USE OF NANO-ENHANCED REACTIVE IRON MEDIA FOR ONSITE WASTEWATER PHOSPHORUS REMOVAL

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ABSTRACT

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Phosphorus is an element which exists naturally in the environment and is required for plant and animal life. Excess of phosphorus can cause significant environmental and health problems, namely eutrophication and the growth of toxic algal blooms in lakes and streams. Onsite wastewater treatment systems are a significant source of environmental phosphorus loading. This laboratory column study explored the use of a nano-enhanced reactive iron media for use in removing phosphorus in onsite wastewater treatment. Actual secondary treated wastewater was used. The capacity was determined to be between 29 and 47 mg P/g, considerably higher than other media that was examined using actual wastewater in a continuously operated reactor. The shape of the effluent removal curve indicates that the likely mechanism of removal is adsorption controlled by the equilibrium complexation of phosphorus with the nano-iron crystals attached the surface of the media. This research could not demonstrate statistically whether empty bed contact time or hydraulic loading were the most important parameters in determining the removal efficiency. As well, it was determined that a wastewater that supports the establishment of a biofilm produces spikes of effluent total phosphorus.

To Dora

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Any words that I write will not be sufficient to express the gratitude that I feel towards those who have encouraged me, believed in me, inspired me, and stayed by my side. This has not always been easy.

Thank you to my parents who instilled in me and my brothers a strong sense of the importance of doing something you can be proud of, and the discipline to do it. Thank you, Mom, for believing I can do anything. Thank you, Dad, for your steadfast support throughout this transformation process to engineer. Your protective arms are always there. Thank you my brothers, Cameron and Mike. You keep me sane with your humor, brains, and love. You are the best brothers in the world. No doubt.

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TABLE OF CONTENTS

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

LIST OF TABLES

.

LIST OF FIGURES

INTRODUCTION

Eutrophication is a process in which water bodies such as lakes, estuaries or slow-moving streams receive excess nutrients, potentially severely impacting the natural ecosystem, human health, recreational potential, and property values. Phosphorus is the limiting nutrient that controls eutrophication in temperate climates. An estimated 40% of US rivers and streams have excessive levels of phosphorus [1]. Sources include the agricultural application of manure and synthetic fertilizers (72% combined), wastewater treatment plant effluent (5%), and onsite wastewater treatment systems (4-25%) [2]. While excess phosphorus exists in aquatic environments worldwide, it is lacking in many soils where it is needed for agriculture. At the current rate of usage, reserves of phosphorus are predicted to last until about 2045 [3]. Though the US and China are the largest producers of mined phosphorus, the two countries are increasingly reliant on imported phosphates for agriculture, with Morocco being the top exporter [4].

This research emphasized removing phosphorus from onsite wastewater. Conventional onsite wastewater treatment systems use septic tanks followed by wastewater dispersion into the soil through a drain field. Removal of phosphorus in this setting is challenging because conventional methods such as biological luxury uptake and chemical precipitation are expensive, requiring elaborate equipment and frequent monitoring.

Onsite use of filter media to sorb phosphorus is advantageous in that the required equipment and operation is minimal. However, research on the availability and use of an economical, predictable, engineered filter media with a high phosphorus sorbing capacity that can then be recovered for beneficial reuse is limited.

The present study researched the use of a nano-iron coated material economically manufactured by MetaMateria Technologies, LLC (Columbus Ohio), for use as a filter media to sorb phosphorus from onsite produced wastewater. Nano-enhancement is a highly engineered process, one effect of which is that the surface area available to sorb phosphorus is very large. This potentially offers considerable advantage in the capacity of the media for solute sorption (i.e. phosphorus). Preliminary studies of earlier generations of similar media produced by MetaMateria showed capacities of approximately 11 mg P/g [5]. The specific goals of this study were to determine the phosphorus capacity of a more advanced media produced by MetaMateria, examine the mechanism of sorption, and provide design information for use of the media in an onsite wastewater system. Unique to this study was the use of actual wastewater, rather than synthetic, which allowed for realistic testing including accounting for the use of sorption sites by wastewater constituents other than phosphorus.

CHAPTER 1
LITERATURE REVIEW

The first section of the Literature Review examines phosphorus in the natural environment, its forms, and how it cycles. A discussion on eutrophication then follows. The next section reviews phosphorus management including lake remediation and at the municipal wastewater treatment plant. Further discussion describes the technology of decentralized wastewater treatment and phosphorus removal in that context. Next is a section discussing the use of phosphorus sorbing media for use for onsite wastewater treatment, including nano-scale sorbents.

1.1 Phosphorus in the Environment

Phosphorus is a mineral necessary for life. One of its main roles is in the transfer of energy within living organisms but it is also a component of genetic material and cell membranes. Phosphorus is highly reactive and generally exists in nature as part of the phosphate molecule (PO_4), with elemental phosphorus being extremely rare [6]. It does not exist in nature in gaseous form. Phosphorus exists in minerals, soils, living organisms, and water. Natural inorganic deposits occur primarily in the mineral apatite. In soil, phosphate exists mainly adsorbed to soil particles or incorporated into organic matter. Most phosphorus compounds exist in solid form [6].

Soil phosphorus can be thought of as existing in one of three pools: solution, active, and fixed. The solution pool is the smallest, and consists primarily of orthophosphate and can contain some dissolved organic phosphorus as well. This is the only pool from which plants can use phosphorus (in the form of orthophosphate) and the only pool which has measurable mobility. The solution pool is continuously replenished by the active pool, which is the solid phase that is relatively easily released into solution. The active pool consists of inorganic phosphate sorbed to active sights of soil particles in the form of phosphate-calcium and phosphate-aluminum compounds and organic phosphorus that is easily mineralized. The amount of phosphate sorbed by soil exists in equilibrium with the amount in solution. In this way, soil particles act as a source or a sink for phosphate to the surrounding water, depending on the conditions [7].

