charge (pH)	6.18	6.87	9.28	12.46	11.60	11.97	9.47
X-ray diffraction crystal structure <sup>c</sup>	Q	None	C	C, Ag, L	Q	D, C, Q	D, C

<sup>a</sup> Plant available quantity

<sup>b</sup> Data verified for accuracy by measuring a standard powdered activated carbon of known characteristics

<sup>c</sup> Abbreviations: Q = quartz, C = calcite, D = dolomite, Ag = aragonite, L = larnite

Table 4-2. Average Metal Composition (mg/kg) of Low-Cost Materials rounded to 3 significant figures

	Al	Ca	Fe	As	Pb	Cu	Mg	Mn	Zn
FS	2470	26000	149000	18.4	12.0	8.42	863	243	626
SS	13900	99900	12400	0.140	7.65	27.7	26600	6720	167
AS	93500	2470	2920	122	7.71	276	650	107	107
IS	56900	177000	2210	1.38	0.556	4.21	21400	1790	39.2
RC	4330	139000	3920	5.49	6.08	15.0	16500	64.7	70.4
LS	722	155000	880	2.67	1.89	5.26	80500	45.7	656
STD REF 2709 <sup>a</sup>	24200	17100	28100	13.8	13.0	29.4	12400	424	1030

<sup>a</sup> All elements in STD REF 2709 were within NIST 2002 specified ranges (NIST, 2002; USEPA, 1996).

Table 4-3. Water Quality Characteristics for Lake Jesup and Sanford Avenue Canal

Month	pH	Turbidity	TOC	SUVA	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	TN	OP	TP	OP:TP
2009		NTU	mg C/L	L/mg C-m	mg/L	mg/L	mg N/L	mg N/L	µg P/L	µg P/L	
Lake Jesup											
Jan.	7.02	2.86	16.1	3.8	109	23.9	< 0.5	1.0	17.2	111	0.15
Mar.	7.33	15.8	17.3	2.9	175	35.6	< 0.5	1.3	7.3	206	0.04
Apr.	7.40	22.3	17.8	3.2	269	57.1	< 0.5	0.7	5.6	274	0.02
Sanford Avenue Canal											
Jan.	7.14	2.47	23.2	4.8	122	22.6	0.6	1.2	86.2	137	0.63
Mar.	7.67	3.70	18.3	4.4	188	40.6	0.6	0.9	159	194	0.82
Apr.	7.63	4.18	14.8	4.3	197	35.3	0.7	0.1	232	289	0.80

Table 4-4. Water Quality Characteristics for Sanford Avenue Canal and Lake Alice

Date	pH	Turb.	TOC	SUVA	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	TN	OP	TP	OP:TP	
2009		NTU	mg C/L	L/mg C-m	mg/L	mg/L	mg N/L	mg N/L	µg P/L	µg P/L		
Sanford Avenue Canal												
Apr.	Raw	7.59	4.18	14.44	4.44	185.15	33.02	1.28	-	221.78	329.07	0.67
	Filt <sup>a</sup>	7.74	-	14.58	4.07	185.15	33.02	1.28	1.22	215.23	250.30	0.86
Jun.	Raw	6.93	-	33.56	4.86	54.51	6.30	9.38	0.84	107.10	195.11	0.55
	Filt <sup>a</sup>	7.57	-	31.48	5.22	54.51	6.30	9.38	0.84	107.10	142.95	0.75
Lake Alice												
Jul.	Raw	7.70	-	7.16	3.19	13.67	18.70	-	0.49	421.26	481.69	0.87
	Filt <sup>a</sup>	7.70	-	7.08	3.09	13.6	18.3	-	0.44	387.12	423.43	0.91
Aug.	Raw	7.55	-	8.26	2.72	15.86	20.76	-	1.95	506.90	528.85	0.96
	Filt <sup>a</sup>	7.50	-	8.06	2.83	-	-	-	0.59	372.37	327.27	0.83

<sup>a</sup> Sample filtered through a Whatman GF/A Filter

Table 4-5. Removal of P by PX using Sanford Avenue Canal April water in Bench-Scale Continuous Flow Study

BV	TP Removed, µg P/L	OP Removed, µg P/L	TP Remaining, µg P/L	OP Remaining, µg P/L	P Remaining, µg P/L
0	0.00	0.00	246.90	216.90	30.00
120	183.22	177.64	63.68	39.26	24.42
600	158.59	149.57	88.30	67.33	20.97
1080	144.34	144.61	102.56	72.29	30.27
1560	141.29	137.12	105.61	79.78	25.83
2880	123.98	124.01	122.92	92.89	30.03
3360	107.82	107.50	139.08	109.40	29.68
3840	108.32	109.10	138.58	107.80	30.78
4320	103.06	102.60	143.84	114.30	29.54
5760	97.17	95.40	149.73	121.50	28.23
6240	94.51	97.40	152.39	119.50	32.89

Table 4-6. Removal of P by AS Using Sanford Avenue Canal April Water

BV	TP Removed, µg P/L	OP Removed, µg P/L	TP Remaining, µg P/L	OP Remaining, µg P/L	P Remaining, µg P/L
0	0.00	0.00	250.70	213.50	37.20
120	184.75	187.14	65.95	26.36	39.59
600	175.38	165.73	75.32	47.77	27.55
1080	167.84	157.97	82.86	55.53	27.33
1560	155.64	148.81	95.06	64.69	30.37
2880	129.04	125.80	121.66	87.70	33.96
3360	125.58	124.06	125.12	89.44	35.68
3840	128.37	118.87	122.33	94.63	27.70
4200	133.70	116.78	117.00	96.72	20.28
4920	109.92	103.20	140.78	110.30	30.48
5760	104.81	99.40	145.89	114.10	31.79

Table 4-7. Comparison of AS1 and AS2

Parameter	AS 1	AS 2
Al <sup>a</sup> (mg/kg)	2461.00	3385.00
Ca <sup>a</sup> (mg/kg)	1142.00	554.00
Fe <sup>a</sup> (mg/kg)	63.60	46.39
Organic Matter <sup>b</sup> , OM	44.10 %	52.23%

<sup>a</sup> Plant available quantity

<sup>b</sup> Loss on Ignition

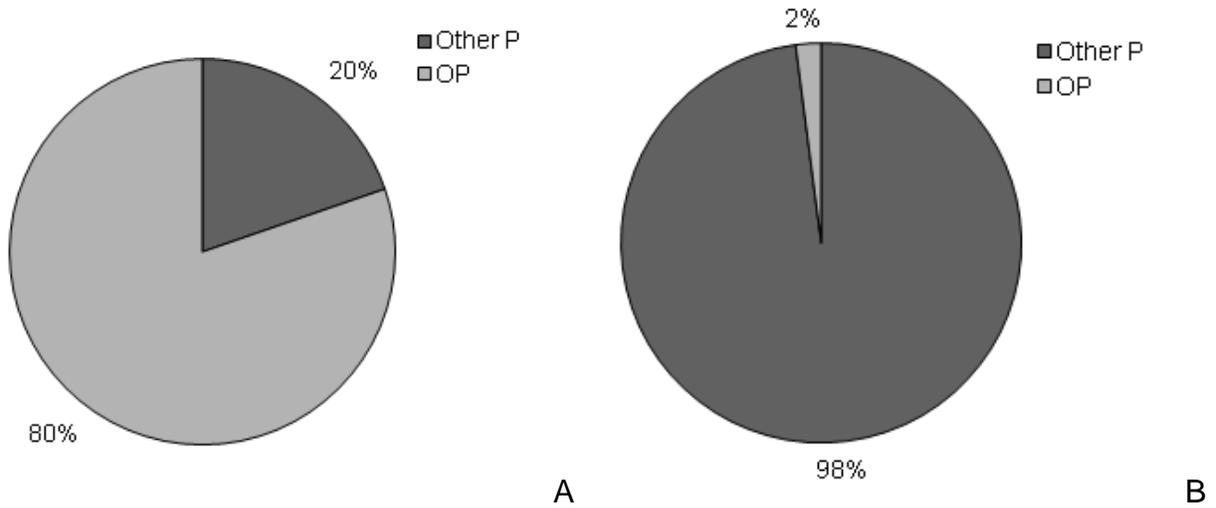
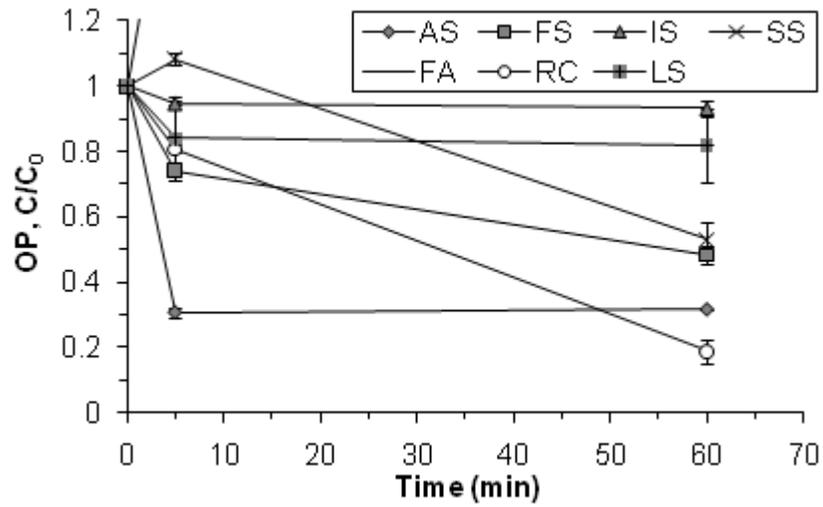
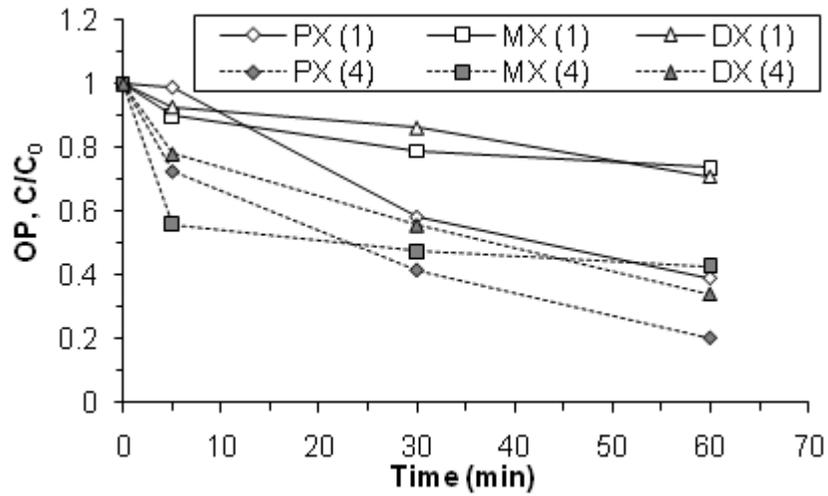


Figure 4-1. Composition of OP of A) Sanford Avenue Canal, and B) Lake Jesup using batches of water from April. Initial Sanford Avenue Canal April TP = 289 µg/L, and Lake Jesup April TP = 274 µg P/L.

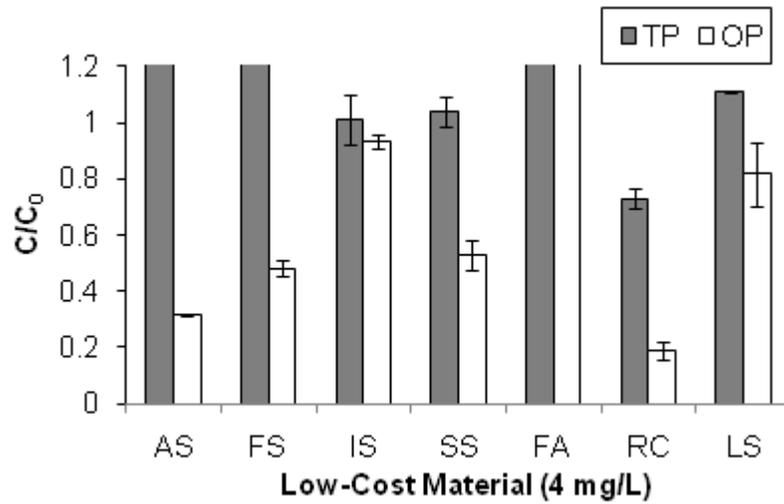


A

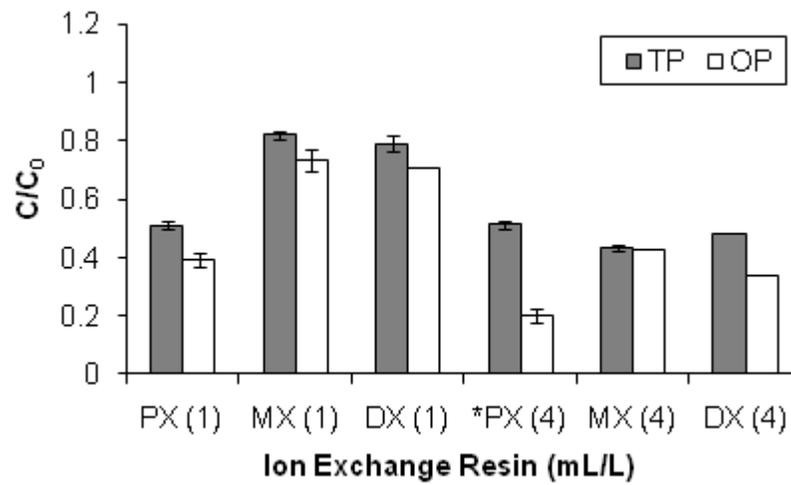


B

Figure 4-2. Rate of OP removal by A) LCMs (4 g/L), and B) IEX resins (1 and 4 mL/L) in Sanford Avenue Canal water.  $C/C_0 = 2.45$  for FA at 60 min. Initial OP = 88.9 to 159.4  $\mu\text{g P/L}$ .