The fixed pool consists of inorganic phosphate compounds that are very insoluble and organic compounds that are resistant to mineralization by soil microorganisms. This pool generally has little impact on living organisms, with conversion from fixed to active pools being very slow [7].

Water quality is affected by the ability of a soil to hold phosphate in the active pool. A soil cannot hold increasing amounts of phosphate in the solid phase without also increasing phosphate in the solution phase [7]. This is how loading soils with excess phosphate results in increased phosphate to nearby water bodies.

Phosphorus in marine and freshwater systems exists in organic form or inorganic form, and both forms exist in soluble or insoluble phases. The insoluble phase generally consists of living or dead plankton, precipitates, adsorbed to particulates, and macromolecular colloidal phosphorus. The soluble phase includes the inorganic forms of ortho and polyphosphate (primarily ortho), and organic phosphorus excreted by organisms.

The organic form consists of phosphate associated with a carbon particle, as is the case with plant and animal tissue. The inorganic forms are orthophosphate and polyphosphate. Polyphosphate, also called condensed phosphate, is a more complex molecule with two or more phosphorus atoms. It is a strong complexing agent for select metal ions and is used primarily in detergents and in the treatment of boiler waters. In water, polyphosphates are unstable and undergo hydrolysis to revert back to orthophosphate [8].

1.1.1 Phosphorus Cycle in an Aquatic System

Phosphorus continuously changes form as it cycles through the aquatic environment. Plants use inorganic phosphorus and animals use both inorganic and organic phosphorus. In an aquatic system dissolved inorganic phosphorus is ingested by phytoplankton and is altered to organic phosphorus. The phytoplankton is then ingested by detrivores or zooplankton. Over half of this phosphorus is excreted as inorganic phosphorus, which is rapidly consumed again by phytoplankton. The organic fraction of phosphorus excreted by animals, and which is part of the composition of dead plants and animals, sinks to the bottom where bacterial decomposition converts it back to inorganic phosphorus. A portion of this inorganic phosphorus returns to the water column when the upper most layer of the bottom sediments is stirred up by benthic invertebrates, human activity, water chemistry changes, and/or water currents [6], [9].

In a stream system, the current tends to carry the phosphorus cycle downstream. The phosphorus is stationary when it is taken up by plants or bound to particles that settle into lake and reservoir sediment (which serve as phosphorus sinks). Continuous accumulation of sediment can leave some phosphorus too deep within the substrate to be introduced into the water column, removing it permanently from biocirculation [6], [9].

An example of a water chemistry change is what occurs in the case of the reducing conditions of a hypolimnion, often experienced during summer months, which can cause the release of phosphate from the benthos [10]. This large release of phosphate can stimulate blooms of phytoplankton (see Figure 1). Consequently, a reduction of phosphorus loading may not be effective in preventing algal blooms for a number of years [6].

The Phosphorus Cycle in an Aquatic Environment

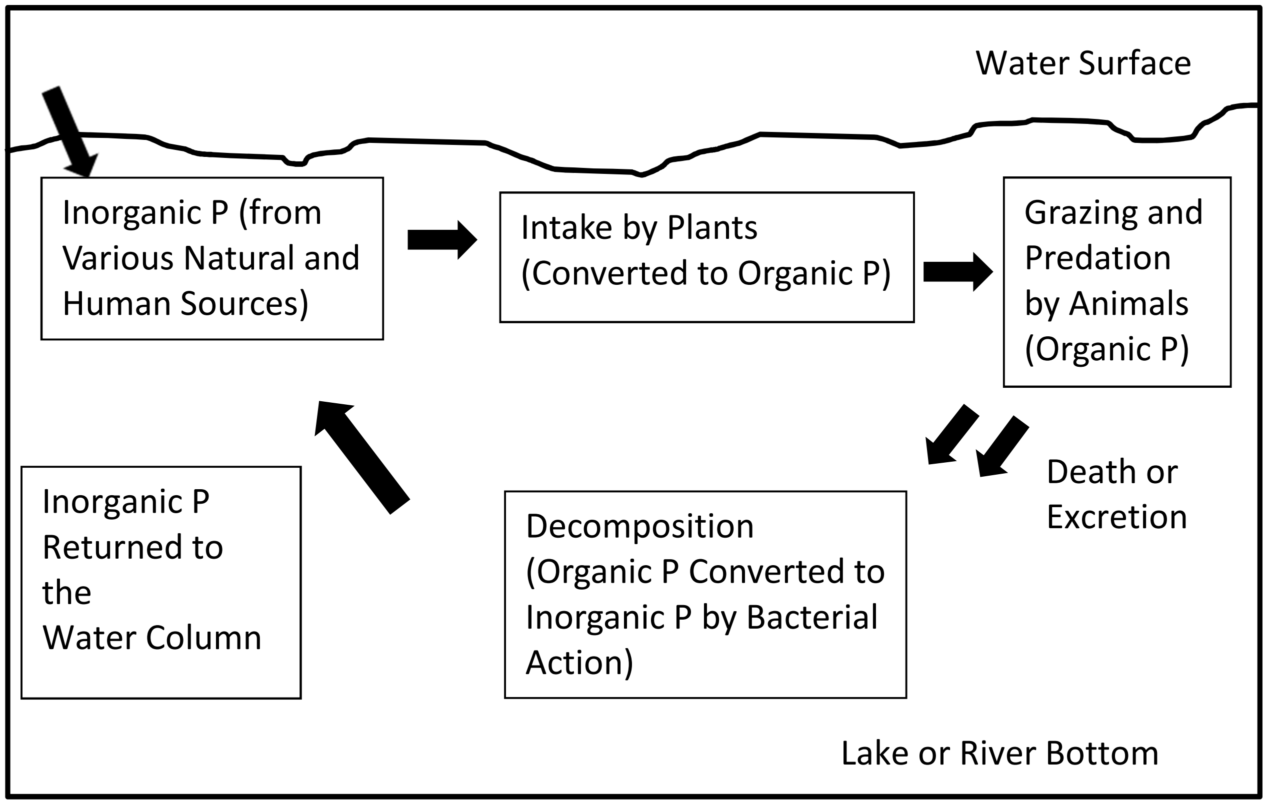


Figure 1. Phosphorus Changes Forms as It Cycles Through the Aquatic Environment [9].