A



B

Figure 4-3. P remaining after 60 min of treatment of Sanford Avenue Canal water for A) LCMs, and B) IEX resins. Peak of  $TP_{AS} = 2.1$ ;  $TP_{FS} = 1.5$ ;  $TP_{FA} = 5.9$ ;  $OP_{FA} = 2.4$ . Initial TP = 125.3 to 286.6  $\mu\text{g P/L}$ ; initial OP = 88.9 to 159.4  $\mu\text{g P/L}$ .

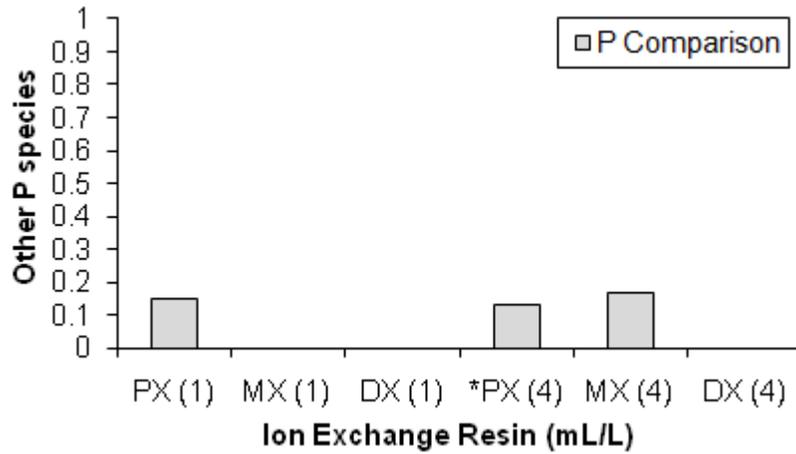


Figure 4-4. P species removed after 60 minutes treatment of Canal Water for IEX resins. Where  $P_{\text{comparison}} = (TP_r - OP_r) / TP_o$ ,  $TP_r = TP$  removed,  $TP_o = \text{Initial TP}$  and  $OP_r = OP$  removed.

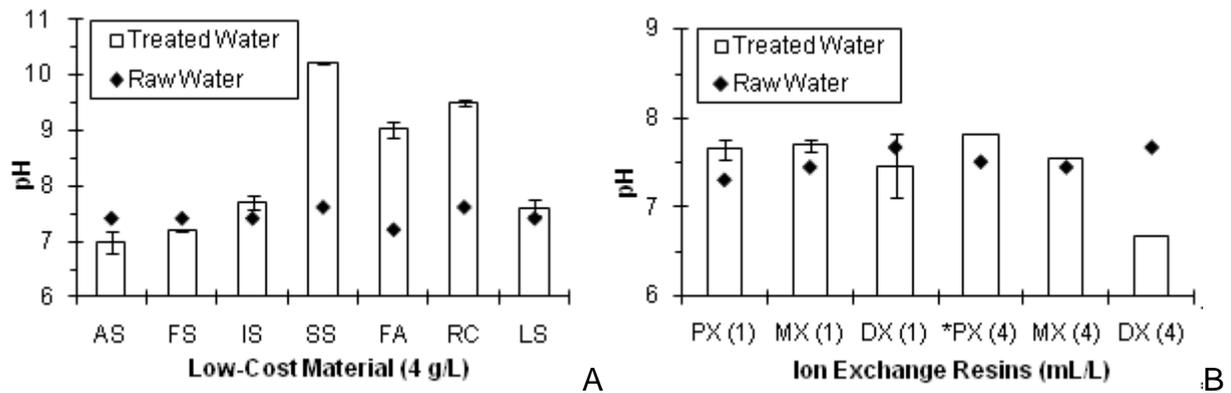


Figure 4-5. Change in pH following 60 min of treatment of Sanford Avenue Canal water for A) LCMs, and B) IEX resins.

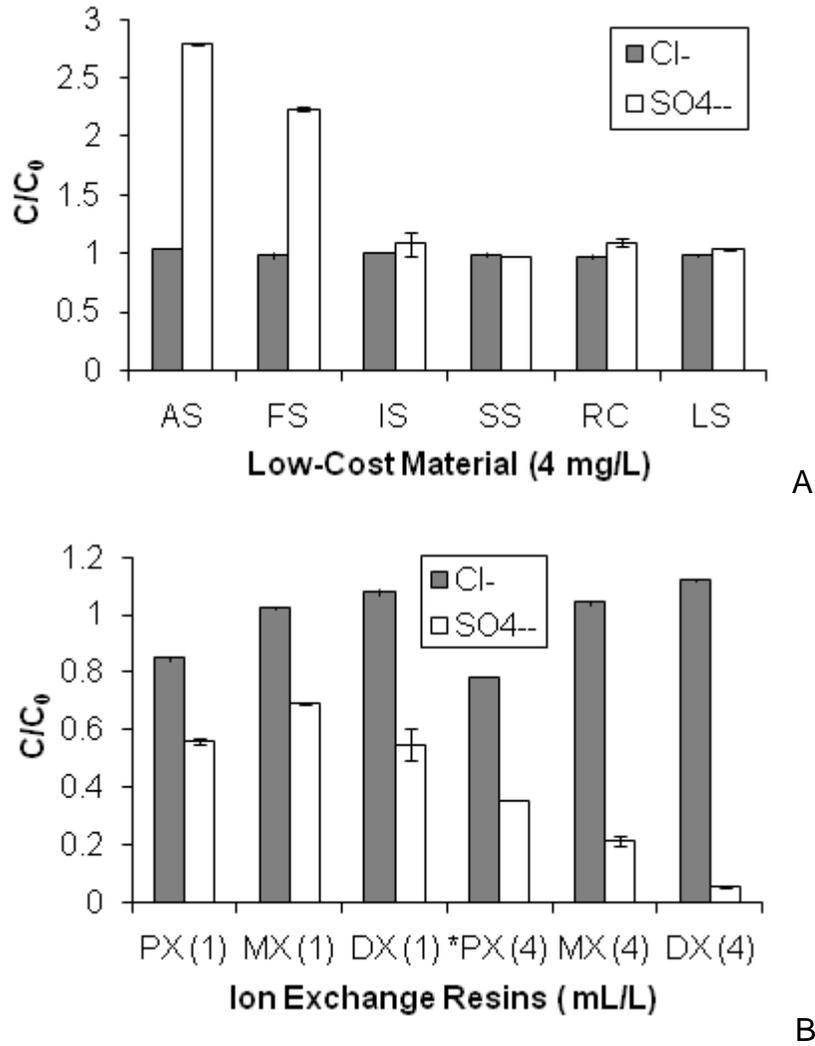
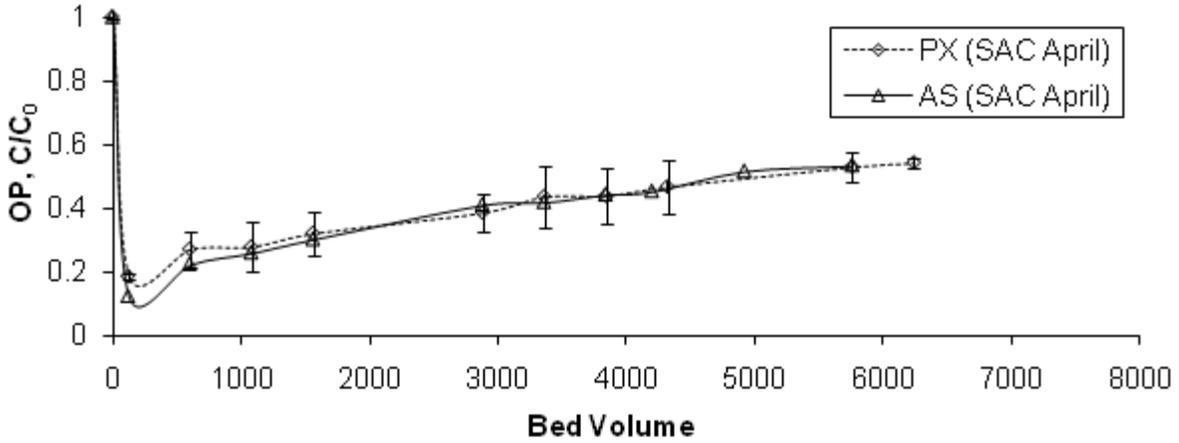
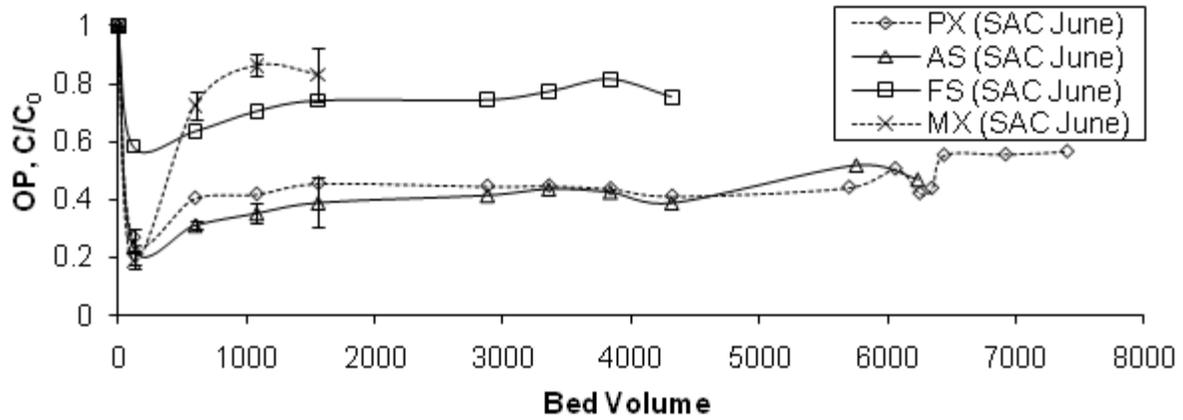


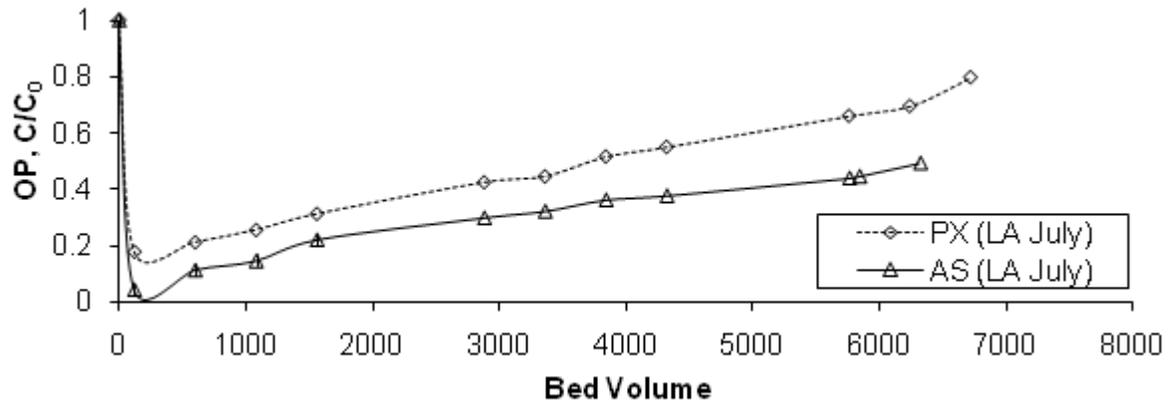
Figure 4-6. Change in chloride and sulfate following 60 min of treatment of Sanford Avenue Canal water for A) LCMs, and B) IEX resins. Initial chloride = 112 to 191 mg/L; initial sulfate = 22.5 to 40.6 mg/L.



A



B



C

Figure 4-7. OP remaining during bench-scale continuous flow treatment by A) PX and AS, B) PX, AS1, MX and FS, and C) PX and AS, in different water batches. Initial OP concentrations of Sanford Avenue Canal (SAC) April = 215.23  $\mu\text{g P/L}$ , and SAC June = 106.83 to 107.63  $\mu\text{g P/L}$ , LA July = 387.12  $\mu\text{g P/L}$ .

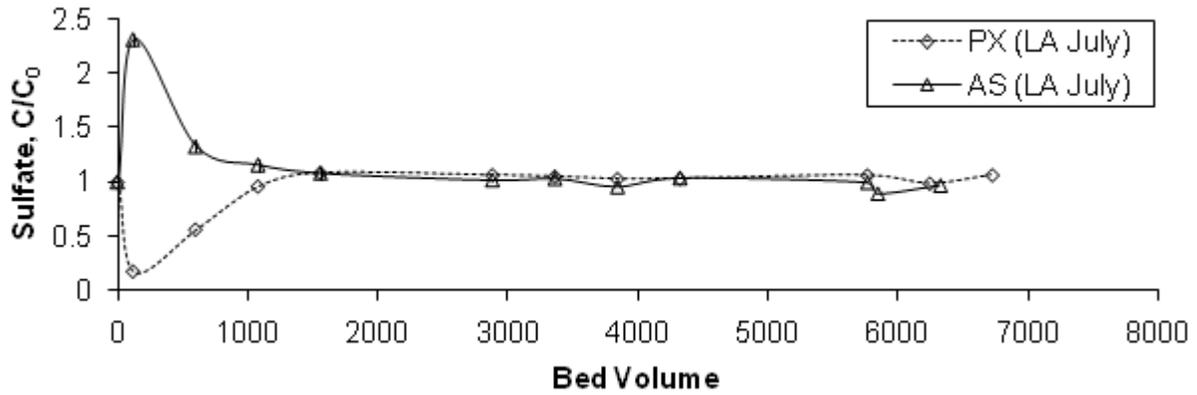


Figure 4-8. Sulfate remaining during bench-scale continuous flow treatment by PX and AS. Initial sulfate concentrations Lake Alice (LA) July = 18.3 mg/L.