Orthophosphate is the most common form of phosphate found in water, and the only one used by plants. Because orthophosphates are triprotic, there are multiple species ($H_2PO_4^-$, HPO_4^{-2}, and PO_4^{-3}) that may be found in solution simultaneously at different ratios for any given pH [11]. In wastewater, HPO_4^{-2} is typically the most prevalent form [12].

1.1.2 Eutrophication

Eutrophication, also called hypertrophication, is the response to the excessive input of nutrients to an aquatic ecosystem. The initial impact is an increase in the growth of phytoplankton (microalgae, macroalgae, and cyanobacteria), called a “bloom”. The bloom begins a chain of events that can eventually lead to two major environmental problems: oxygen depletion and overgrowth of algae. Some algae produce toxins deadly to birds and animals.

Nitrogen and/or phosphorus are the nutrients which in excess stimulate eutrophication. Excess phosphorus is the most important cause of eutrophication in freshwater systems, where it is the limiting nutrient for plant growth. As phytoplankton grow, they assimilate other necessary nutrients for plant and animal growth (leaving less resources for other organisms). As phytoplankton die, sink to the bottom, and decompose, the nutrients which are contained in the organic matter are converted to inorganic matter by bacteria.

The decomposition process uses oxygen, and can eventually deprive the deeper waters of oxygen, killing fish and other organisms. In eutrophic conditions, there is more turbidity, thus sunlight is inhibited from reaching bottom dwelling organisms. The lack of sunlight leads to wide swings in dissolved oxygen content of the water, and to a precarious balance in the availability of oxygen to organisms that require it. Dissolved oxygen increases during the day when photosynthesizing plants produce oxygen and decreases at night when it is used by respiring algae and microorganisms that feed on the increasing mass of dead algae. If the oxygen level becomes too low, fish and other animal suffocate and die [13], [14], and [15]. In extreme cases, anaerobic conditions arise, promoting the growth of Clostridium botulinum, a deadly toxin producing bacterium [16].

Though eutrophication does occur in nature without human influence, there are strong correlations between land-based activities with associated increased nutrient loading and the presence of toxic algal blooms, as well as a combination of habitat disturbance and species displacement [17], [18], [19].

The International Lake Environment Committee (ILEC) in conjunction with the United Nations Environment Program performed a survey of 217 lakes worldwide, results of which indicated all lakes showed an increase in eutrophication over the past 50 years. Wastewater treatment in some industrialized countries did result in a decrease in nutrient inputs to 66 of the lakes studied, despite that most lakes are still more eutrophic than they were 50 years ago [20].

Harmful algal bloom incidents have increased in the US during the past 25 years to include almost every coastal state [21]. The Midwestern area of the US near the Great Lakes has recently experienced levels of algal blooms in inland lakes not seen in 30 years [22], with record numbers of closings of inland lakes for recreational use, and limitations on drinking water in certain areas [23].

1.2 Phosphorus Management

To manage phosphorus discharges that are impacting the environment it is necessary to physically remove it from the system. Unlike nitrogen, which can be denitrified to nitrogen gas and leave the system passively, phosphorus cannot be easily converted to a gas and passively exit the system [24]. The first subsection reviews lake management of phosphorus, followed by municipal wastewater treatment, then decentralized wastewater treatment.

1.2.1 Lake Management

Ideally, measures are taken to prevent excess phosphorus from entering a lake, however it occurs, and there are technologies for remediation.

Since the passage of the Great Lakes Legacy Act in 2002, about $288 million has been spent on the remediation of 10 water bodies identified as areas of concern in the area of the Great Lakes, with phosphorus a major contaminant [25].

In cases where there exists potential for large amounts of algal-available phosphorus to be released, the use of aeration devises and other remediation techniques may be involved such as: hypolimnetic aeration and hypolimnetic withdrawal, mixing (aeration), dilution, nutrient diversion, dredging, and nutrient inactivation. In *hypolimnetic aeration* for example, air (oxygen) is pumped into the hypolimnion layer such that oxygen levels remain adequate to prevent the release of phosphorus from the sediments, without causing the water layers to destratify. Habitat and food supply are increased as a result of the increased oxygen. However, aerators are expensive to operate and it may be difficult to keep the stratification from occurring. This technique is suitable for deep lakes with an oxygen-deficient hypolimnion [26].

The ILEC survey showed that of the eutrophied lakes and reservoirs where measures had been taken to reduce or remove nutrients without effect, the reason was largely due to large amounts of nutrients stored in sediments and being constantly released into the water. This shows that proper planning and management is needed to avoid future release of nutrients [20].

In general, remediation of a water body is a risky and expensive endeavor. Preventing the need for remediation is preferable from a health and economic perspective.

1.2.2 Municipal Wastewater Treatment

A municipal treatment plant offers numerous advantages for the treatment of wastewater. Professionals routinely monitor and check conditions within a closed system and a range of parameters can be optimized to reach ideal, stable conditions for complex removal techniques. These techniques include biological, precipitation, and ion exchange.

Biological phosphorus removal requires luxury uptake, which is achieved using an anaerobic/aerobic sequence in a biological reactor that allows for microorganisms to accumulate high levels of phosphorus. The phosphorus is removed with the excess biosolids. A disadvantage is that should biosolids accumulate for an extended period of time, phosphorus could be released back into the water [24].

In chemical precipitation and ion exchange, aluminum and iron salts, (and less commonly lime) are used to convert the phosphorus into insoluble compounds that then can be settled out. Though capital costs involved in biological phosphorus removal are generally higher than with chemical removal, the expense of treatment chemicals involved in chemical precipitation results in higher operation and maintenance costs. As well, the addition of treatment chemicals increases the volume of waste sludge, up to 50 percent if lime is used [27].

1.2.3 Onsite Wastewater Treatment

This subsection consists first of a description of onsite (also called decentralized) wastewater and then culminates with a review of phosphorus removal options.

1.2.3.1 Onsite Wastewater

In onsite wastewater treatment the water stays in the local watershed. Depending on the treatment system, operation costs vary from minimal to expensive. Generally the system is located close to the source of generation and the treatment is passive (i.e. soil dispersal) [28].

Onsite wastewater treatment approaches vary in their means of collection, treatment, and dispersal or reuse of wastewater. This type of system can be a part of the permanent infrastructure and managed as a stand-alone facility, or be integrated with centralized sewage systems. Onsite approaches are used in individual dwellings, industrial or institutional facilities, clusters of homes or businesses, and entire communities. Site-specific evaluation of topography, soil type, and proximity of water, is performed to determine the appropriate units to make up the most efficient and effective system for each location [28]. Descriptions of various onsite (decentralized) systems follow.

1.2.3.2 Septic Tank and Drain Field

The simplest type of onsite wastewater treatment unit is as a septic tank followed by a drain field. The septic tank allows for settling of heavier particles and flotation of fats, oils, and grease. A minimum amount of biodegradation of soluble material may also occur.

Septic tank effluent is distributed in a drain field and treated as it percolates through unsaturated soil beneath the trench. State regulation dictates the minimum depth of this unsaturated soil [29]. Biological, physical, and chemical mechanisms remove pollutants from the water.

The mechanism of phosphorus removal from septic tank effluent is primarily by sorption to soil. As mentioned in the previous section on Phosphorus in the

Environment, a soil cannot hold increasing amounts of phosphate in the solid phase without also increasing phosphate in the solution phase. The result can be the discharge of excess phosphorus in nearby water bodies.

In 2007 in the US an estimated 20% of all households used soil-based septic systems, with 50% of those located in rural areas, 47% in suburban areas, and 3% in central cities [30].

1.2.3.3 Advanced Treatment System

An advanced treatment system (ATS) is complex, designed to meet strict treatment goals and/or handle unusual site conditions, where an inexpensive septic tank/drain field system does not work. In some states, an ATS discharge to surface waters, in which case a National Pollutant Discharge Elimination System (NPDES) permit is required [28].

An example of an ATS is located in Louden County, VA. An integrated approach is used consisting of purchased capacity from a centralized plant, a satellite water reclamation facility, and several small cluster systems. This allows the area to increase in population density without changing its rural character. Another example is located in Rutherford County, TN and consists of a septic tank effluent pumping (STEP) system with about 50 subdivision wastewater systems, all of which contain a STEP system, a recirculating sand filter, and large effluent drip disposal system. At each residence is a 1,500 galloon septic tank with pump and controls for discharge to a centralized treatment location. This also allows for high density development despite lack of city sewer and soil type suitable for conventional sewage tank and drain field [28].

1.2.3.4 Constructed Wetland

In a constructed wetland plant life as well as soil plays a critical role in treatment. . In theory, it possesses a rich microbial community to effect the biochemical transformation of pollutants, is biologically productive, and self-sustaining [31].

Constructed wetlands have been gaining attention in the treatment of wastewater and are used worldwide. About 5,000 have been built in Europe and 1,000 in the US, particularly in the Southwest. Identified phosphorus removing mechanisms are assimilation and release by vegetation and micro-organisms, and sorption to soils and sediments [31].

1.2.3.5 Onsite Wastewater Treatment and Phosphorus Removal

Since the 1970s, sorption of phosphorus to the substratum has been recognized as one of the most important removal mechanisms [32]. In Michigan phosphorus is adsorbed in natural soils by aluminum and iron located in the B horizon, typically 15 to 61 cm (about 6-24 inches) deep [33]. In a study using soil in Canada, Baker et al. [34] found an average capacity of 113.2 mg P/kg, ranging from 6.3 to 501.0 mg P/kg. Even in the case of a constructed wetland system or other filter based system, local sand and soils are often used as the substrate for phosphorus removal in onsite systems without knowledge of the phosphorus-retaining capacities [35].

If the locally available substrate is not effective in removing phosphorus, or because of high seasonal groundwater and if there is the possibility of impacting a nearby lake, alternative means of removal is needed [36], [37]. Conventional methods are not practical as onsite treatment systems do not receive daily attention; even routine maintenance on an ATS is not scheduled more than once every 3 months. Biosolids need to be routinely removed for biological phosphorus. Typical chemical precipitation is also difficult as a feed pump and supply chemical is required and precipitates routinely required. Alum injection in a septic tank can require tank pump-outs 2 to 3 times per year [27].

1.3 Phosphorus Sorbing Media

The following subsections provide a general overview of phosphorus sorbing media in wastewater treatment then describe the sorption mechanism and issues surrounding effectiveness. A description of various phosphorus sorbing medias studied for use in onsite wastewater treatment is then described, including details on recently developed media that contain nano-particles.