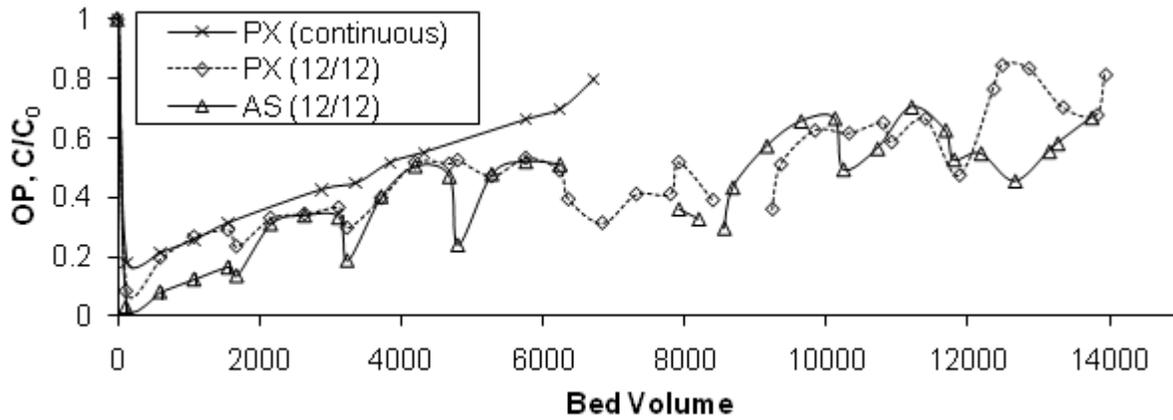


Figure 4-9. Cyclic Flow, 12 hours treatment and 12 hours resting period, compared to continuous treatment. Lake Alice water was used from July and August for bench scale continuous and 12/12 experiments respectively. Initial OP concentration of Lake Alice (LA) July = 387.12  $\mu\text{g P/L}$ , and LA August = 396.15  $\mu\text{g P/L}$ .

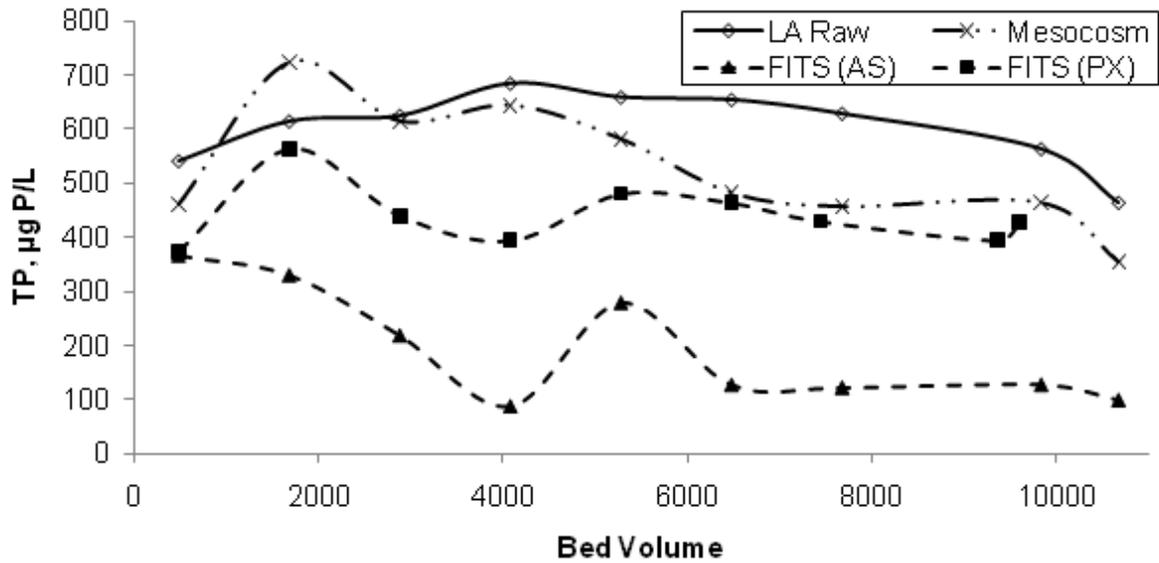
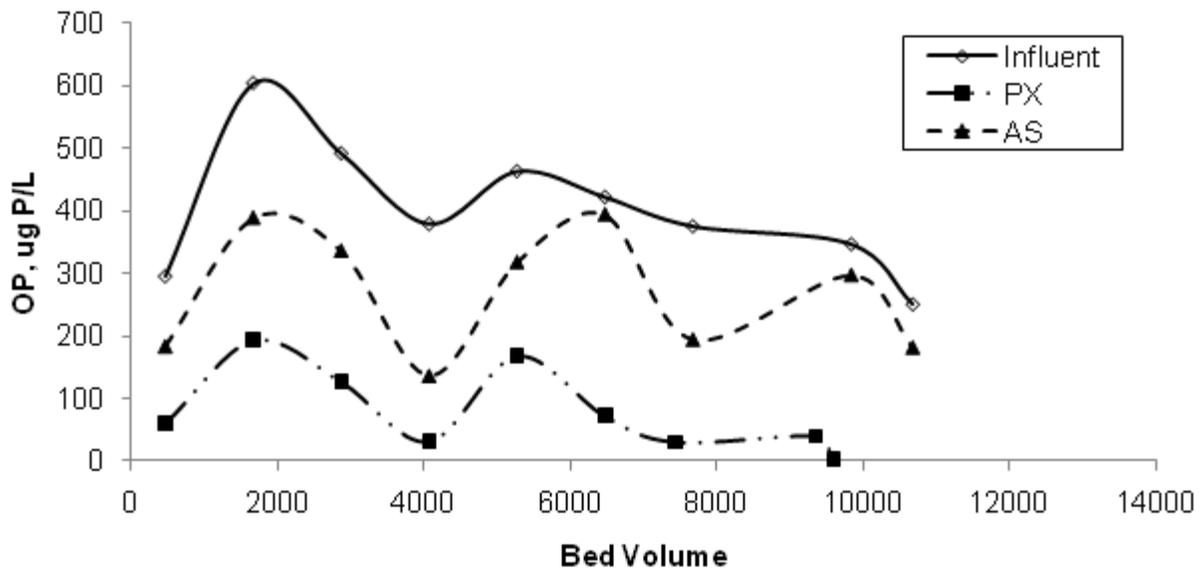
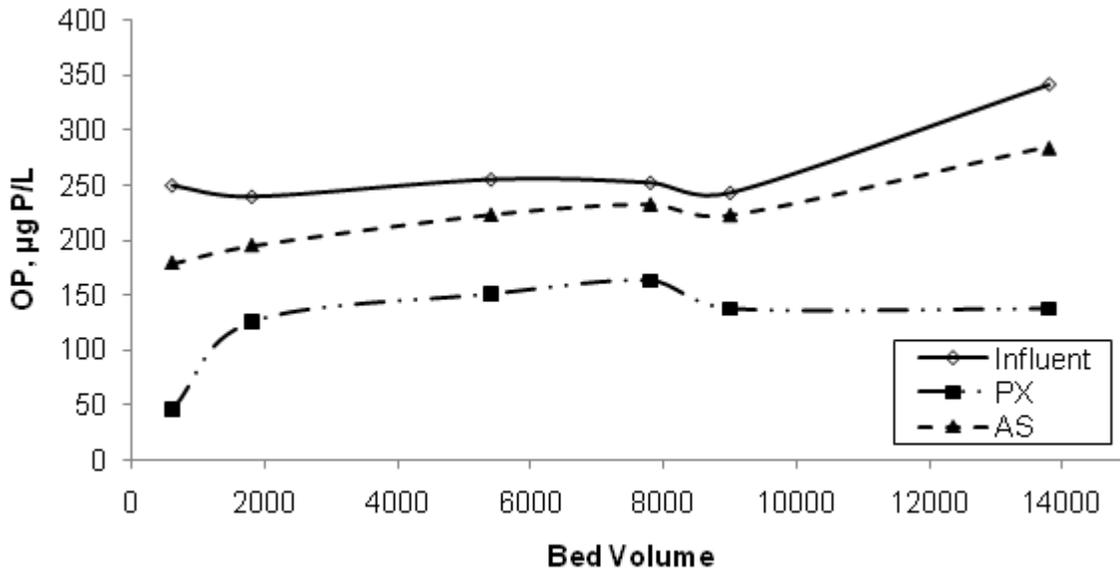


Figure 4-10. TP removal by FITS through mesocosm and fluidized beds between 10/09/2009 to 10/19/2009 during pilot study.



A

Figure 4-11. OP Removal by fluidized beds from mesocosm (influent) water and fluidized beds between A) 10/9/2009 to 10/19/2009, and B) 12/01/2009 to 12/12/2009 during pilot study.



B

Figure 4-11. Continued.

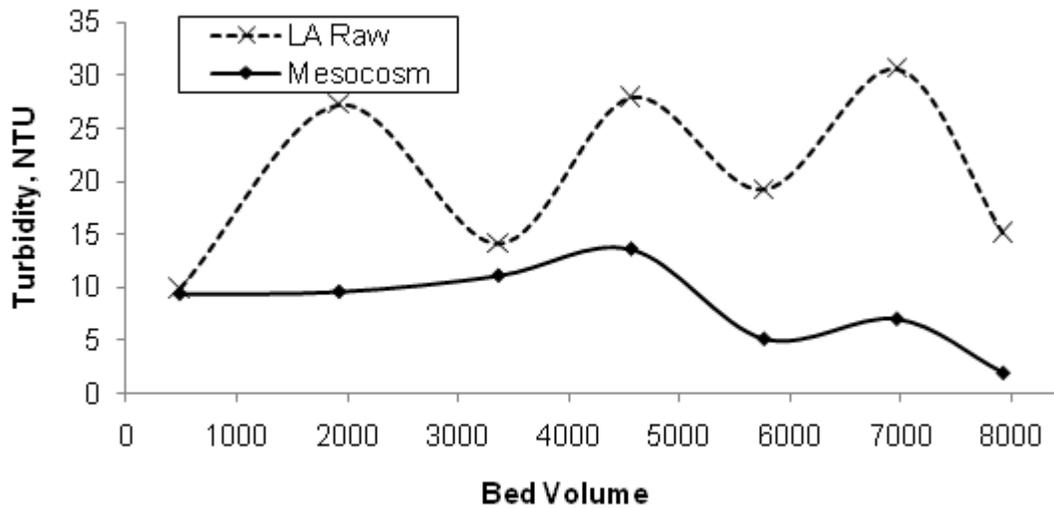


Figure 4-12. Turbidity in Lake Alice (LA) during algae bloom and removal by mesocosm respectively between 10/02/2009 to 10/09/2009 during pilot study.

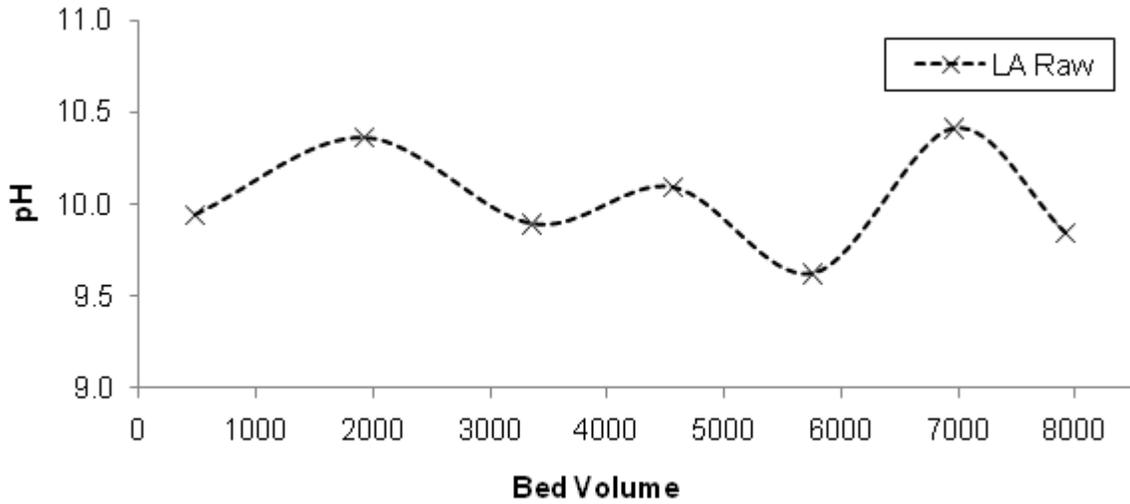


Figure 4-13. Change of pH during algae bloom in Lake Alice (LA) pH between 10/02/2009 to 10/09/2009 during pilot study.