1.3.1 General Advantages of Phosphorus Sorbing Media

The use of low cost and easily available sorption materials for wastewater treatment has been greatly studied in recent years. As well, an exponentially increasing number of studies on the use of highly manufactured nano-scale sorbing material (including carbon nanotubes, nano-zerovalent iron, metal oxide-based, and polymeric nanoparticles) for treating contaminated water has occurred over the past twenty years [38]. The vast majority of the nano-scale studies target metals, lead, and bacteria. Literature on the use of nano-scale constructed sorbents for phosphorus is limited to batch studies using synthetic wastewater.

1.3.2 Phosphorus Sorbing Medias Studied for Use in Onsite Wastewater Treatment

Phosphorus sorption media uses charged cations (iron oxides, aluminum oxides, and calcium oxides) to attract phosphates. The cation forms surface hydroxides that can exchange with phosphates, forming mineral complexes with orthophosphate. The media's selectivity and effectiveness depends on other ions that are present, pH, dissolved oxygen levels, contact time, and the relative concentrations of the constituents [38], [39].

Many studies comparing various natural and manufactured media, including those based on limestone, furnace slay, iron fillings, activated aluminum, and iron-coated inorganic foams have been reported in the literature [5], [34], [39], [40], [41], and [42]. Johansson Westholm published an excellent review article (2006) of studies performed on various substrates (ranging from natural to highly manufactured materials), specifically for potential use in onsite phosphorus removal. Included were batch, column, and field experiments. None of the substrates presented in the article were manufactured on the nano-scale. Wastewater sources varied from artificially made to natural [42]. A summary of various sorbing media studied, including some reviewed in the Johansson Westholm article appears in Table 1.

Table 1. Select Filter Media Investigated for Phosphorus Sorption Capacity.

Sorbent	Experiment Type	Notable Results	Source
Natural Soils Surveyed in Canada	batch and column; artificial P solution	average capacity of 113.2 mg P/kg, ranging from 6.3 to 501.0 mg P/kg	Baker, et al. (1998)
Wollastonite (powder and tailings)	batch; artificial P solution	98-100% removal after 72 hrs.	Brooks et al (2000)
	column; secondary wastewater	>85% removal after 411 days.	Brooks et al (2000)
	column; secondary wastewater	39% after 100 days	Brooks et al (1999)
	batch; artificial P solution	capacity 2 mg P/g	Goerhring et al (1995)
Wollastonite (tailings)	field; pre-treated dairy wastewater fed to constructed wetland	45% removal after 175 days.	Hill et al (2000)
Crystalline and amorphous blast furnace slag	column; artificial P solution	95-100% removal without sign of saturation	Johansson Westholm et al (1999)
Activated Alumina	column; secondary wastewater		Safferman et al (2004)
Meosporous Silicates Impregnated with 30% Aluminum	batch; artificial P solution	0.826 g/umol-min	Shin et al (2004)
MetaMateria FeOOH	column; secondary wastewater	capacity 11.4 mg P/g	Safferman et al (2008)
Filtralite™ (LWA material with natural additives)	batch; artificial P solution	capacity 2.21 mg P/g	Zhu at al (1997)
	field; pre-treated dairy wastewater fed to constructed wetland	34% removal after 18 mos	Hill et al (2000)

1.3.3 Benefits of Nano-Scale Technology and Phosphorus Sorbing Nano-Scale Medias Found in the Literature

Nanotechnology refers to the manipulation of materials and systems at the nanoscale (less than 100nm). The field of study is relatively new in materials development and has moved quickly from the laboratory to practical applications [38].

Nano-sorbents have a high porosity, small size, and active surface. These qualities enable sequestering contaminants of varying molecular size, hydrophobicity, and species. In the manufacturing process, raw materials can be used efficiently, as large surface area enables the requirement of less material. Nano-adsorbents work quickly, and can be chemically regenerated after being exhausted [38]. Just two nano-adsorbents have been found in the literature for use in the wastewater treatment of phosphorus.

A batch study published in 2010 by Chouyyok et al used Anion-SAMMS (Self-Assembled Monolayers on Mesoporous Supports) technology and achieved a capacity of 43.3 mg P/g. In Anion-Samms (also called metal capped ethylenediamine-SAMMS), cationic Cu(II) – EDA complexes, or in the case of this study, Fe(III) – EDA complexes, bind to the silica wall of the SAMMS and are capable of binding toxic anions such as arsenate and chromate. Influent concentrations varied from 0.02 to 18.53 mg P/L, and sorption was equilibrium driven. In a study by Yokoi, phosphate was reported as a competing anion for the metal. With this information, Chouyyok found the technology to be effective in sorbing phosphorus [43].

Another batch study published in 2007 by Deliyanni et al determined the phosphate sorption capacity and rate of uptake for akaganete (β-FeO(OH)), a natural iron oxyhydroxide mineral. Researchers prepared the media to contain nano-crystals with a high surface area and added a cationic surfactant (*N*-cetyl-*N,N,N*-trimethylammonium bromide-HDTMA). Sorption was equilibrium driven. As in the case of Anion-SAMMS, the akaganete technology had already proved successful in the sorption of arsenate. The nanocrystalline akaganete capacity was 59.62 mg P/g and the capacity of the media with the surfactant was determined to be 451.20 mg P/g [44].

1.4 Summary: What is Known and Not Known in the Field of Onsite Wastewater Phosphorus Removal

Phosphorus is a nutrient necessary for life and a healthy ecosystem. There is a demonstrated need to keep excess phosphorus from entering lakes and streams and several management methods. Many of these methods are appropriate for use in a wastewater treatment plant but are too costly and labor intensive for use in other arenas. A material which works passively, at a low cost, and minimizes labor requirements, is ideal for onsite wastewater application. Phosphorus sorbing media fits this category.