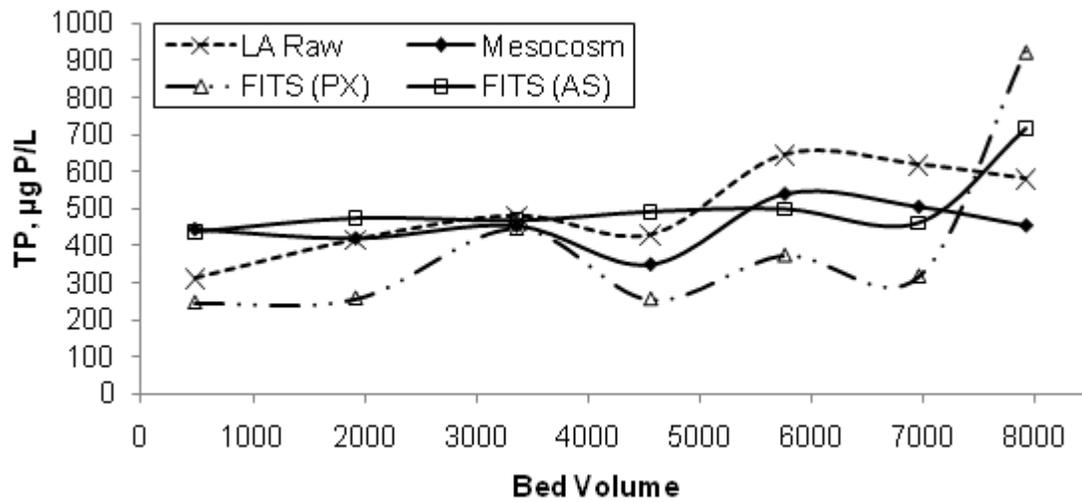


Figure 4-14. TP removal from Lake Alice by FITS between 10/02/2009 to 10/09/2009 during pilot study.

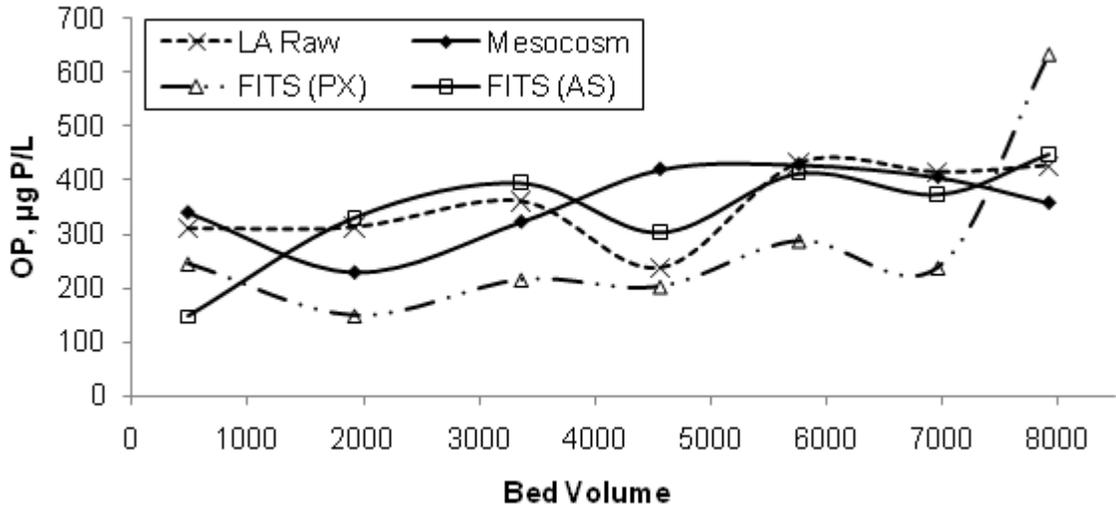


Figure 4-15. OP removal from Lake Alice by FITS between 10/02/2009 to 10/09/2009 during pilot study.

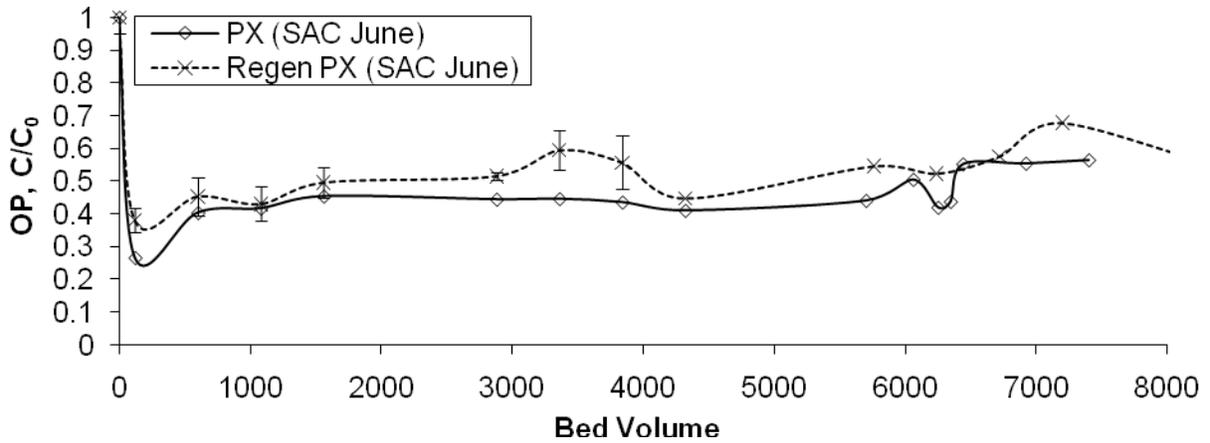
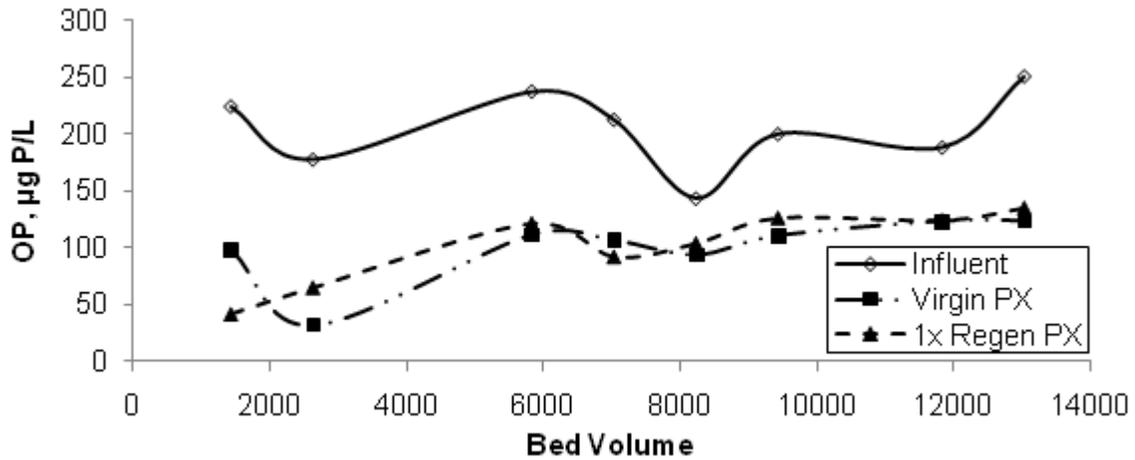
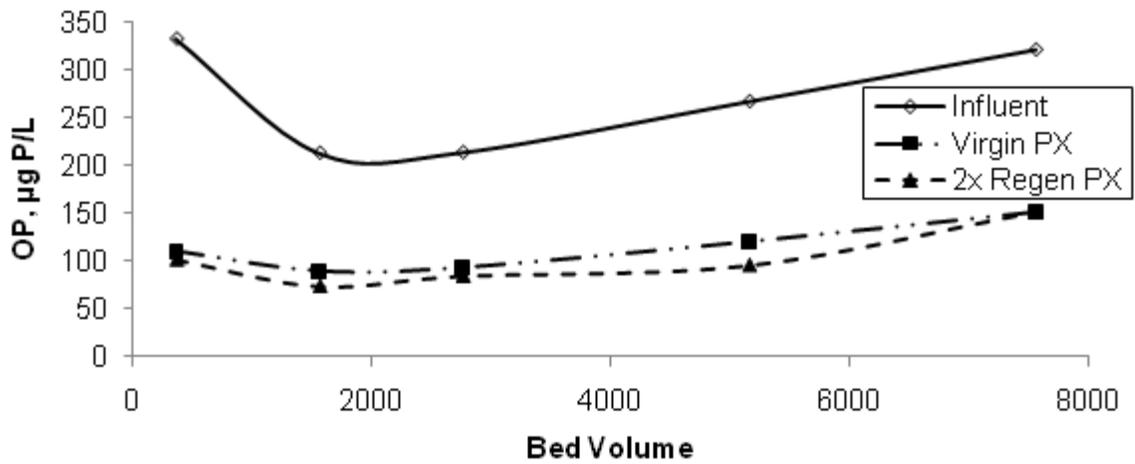


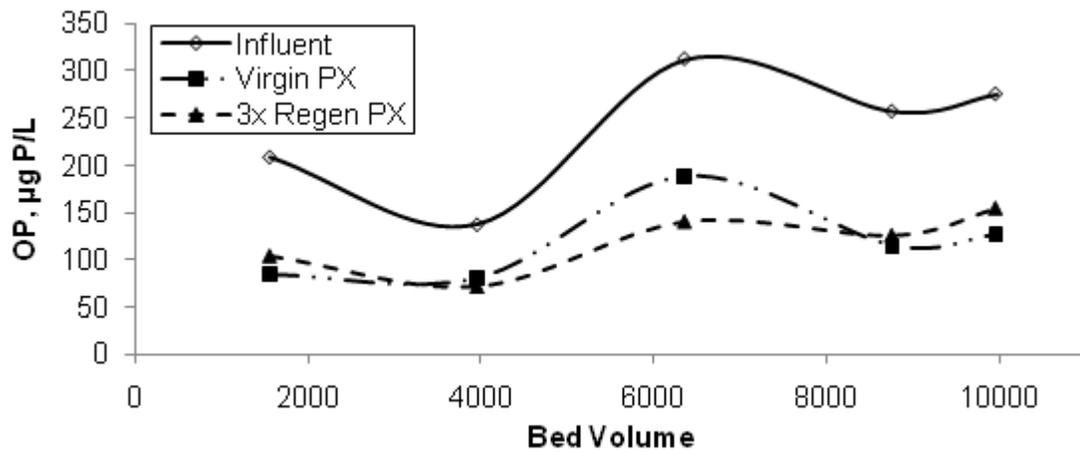
Figure 4-16. Removal of OP by Regenerated PX from the bench-scale continuous flow studies. Initial OP for Sanford Avenue Canal (SAC) June = 107.10 µg P/L and 90.49 µg P/L for PX and Regenerated PX respectively.



A

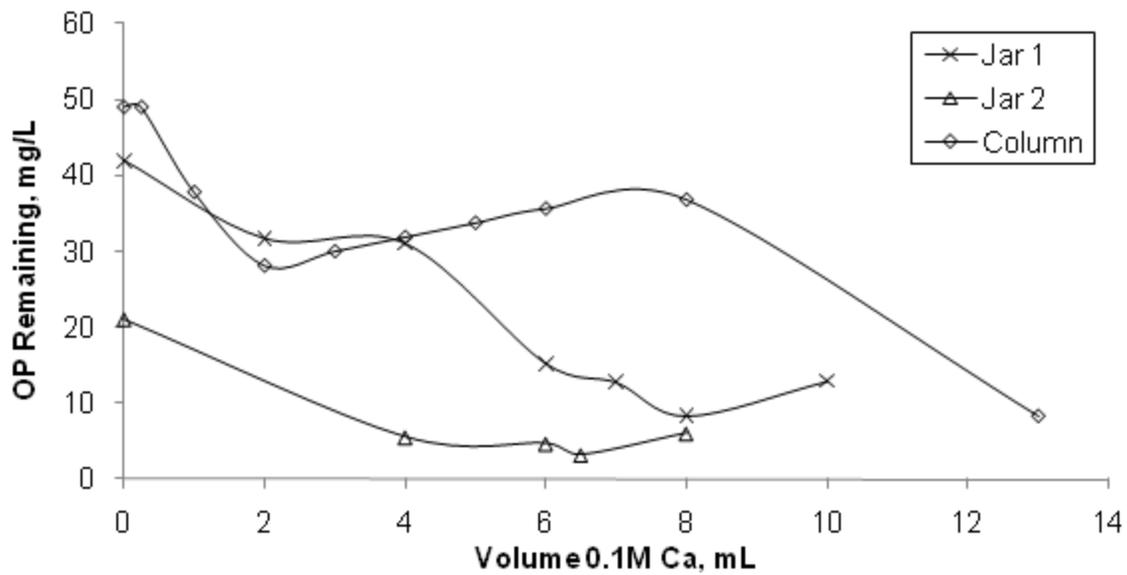


B

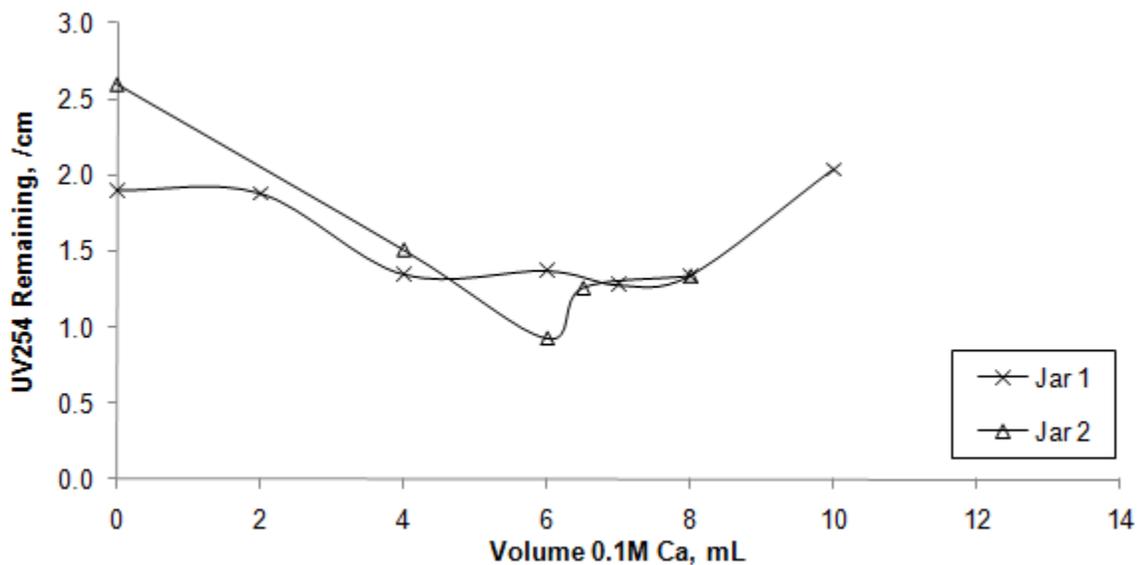


C

Figure 4-17. OP removal from mesocosm (influent) water by batches of PX regenerated A) 1x (11/02/2009 to 11/13/2009), B) 2x (12/15/2009 to 12/21/2009), and C) 3x (01/12/2010 to 01/20/2009) during pilot study.



A



B

Figure 4-18. Volume of 0.1M CaCl added to precipitate A) OP, and B) NOM from DWSs from various starting concentrations. Initial OP, Jar 1 = 42mg P/L, Jar 2 = 21 mg P/L, Column = 49 mg P/L. Initial UV<sub>254</sub> Jar 1 = 1.9 cm<sup>-1</sup>, Jar 2 = 2.6 cm<sup>-1</sup>.

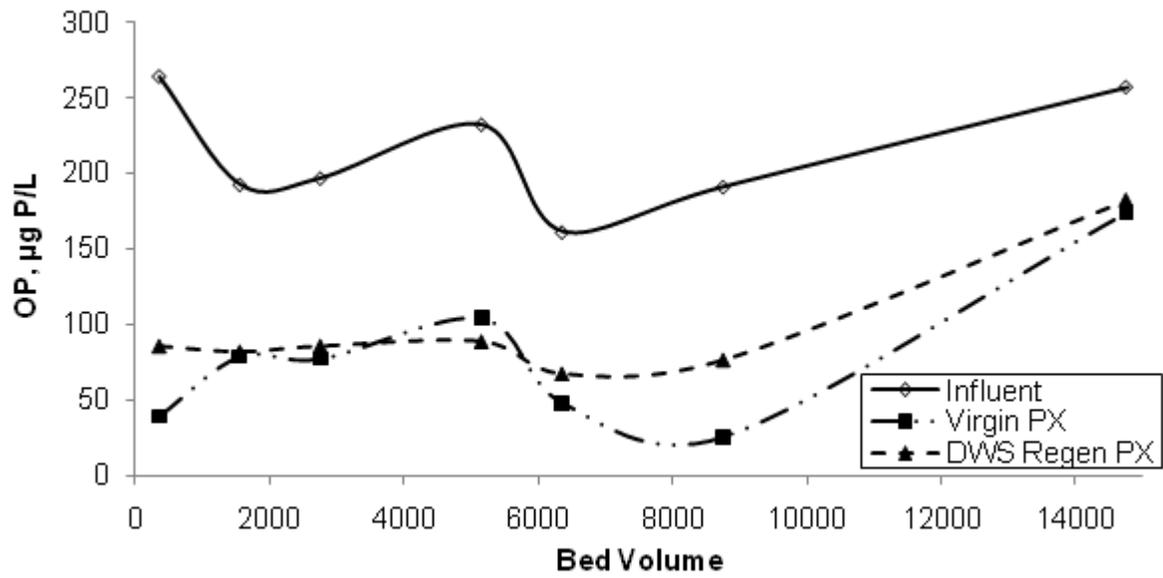


Figure 4-19. OP removal from mesocosm (influent) water by PX regenerated by cleaned DWS between 11/18/2009 and 11/30/2009. Resin used on FITS.

## CHAPTER 5 CONCLUSION

### **Evaluation of Materials**

#### **Low-Cost Materials**

The low-cost materials (LCMs) performed similar to the results depicted in past research. Materials such as recycled concrete (RC) and steel slag (SS) made great improvements in reducing orthophosphate (OP) levels but they significantly changed the pH and resulted in calcium precipitate. As expected, alum sludge (AS) and ferric sludge (FS) are good prospects for the removal of OP because under a fixed volume of water, they both performed well. However, under continuous flowing conditions, AS was the best LCM because of its affinity for OP and the fact that it is very porous due to the activated carbon content, which individually removes P. AS was fairly inert to other water quality characteristics like pH, if carefully prepared for usage. The major disadvantage of using an LCM is that it is infeasible to obtain grain sizes that provide a large enough surface area to be effective. Furthermore, its composition tended to vary in different batches in time and was more sensitive to water quality changes, as was observed in the case of AS. This in itself can introduce a random error in any predictive study that is endeavored. In relation to a past experiment done with fly ash (FA), this material had provided 99% P removal (Ugurlu and Salman, 1998), however the batch obtained for this project greatly contaminated the water. In summary, LCMs are cheap and their beneficial reuse should be a priority. Therefore, if a good batch is received and tested, it can be mixed into a treatment process if it encompasses an effective grain size because it is difficult to prepare in large quantities.

## **Commercially Available Resins**

Commercially available ion exchange (IEX) resins performed in a consistent manner and can engender the possibility of a predictable treatment system. PhosX (PX) resin was proven to be a robust material at removing OP from the surface water, despite competing anions. It had consistently achieved over 60 percent removal of OP when applied to the Floating Island Treatment System (FITS). MIEX (MX) is a great material for treating fixed volumes of water as it immediately exchanges its surface area sites for OP and natural organic matter (NOM) ions in the water. In contrast, this proves to be a disadvantage because when it is applied to a continuously flowing treatment system, it becomes exhausted early and is hence, useless in treatment of continuously flowing water.

## **Pilot Application**

Fluidized beds were built to simulate the small-scale column studies. Their inclusions in the treatment process of the FITS have proven to be greatly beneficial. PX and AS passed the screening process, and were deemed the best options of P selective materials, based on OP threshold and effects on other water quality. However, AS did not perform as well as it did in the bench-scale experiments mainly, because of the two major disadvantages of LCMs, as described above. PX resin treated the surface waters effectively and consistently. However, the presence of algae blooms increases the pH and can adversely affect the adsorption process of PX. As compared to the column studies, the results were very similar because real surface water was used in the screening process. Also, the BV/min were kept constant which proved to be a major controlling factor for replicating the performance observed in bench-scale column

studies. Overall, the bench-scale column experiments were successfully scaled up and the concept applied to the pilot study closely resembled the bench-scale experiments.

### **Sustainability of Process**

In addition to the fact that the FITS is solar powered, and safe for the environment, the PX resin can also be successfully regenerated multiple times and performs just as well as a fresh batch. This is an advantage, with inclusion of great performance, which can counteract its disadvantage of being costly. However, with regeneration comes a dirty brine solution, also referred to as dirty wash solution (DWS), contaminated with the P and other constituents that were removed in the treatment process. The P in the solution can be precipitated with calcium, which can then be separated from the solution by filtration and reused in another industry for fertilizer. Afterward, this cleaned solution can be reused to wash another batch of exhausted PX. This PX regenerated with the reused DWS performs well in comparison to fresh PX. Upon final disposal of the DWS, the environmental hazards must be considered. The DWS contains not only P but has a high pH, concentrated NOM, and possibly other contaminants. Firstly, P will be precipitated and in this instance, to further treat the DWS, NOM can be completely removed by neutralizing the solution after the precipitate is removed and then possibly treating it with MX. This clean, neutral solution can then be tested for other hazardous contaminants and then disposed of. MX from previous jar testing results and past research presented itself as an ideal material for NOM removal in a fixed volume of water (Banerjee, 2010; Boyer and Singer, 2008). Overall, the design of the treatment process and selection of materials were successful and proved to be sustainable and beneficial to the environment.

## Recommendations for Further Research

Based on the results of this project it was found that further research must be done to explore and exploit the possibilities that it can be of benefit. Recommendations for future research are outlined below:

- The fact that OP is the main cause of eutrophication indicates that it must be targeted. Therefore, the oxidation of organic P to convert it to OP may be useful for complete remediation. Processes such as solar irradiation (Frost and Xenopoulos, 2002) and a chemical-UV combination oxidation will be highly beneficial (Ridal and Moore, 1990).
- The concept of the FITS is successful but can be optimized to work more effectively. Applying an oxidation process before the fluidized beds, and investigating into different contact times with materials or flow rates (BV/min) are good options. Contact times will help to determine whether there is a relationship between the BV/min and either removal percentage, or duration of treatment, or both.
- Number of times commercially available P-selective resins can be regenerated and reused.
- A method to completely clean the DWS before disposal should be developed.
- A model based on all dissolved constituents present and a material's affinity for them can be developed. This could be used to accurately predict the performance of a treatment system and capacity of a material selected for targeted contaminants. The relationship between NOM and P during treatment may prove to be useful here.
- This study opens a new perspective on water treatment. Investigations into applying this process for pre-treating surface water before entering a drinking water facility may prove to be useful; for example, to remove arsenic from water (Moller and Sylvester, 2009). In Florida, most of the drinking water supply comes from ground water, which is becoming depleted and plans to withdraw water from surface water bodies (WSTB et al., 2009) are currently being considered by municipalities. Conversion from a ground water to a surface water facility or building new facilities may be costly. Therefore, the pre-treatment of surface water before entering treatment facilities, such as previously designed ground water plants, may be feasible.

APPENDIX A  
LOW COST MATERIAL PROPERTIES

Table A-1. Metal Composition (mg/kg) of Low-Cost Materials

	Ag	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe
<b>Material</b>												
<b>AVG FS</b>	0.4	2470.7	18.4	5.1	87.0	0.0	26013.3	6.5	18.6	9.0	8.4	148529.9
<b>AVG SS</b>	0.4	13869.0	0.1	31.1	58.7	0.0	99906.3	4.3	3.1	637.8	27.7	123475.8
<b>AVG AS</b>	0	93468.9	121.9	20.8	17.6	0.0	2468.1	0.0	0.0	80.2	276.1	2921.9
<b>AVG IS</b>	0	56868.8	1.4	75.7	322.4	6.5	177231.3	0.0	3.3	22.2	4.2	2207.9
<b>AVG RC</b>	0	4326.9	5.5	24.3	31.6	0.4	139020.4	0.2	1.9	14.3	15.0	3923.3
<b>AVG LS</b>	0	722.3	2.7	14.0	1.6	0.0	154883.9	0.0	0.0	10.0	5.3	880.2
<b>STDREF 2709<sup>a</sup></b>	0.6	24159.7	13.8	32.9	342.2	0.4	17066.0	0.9	11.0	71.1	29.3	28108.1

	K	Mg	Mn	Mo	Na	Ni	Pb	Sb	Sn	Sr	V	Zn
<b>Material</b>												
<b>AVG FS</b>	292.3	863.2	242.7	109.8	0.0	13.3	12.0	7.6	4.5	92.4	479.1	626.1
<b>AVG SS</b>	576.2	26563.2	6722.9	10.0	0.0	6.4	7.6	2.5	0.9	134.4	759.3	166.9
<b>AVG AS</b>	495.5	650.2	107.3	56.4	6467.7	9.2	7.7	0.0	22.0	315.3	29.0	106.6
<b>AVG IS</b>	3365.1	21396.2	1790.5	0.0	1706.2	1.4	0.6	0.0	0.0	281.6	24.8	39.2
<b>AVG RC</b>	478.2	16541.8	64.7	2.8	2005.1	7.2	6.1	0.4	2.9	214.3	15.2	70.4
<b>AVG LS</b>	309.8	80445.0	45.7	1.1	2563.5	3.7	1.9	0.0	1.3	156.1	9.7	655.7
<b>STDREF 2709<sup>a</sup></b>	4162.6	12425.3	424.4	0.0	783.1	65.3	13.0	0.6	0.0	91.6	63.9	1026.8

<sup>a</sup> All elements in STD REF 2709 were within NIST 2002 specified ranges (NIST, 2002; USEPA, 1996).