Various substrates ranging from natural soils and minerals to highly manufactured materials have been used in phosphorus sorption. This includes media using nano-scale technology, although use for phosphorus is still limited. The present study on the use of nano- scale material for phosphorus removal is unique in that is uses natural wastewater and the substrate is known to be economically produced.

CHAPTER 2
PROJECT OBJECTIVES

This study explored the use of an economically produced, nano-scale media for its potential in removing phosphorus from onsite produced wastewater. The sorption capacity, ability to treat wastewater to a desired effluent level, and the removal mechanism were investigated.

2.1 Hypothesis

The hypothesis for this research is that a cost-effective phosphorus sorbing media can be used in an onsite system for an extended period, only requiring minimum operational attention and maintenance. The mechanism is equilibrium driven allowing for predictable performance.

2.2 Objectives

Based on the hypotheses, the project has the following objectives.

1. Determine the capacity of the media to remove phosphorus (proof-of-concept).
2. Examine the mechanisms of phosphorus removal to aid in determining design parameters.

CHAPTER 3
METHODS

The study was conducted in two phases. The first phase was a proof-of-concept study on the long-term capacity of the nano- enhanced media for soluble phosphorus in onsite waster.

The second phase addressed operational parameters by examining the hydraulic loading, empty bed contact time (EBCT), and mechanism of removal. The hydraulic loading is a measure of the flux of fluid flowing across a cross section of the media bed, and has units of volume per time per surface area. Empty bed contact time is a measure of how long a solution is in the volume occupied by the media without considering the volume the media occupies, and has units of time. Additionally, phase two wastewater had a higher organic content, which allowed for discovery of how this impacted the media.

This section first reviews the nano-enhanced media, reactor design, reactor construction, source wastewater, and the operation protocol. The technique to determine the media's capacity and impact of hydraulic loading and EBCT is then discussed.

3.1 Filter Media

The media was an inexpensively produced nano-iron coated iron foam manufactured by MetaMateria Technologies and has been under development for over 10 years (Figure 2). Phase 1 used a different generation of media than Phase 2 but the primary difference was in the efficiency of manufacturing. Details regarding the nature and cost of the media are available from Metamateria [45], but certain manufacturing procedures are proprietary.

Figure 2.”For the interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of the thesis.” Granular, Iron Foam Substrate Coated with Nano Iron. (Photo Courtesy of Dr. Steven Safferman).

3.2 Reactor Design and Construction

Figure 3 is a schematic of the reactor. A bottom-to-top flow pattern was used to achieve optimal wastewater distribution and reduce chances of short-circuiting.

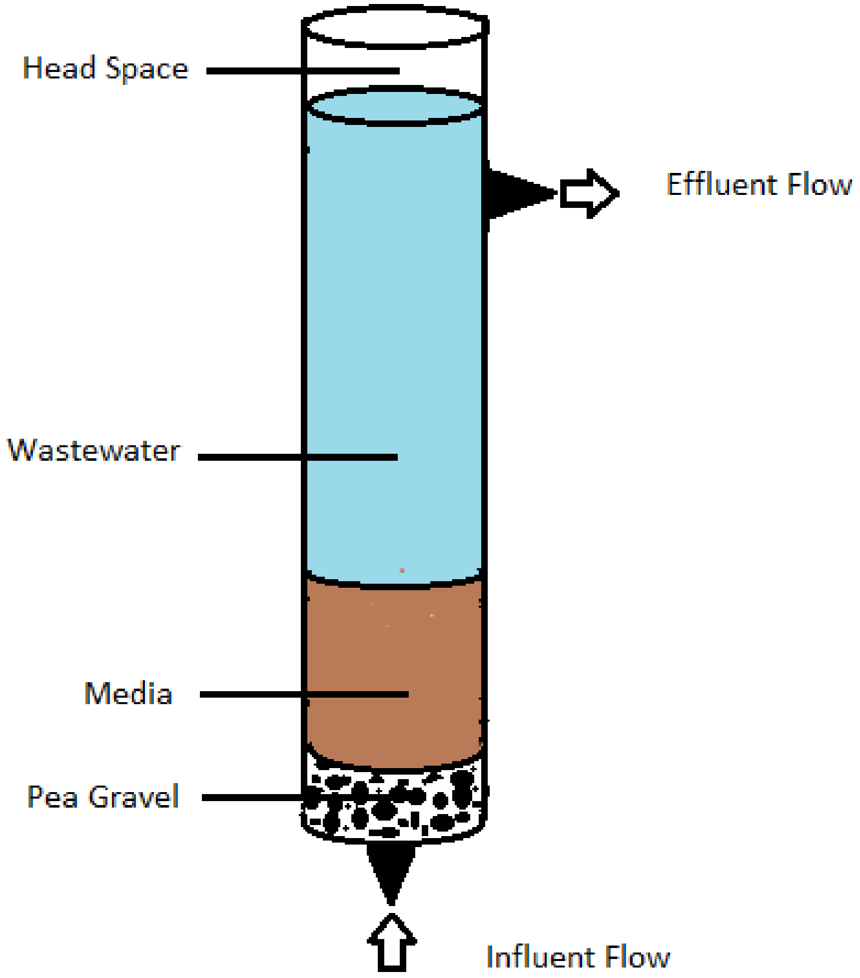


Figure 3. Reactor Schematic Showing Direction of Wastewater Flow.

The reactors were constructed from PVC pipe, approximately 0.61 m (2 ft.) in length, and ranged in diameter from 3.81 to 7.62 cm (1.5 to 3.0 inches) depending on the phase of the study. The specific reactor assembly steps are listed below.

- PVC pipes were cut to size and at the effluent location; a hole was drilled and pipe-tapped to allow for a hose barb to be installed. The threads were wrapped in plumbing tape before installation.
- Bottom end-caps were glued to the reactors, a hole was drilled for the influent, and a hose barb was installed as previously described.
- Reactors were cleaned with phosphate-free detergent and rinsed with deionized (DI) water.
- End-caps were loosely installed on the tops of the reactors but not glued.
- Media was rinsed repeatedly (approximately ten times to remove any coating that had come loose) with DI water until rinse water became translucent and then air-dried for several days.
- Approximately 150 mL of the air dried media was used in each column.
- A portion of media was set aside to be tested for phosphorus and moisture content and examined by scanning electron microscope.

Columns were then loaded with pea stone and media as follows.

- Columns were loaded first with pea stone to prevent media from escaping and distribute the wastewater. The stones were rinsed with DI water and 100 mL were placed in the bottom of the reactor, which occupied approximately 3.05 cm (1.2 in).
- A volume of 150 mL of air dried MetaMateria nano-enhanced iron coated media was weighed, and added to each reactor atop the stones. This resulted in an approximately 7.6 to 12.7 cm (3 to 5 inches) headspace.

- Columns were mounted on a specially constructed stand and flexible 1.6 mm tubing was used to connect the influent, pumped from the reservoir by the positive displacement pump. Flexible tubing was also used to drain the effluent.

3.3 Source Wastewater

Wastewater used in the study was collected from actual onsite treatment systems to enable a comprehensive evaluation of the media's capacity in the presence of competing ions. Phase one wastewater and phase two wastewater came from different sources.

Phase 1 wastewater was obtained from an onsite advanced treatment system (ATS) at a retail facility in Okemos, Michigan. The ATS consisted of a series of septic tanks, recirculating sand filter, pump chamber, and drain field. The wastewater was obtained from a pump chamber where effluent from the sand filter was stored before either being sent back to the sand filter or disposed of into the drain field. The parameters used to characterize the wastewater in phase one were nitrate, ammonia, alkalinity, pH, total COD, and total phosphorus. The same parameters were measured in phase two, with the addition of silica, sulfate, BOD_5, TKN, arsenic, calcium, magnesium, manganese, soluble COD, and soluble phosphorus (specific methods are described in Section 5).

Phase 2 wastewater was obtained from a housing development in Dimondale, Michigan. With its higher organic content, the quality of the effluent wastewater is more typical of that found in most onsite treatment systems. As in Phase 1, the treatment sequence was a septic tank located at each house, an ATS recirculating sand filter, and pump chamber. Rather than being discharged to a drain field, treated wastewater was discharged to a pond (which also serves an aesthetic function for the community). The wastewater was obtained from a small chamber immediately before being discharged to the pond.

3.4 Operation of Systems

Throughout the course of each phase, input and output phosphorus concentrations (the primary analytical parameter) were monitored on an approximately weekly basis but more frequently at the beginning of the study. Flow was delivered by positive displacement pumps and rates were monitored on a regular basis by timing the collection of a given volume.

The sequential subsections describe the specific operation associated with each research phase.

3.4.1 Phase One Operation

Phase 1 ran from July 8, 2009 to March 8, 2010 (604 days). Its primary goal was to determine the capacity of the media to maintain an effluent phosphorus level below 2 mg/L (a common regulatory limit at the time of the research). To do so, the flow rate was initially adjusted, but not optimized, to meet this target.

The system consisted of two reactors operating in series. Each reactor had a diameter of 3.81 cm (1.5 inches). This configuration allowed the target breakthrough level of 2 mg/L to be exceeded in the first column so that more of the media's capacity could be used. The second reactor served as a polishing unit to reduce the phosphorus level to the desired level. Figure 4 is a schematic of the system and Figure 5 is a photograph. Phase 1 ended when the effluent phosphorus consistently exceeded the 2 mg/L effluent target.

Results of influent and effluent phosphorus concentrations were recorded in a spreadsheet that included calculations of the cumulative mass loading. This was calculated by subtracting each discreet measured effluent phosphorus concentration from the discreet measured influent concentration and multiplying the result by the average flow rate and time between two sequential measurements. This approach can only be considered an estimate as the time between measurements varied and there were five occasions when the columns were clogged or operation errors occurred. In these cases, the specific time of such occurrences had to be estimated. Also, keeping the slow flow rate constant was challenging. Flow rates were measured approximately weekly or more and adjusted as necessary. Appendix A shows the dates that phosphorus concentrations and flow rates were measured and when phosphorus concentrations are reported as estimates.

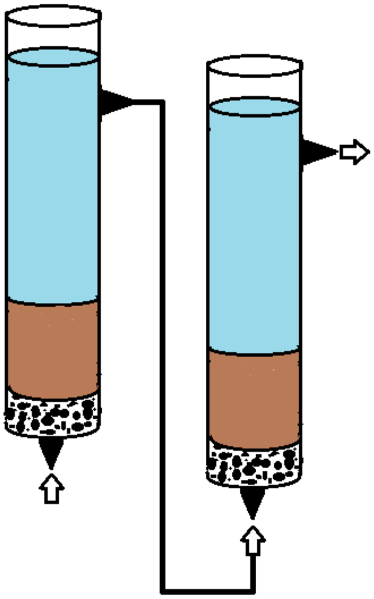


Figure 4. Phase 1 Schematic, Two Reactor Columns Operating in Series.

Figure 5. Photograph of Phase 1 Experimental Setup.

It is unclear as to whether clogging was an artifact of the small system (including the small diameter tubing) or whether the media bed itself was the cause.