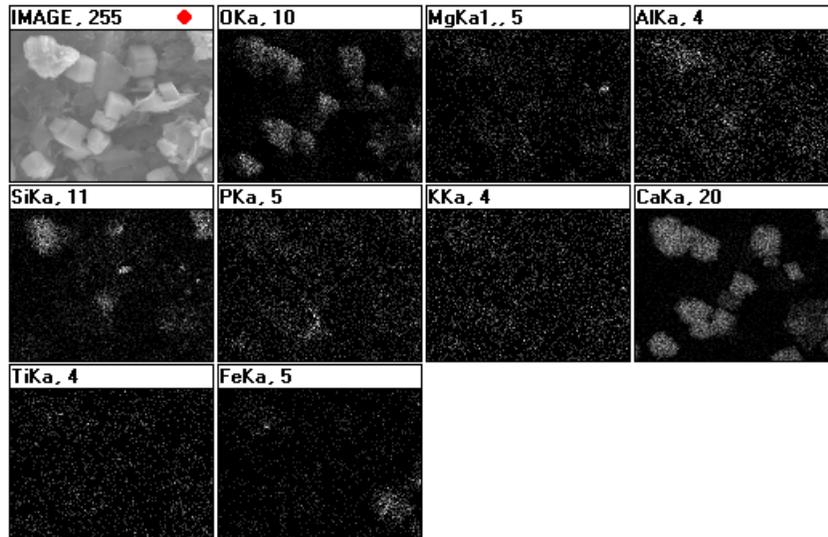


Figure A-1. Elemental spectrum and dot map of Steel Slag done by scanning electron microscopy (SEM) and energy-dispersive x-ray fluorescence elemental microanalysis. This helped to identify calcium silicate as a dominant mineral.

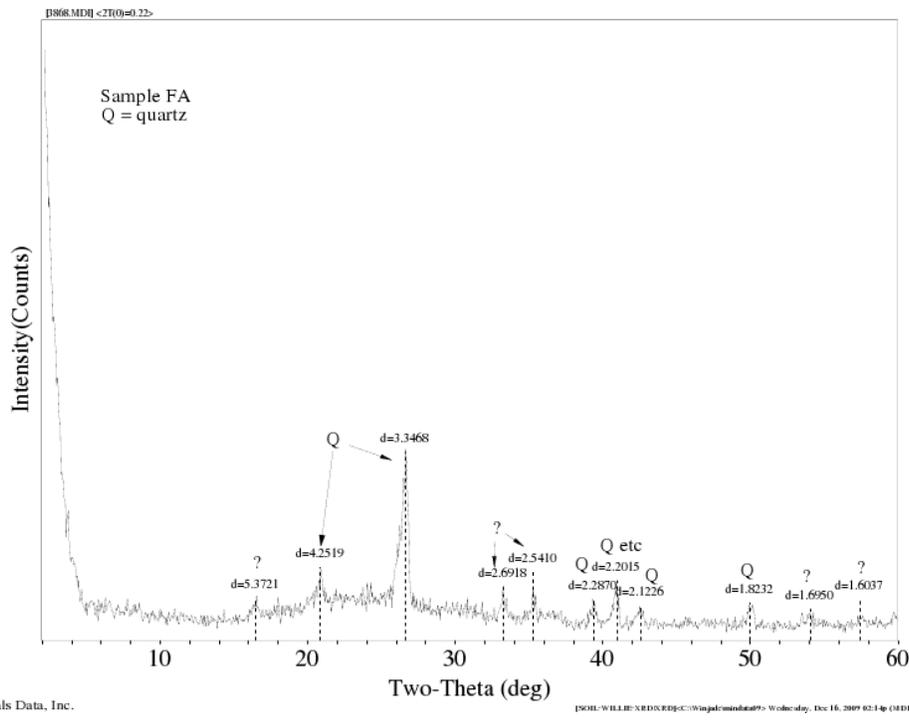
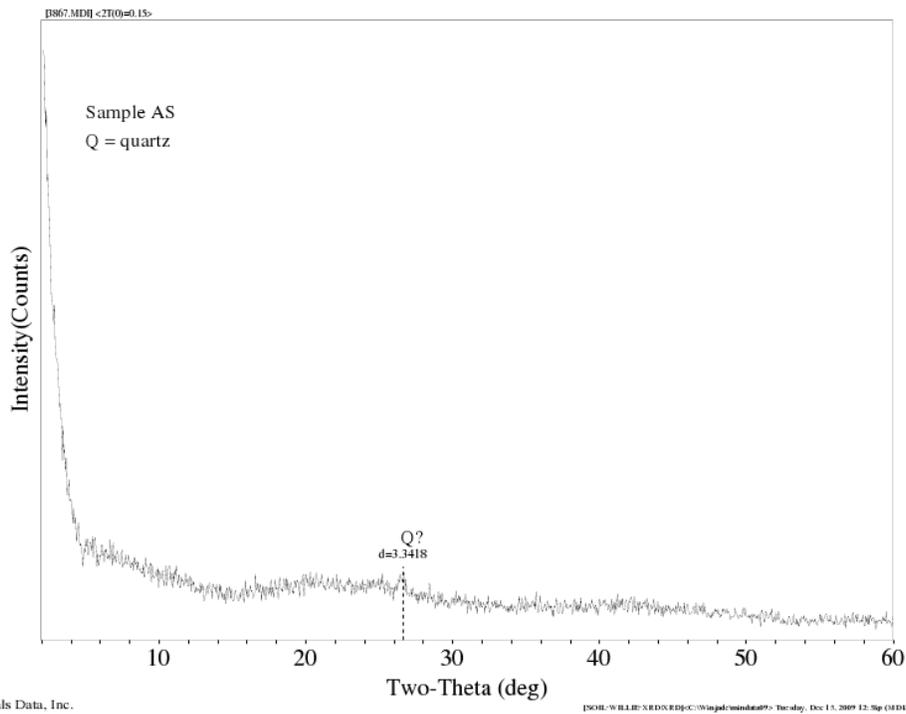
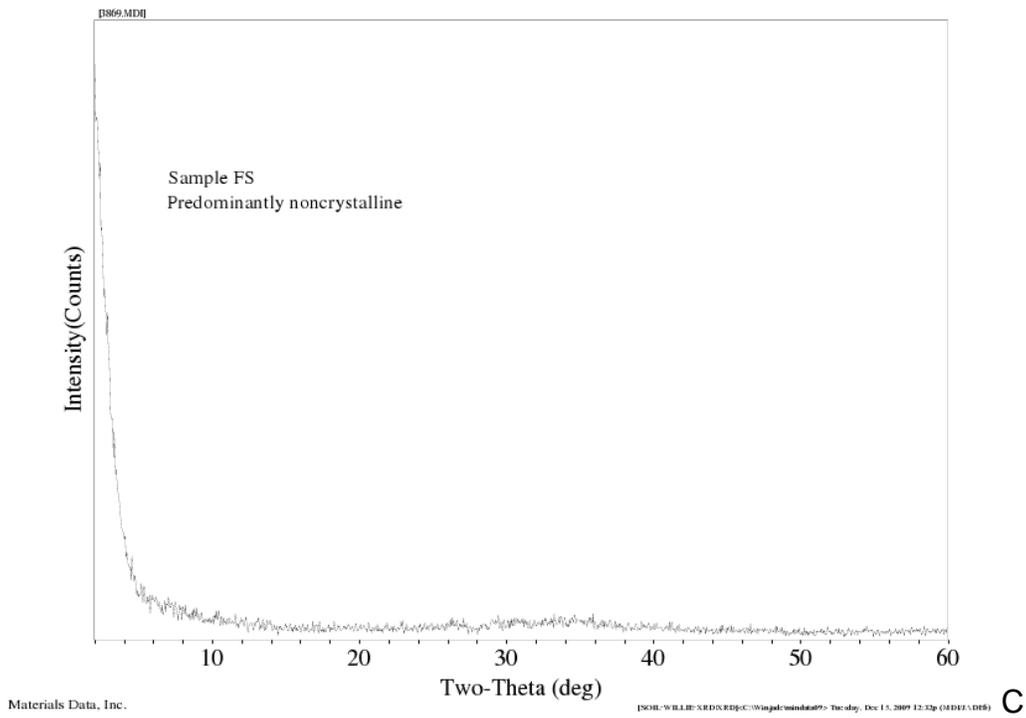
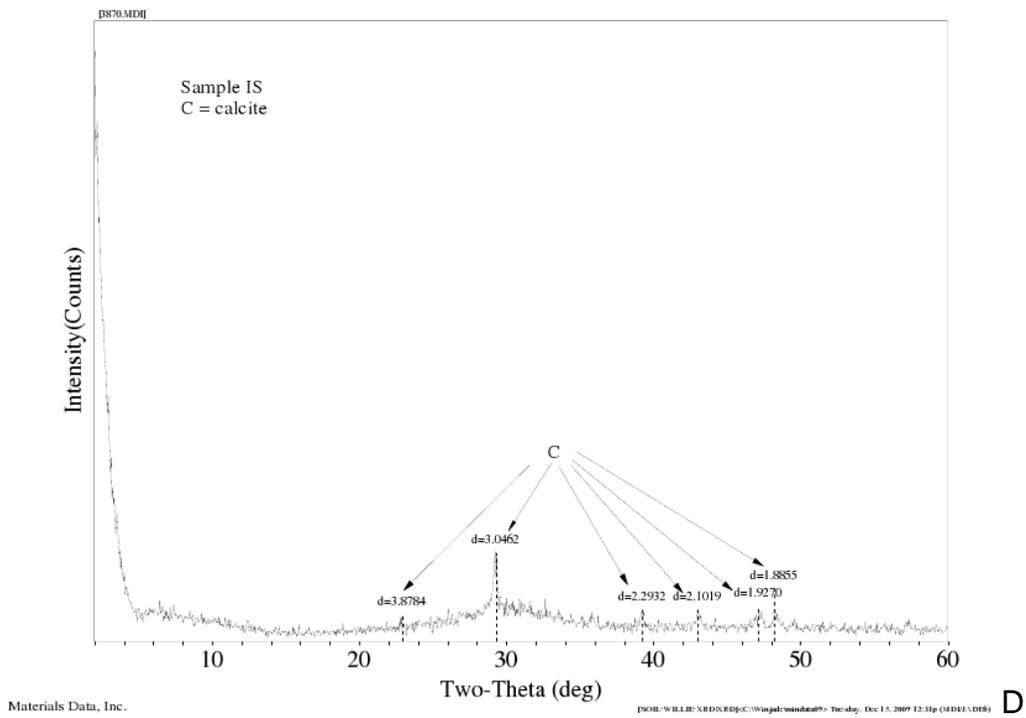


Figure A-2. X-ray diffraction peak graphs of A) alum sludge, B) fly ash, C) ferric sludge, D) iron slag, E) limestone, F) recycled concrete, and G) steel slag showing mineral compositions

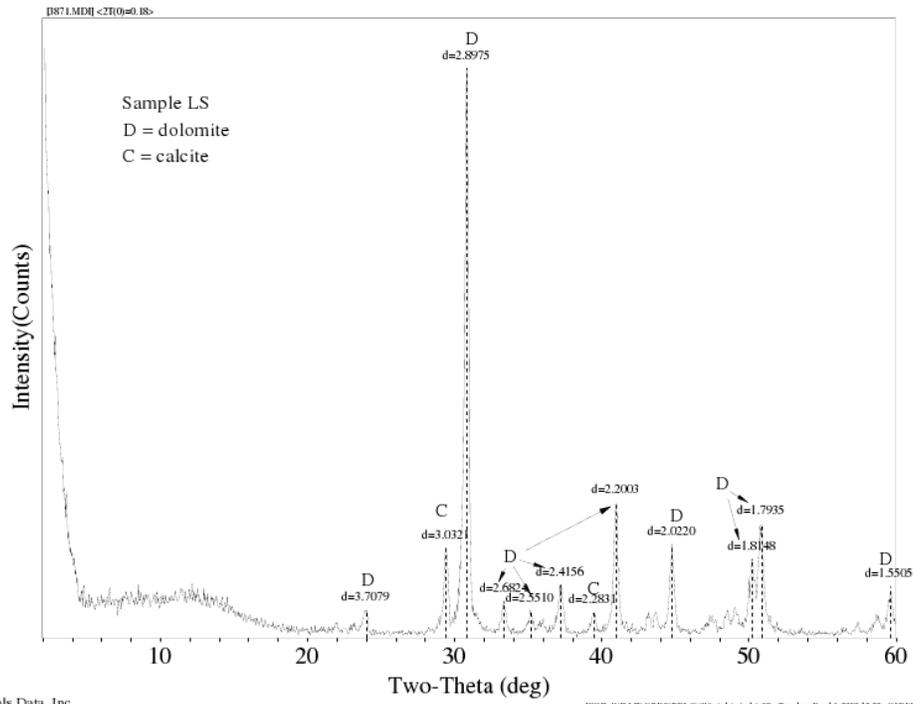


C

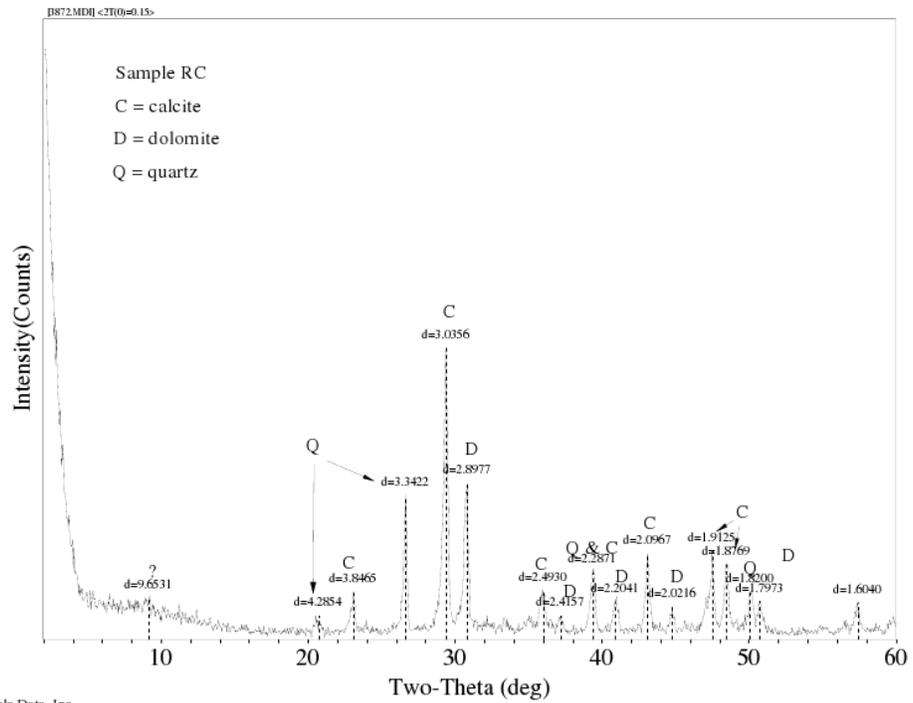


D

Figure C-2. Continued.



E



F

Figure C-2. Continued.

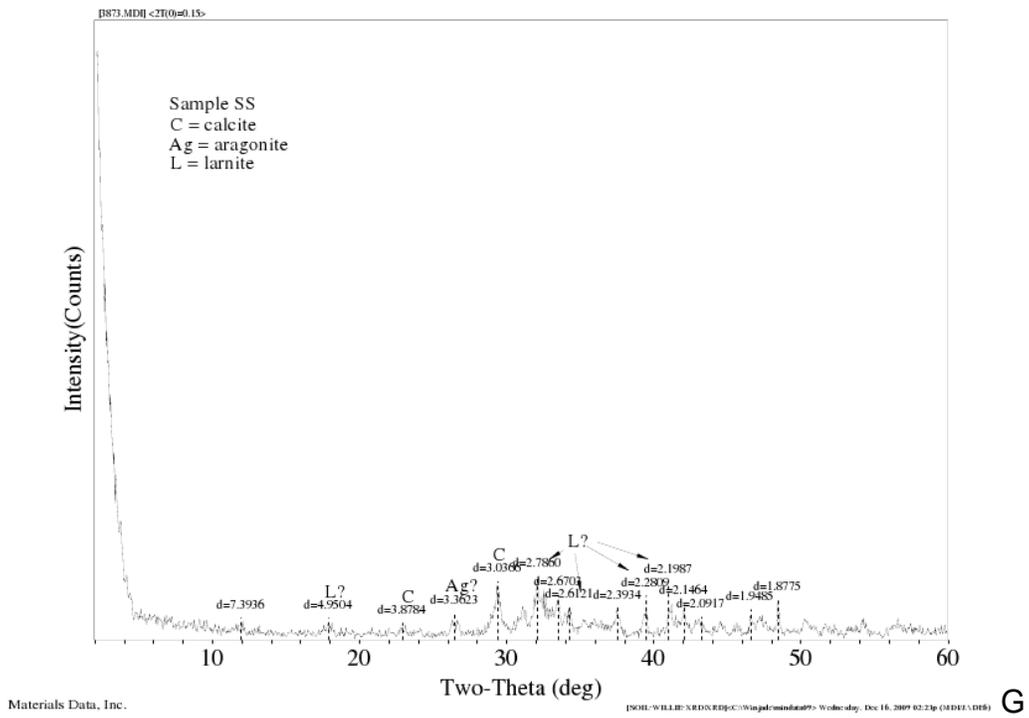
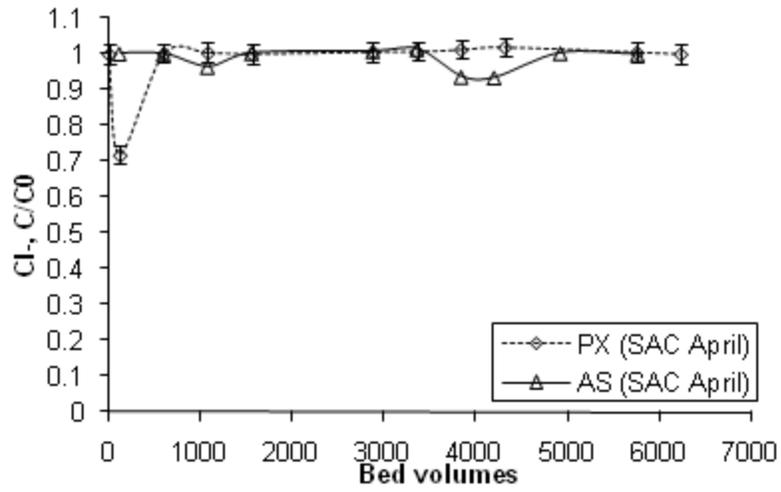
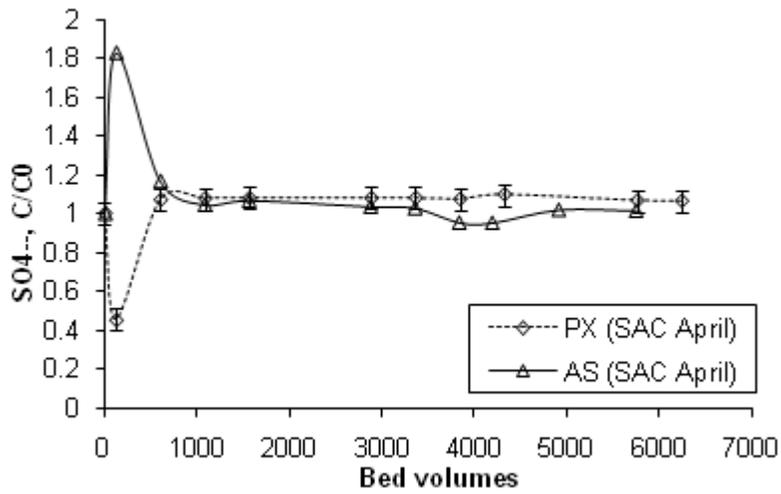


Figure C-2. Continued.

APPENDIX B  
COLUMN TESTING RESULTS



A



B

Figure B-1. Change in A) Chloride, and B) Sulfate during column testing by PhosX (PX) and Alum Sludge (AS). Initial Chloride = 193.84 mg/L, Sulfate = 29.7 mg/L.

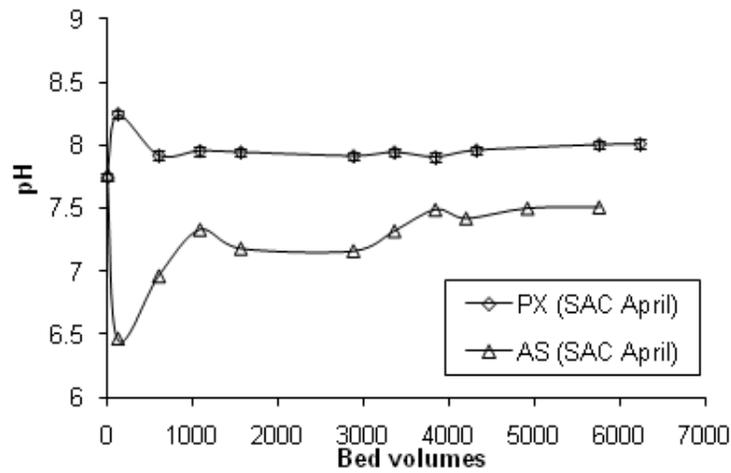


Figure B-2. Change in pH during column testing by PhosX (PX) and Alum Sludge (AS).

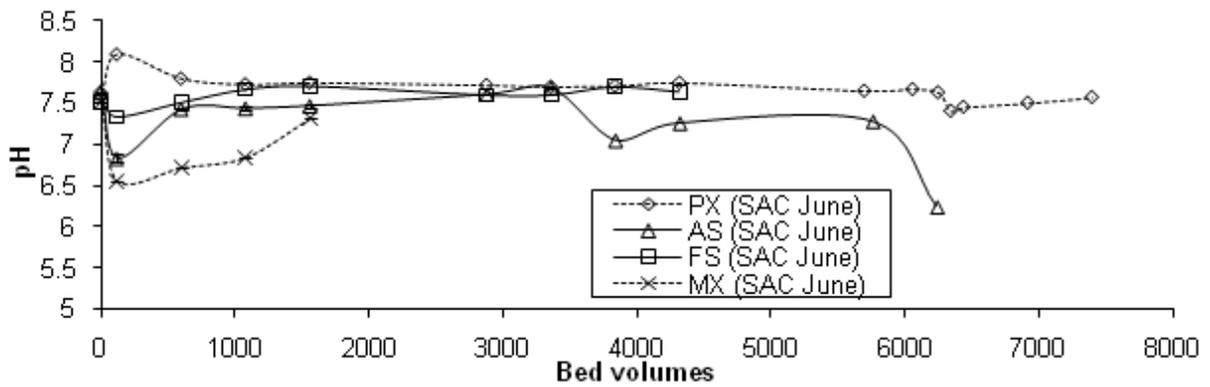


Figure B-3. Change in pH during column testing by PhosX (PX), MIEX (MX), Alum Sludge (AS), and Ferric Sludge (FS).

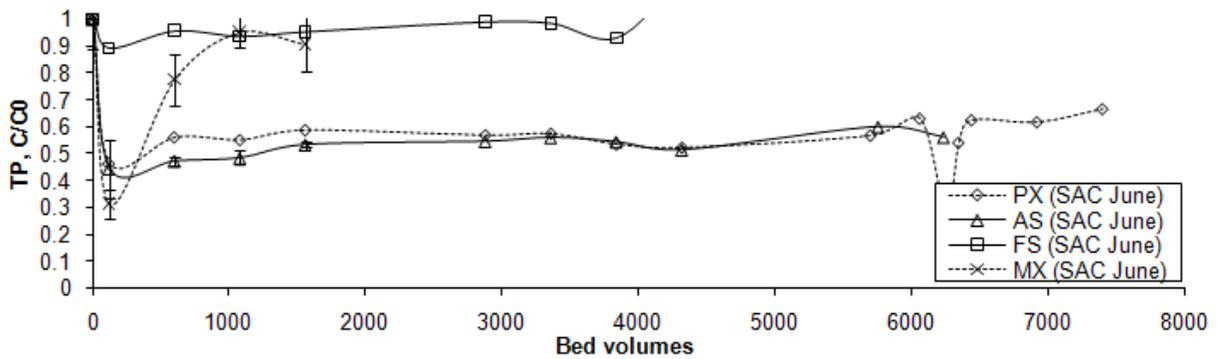


Figure B-4. Change in Total Phosphorus (TP) during column testing by PhosX (PX), MIEX (MX), Alum Sludge (AS), and Ferric Sludge (FS). Initial TP = 125.99 ug P/L to 152.87  $\mu\text{g}$  P/L.

APPENDIX C  
FLOATING ISLAND TREATMENT SYSTEM RESULTS

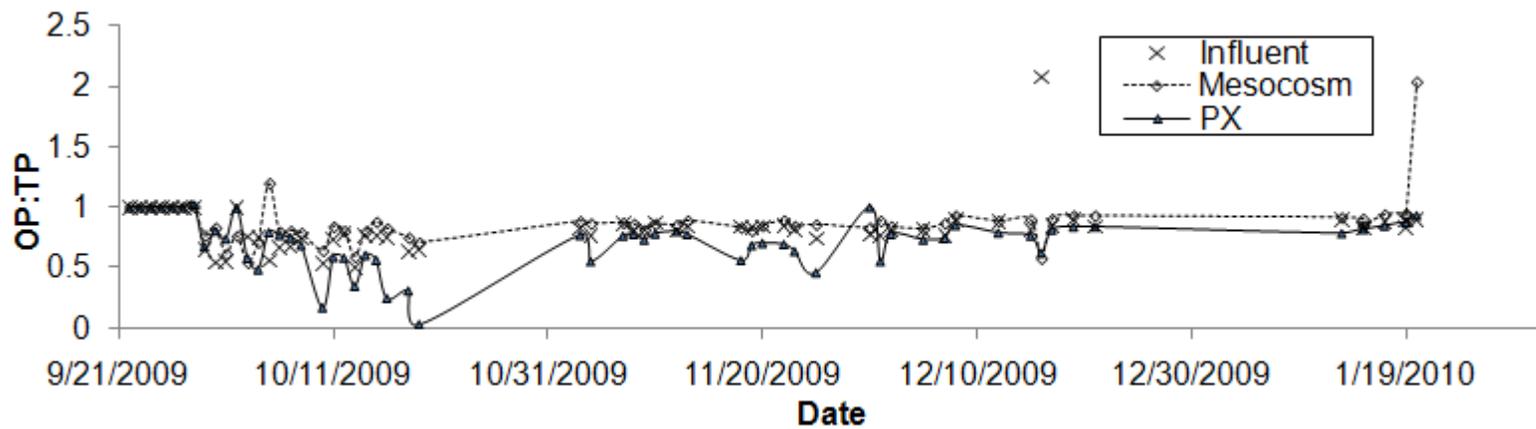


Figure C-1. Phosphorus speciation throughout operation of Floating Island Treatment System showing treatment by mesocosm and PhosX packed fluidized bed.

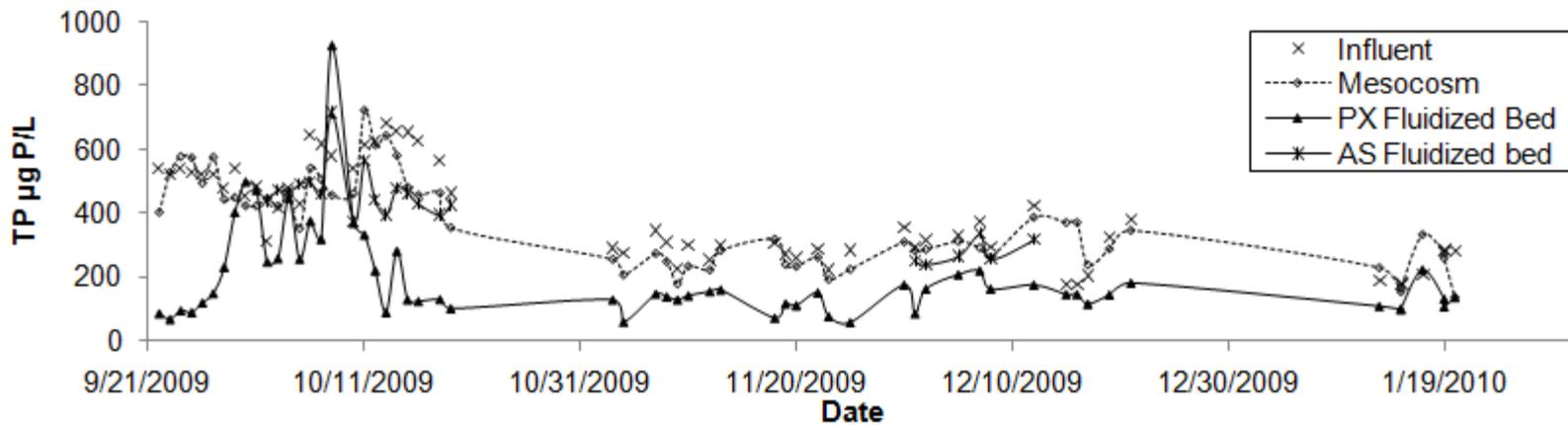


Figure C-2. Total Phosphorus Removal by Floating Island Treatment System through Mesocosm and Fluidized beds.

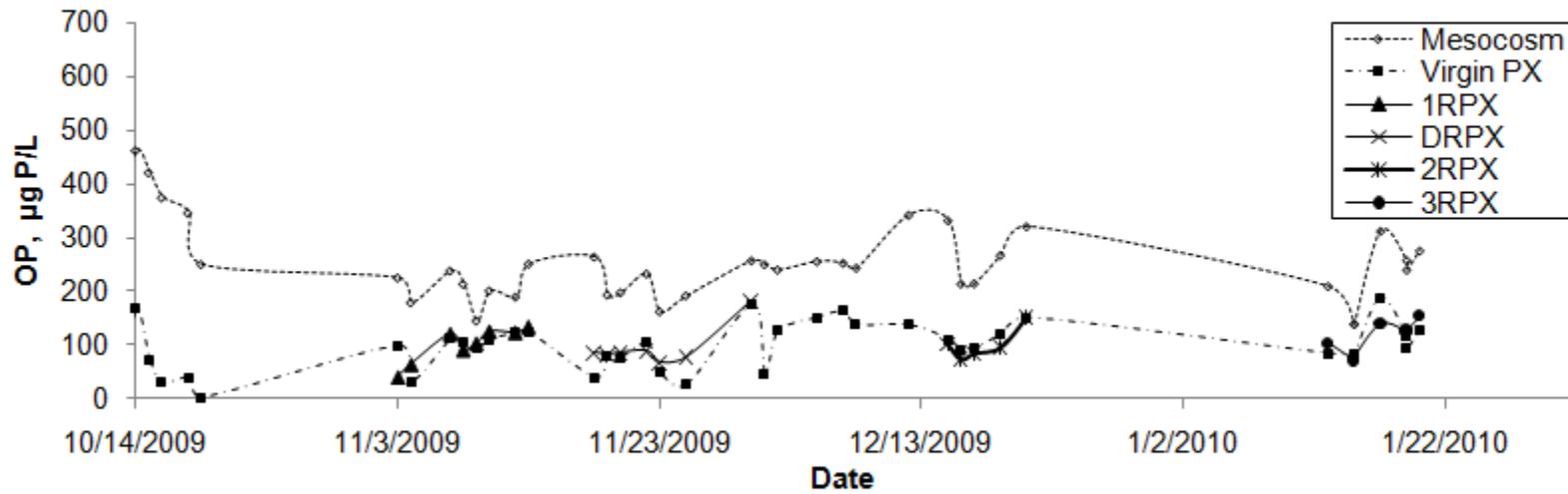


Figure C-3. Orthophosphate Removal by Floating Island Treatment System through virgin PhosX and Regenerated PhosX Fluidized beds.

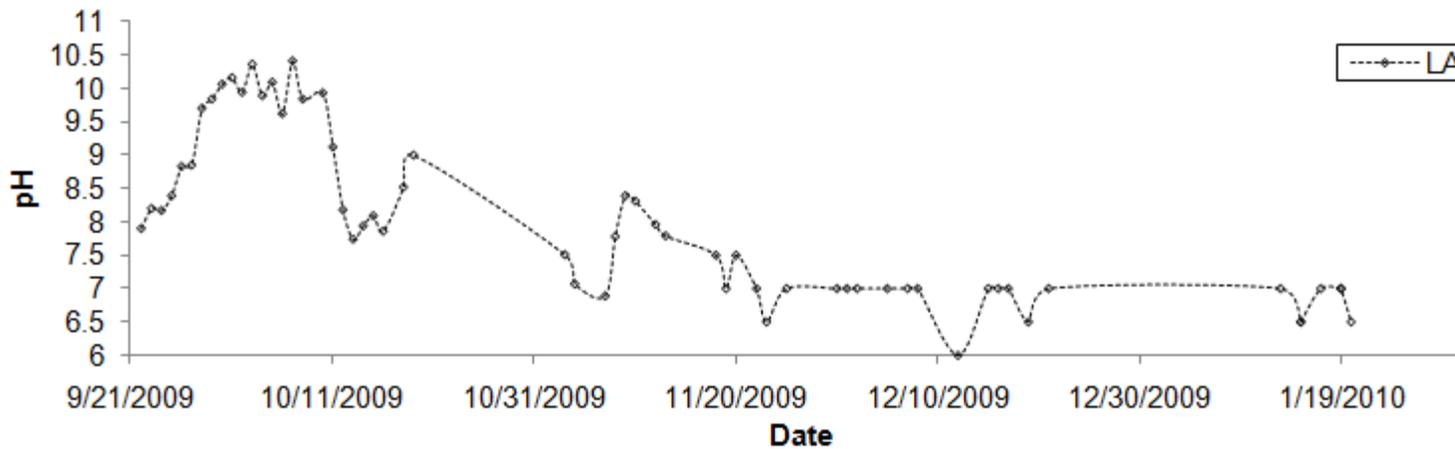


Figure C-4. Change in pH in Lake Alice throughout operation of the Floating Island Treatment System.

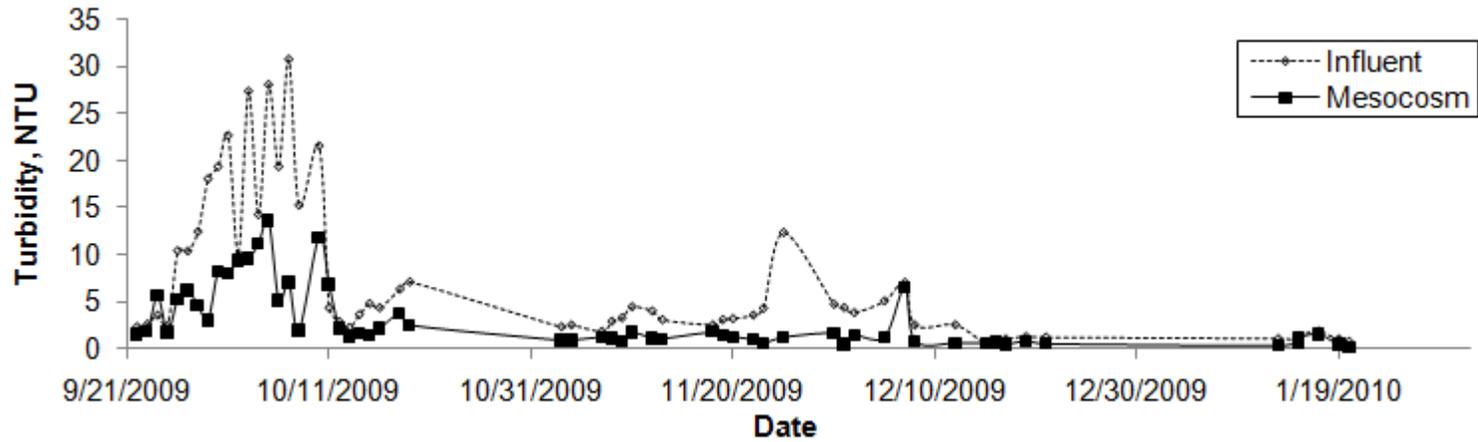


Figure C-5. Change in turbidity in Lake Alice and removal by mesocosm throughout operation of the Floating Island Treatment System.

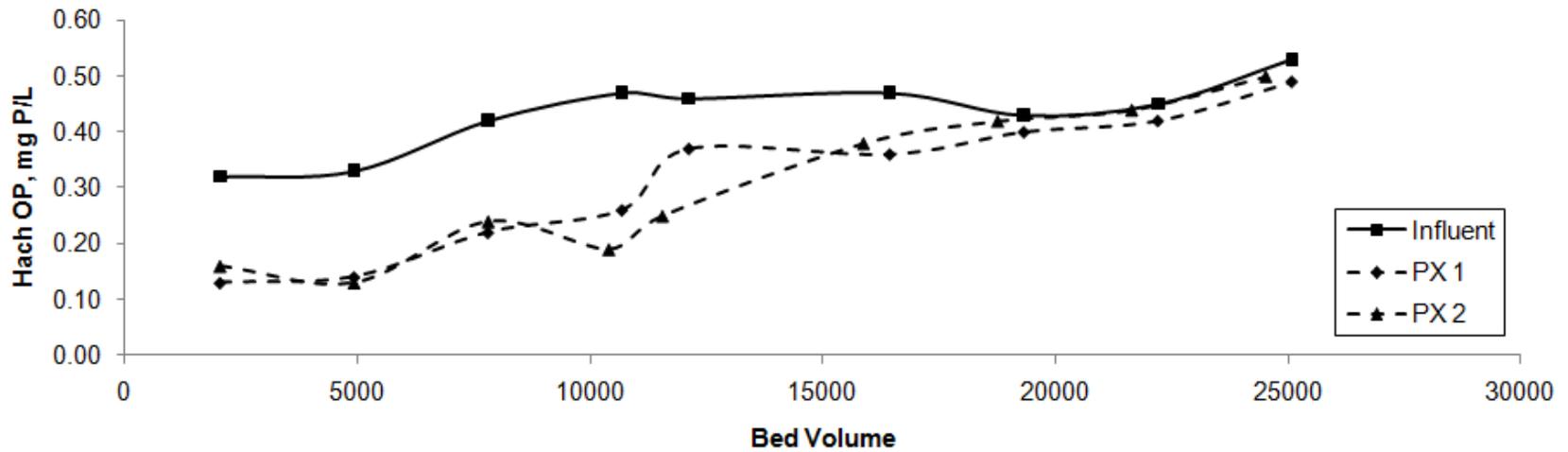


Figure C-6. OP removal by fluidized beds from mesocosm (influent) water comparing PhosX (PX) dosed at 0.25 gals flowing at 0.5 gpm for 12 hrs per day until total exhaustion of PX between 03/23/2010 to 04/10/2010 during pilot study.

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## BIOGRAPHICAL SKETCH

Amar Prem Persaud was born in 1984 in London, England. He attended elementary school in New Jersey, USA and then The Bishops' High School in Guyana, South America. He attained a Diploma in Civil Engineering from the University of Guyana in 2003 and later graduated with a B.S. in Civil Engineering at Florida Atlantic University in 2006 at which time was awarded Outstanding Undergraduate Leadership. He then ventured off into broadening his horizons by working in the engineering consulting industry for two years. This started in Florida where he did structural and geotechnical inspections with GFA International until the end of 2006. The opportunity then arose to gain project management experience in Guyana with Vikab Engineering Consultants, which he could not help but take advantage of. The duties for this job became relaxed after the third quarter of 2007, so with his ambition to gain progressive experience he relocated to California to work with Leighton and Associates conducting underground explorations, slope stability analyses and other geotechnical engineering work specific to the Californian terrain. The world's practices were leaning toward a sustainable environment; therefore, in 2008 he relocated to Florida and committed himself to attaining a M.E. in environmental engineering with a focus on the hydrological sciences, ecology, and policy at the University of Florida. Finances became tight as savings dwindled when at that moment he met his new advisor, Dr. Treavor Boyer, in short pants at the Einstein Bros. Bagel on the UF campus and a light at the end of the tunnel became visible. With both of them starting a new career, the initial research goals to manage the physical-chemical experimentation phase and help develop a sustainable phosphorus removal system for surface waters were presented by the St. John's River Water Management District. "With Amar's experience, he is the man for the

job," said Dr. Boyer. This research later expanded into a Master's Thesis focusing on phosphorus removal from organic rich surface water bodies. His main career goal is to get involved in construction and environmental planning by adopting a synergistic approach to the development of civilization with the security of natural resources.