The total mass of phosphorus sorbed onto the media when phase one was discontinued was analytically measured and compared to that found from the cumulative mass loaded, as described in the introduction to this chapter. To obtain the analytically measured amount of phosphorus sorbed to the media, the reactors were disassembled and five samples were collected from different regions within each column. These samples, as well as unused media, were analyzed for phosphorus content using nitric acid digestion (EPA method 3050b), and inductively coupled plasma-atomic emission (EPA method 6010B). This work was conducted by Brookside Laboratory in New Knoxville, Ohio, USA. The percent recovery of the phosphorus was then calculated by subtracting the phosphorus sorbed from that loaded, dividing by the amount loaded, and multiplying by 100.

Also at the end of Phase 1 scanning electron microscopy (SEM) images and electron dispersive spectroscopy (EDS) analysis were completed on samples gathered as above, and on unused media. The sample preparation, SEM and EDS analyses were performed by the Center for Advanced Microscopy at MSU. These studies allowed for qualitative analysis of any attached biofilm and for the amount of phosphorus sorbed. The specific steps in sample preparation and analysis are taken from the Center for Advanced Microscopy SEM Samples Preparation Guide, and are listed below.

- Samples were placed in microporous baskets and fixed at 4ºC in 4% glutaraldehyde buffered with 0.1 M sodium phosphate at pH 7.4. Following a brief rinse in the buffer, samples were dehydrated in an ethanol series (25%, 50%, 75%, 95%) for 10 -15 minutes at each and with three 10 minute changes in 100% ethanol.

- Samples were critical point dried in a Balzers Model 010 critical point dryer (Balzers Union, Ltd., Balzers, Liechtenstein) using liquid carbon dioxide as the transitional fluid, for 4 minutes, 4 times to flush.
- Samples were mounted on aluminum stubs using carbon suspension cement (SPI Supplies, West Chester, PA).
- Samples were coated with osmium (≈10 nm thickness) in an NEOC-AT osmium coater (Meiwafosis Co., Ltd., Osaka, Japan).
- Samples were examined in a JEOL JSM-7500F (cold field electron emission emitter) scanning electron microscope (JEOL Ltd., Tokyo, Japan).
- Energy dispersive X-ray spectroscopy (elemental analysis) was done using and Oxford Instruments INCA system (Oxford Instruments, High Wycomb, Bucks, England), software version 4.13, using a 10 mm^2 detector crystal (6400 SEM or a 30 mm^2 detector crystal (7500F SEM) and an ultrathin window.

3.4.2 Phase Two Operation

Phase two ran from March 23, 2011 to June 17, 2011 (70 days). Its primary goal was to provide design information.

Four single reactors in parallel were used. Initial assembly of each reactor was the same as described Phase 1. The first reactor was designed to have similar operational characteristics as a single column from Phase 1, including the 0.8 mL/min flow rate. The remaining three columns had various hydraulic retention times but EBCTs were identical. Different hydraulic retention times were achieved by using columns of varying diameters. Influent to the four reactors was from a common container. Table 2 shows the design parameters for each column and Figure 5, the experimental setup.

Table 2. Design Parameters of Four Reactors Used in Phase 2.

System Number	Diam. of Column (cm)	Flow (mL/min)	EBCT (min)	Vol. of Media (mL)	Hydraulic Loading (mL/min/cm^2)
1	3.8	0.8	190	150	0.07
2	3.8	2.5	60	150	0.22
3	5.1	2.5	60	150	0.12
4	7.6	2.5	60	150	0.05

Figure 6. Photograph of the Four Reactors Used in Phase 2.

Initially, the primary analytical parameters were influent and effluent total phosphorus. As the study progressed, spikes in effluent concentration of total phosphorus were observed, as well as visible particulate matter in the effluent. It was hypothesized that this was due to the sloughing of biological material growing in the reactors. Consequently, on day 29, the measurement of soluble phosphorus, total COD, and soluble COD were initiated (see Section 5 for details on the analytical methods).

Also, to verify the attachment of biofilm and the presence of phosphorus crystals, samples of the media were taken from the top of the reactors and SEM images were examined and EDS analyses conducted as previously described.

3.5 Wastewater Analysis and Quality Assurance/Quality Control

The analytical methods are provided in Table 3 All methods were United States Environmental Protection Agency (USEPA) accepted. Quality was assessed for all parameters throughout the study with a minimum of 1 field duplicate, 1 lab duplicate, 1 standard, and 1 blank for every 10 to 20 samples. In measuring soluble phosphorus and COD during Phase 2, samples were first filtered through a 0.45 micron filter.

Laboratory tests performed by MSU used reagent kits manufactured by Hach, with a Hach model DR5000 spectrophotometer.

Table 3. Methods used in Wastewater Characterization.

Parameter	Method	Range	Performed by
TKN	4500-N(org)/NH_3	0.1 +	Merit Labs*
Nitrate-N	Hach 8039	0.3 - 30.0 mg NO_3/L	MSU**
Ammonia-N	Hach 8038, Nessler	0.02 - 2.25 mg NH_3/L	MSU
Alkalinity (as $CaCO_3$)	Hach 8203, digital titration	10 - 4000 mg/L as $CaCO_3$	MSU
COD	Hach 8000, reactor method	3 - 150 mg COD/L	MSU
Phosphorus	Hach 8190	0.06 - 3.50 mg PO_4^{3-}/L	MSU
Silica	4500-Si D	0.05 +	Merit Labs
Sulfate	300.0	5 +	Merit Labs
BOD_5	10360	1.0	Merit Labs
Arsenic	200.8	0.002	Merit Labs
Calcium	200.8	1.0	Merit Labs
Magnesium	200.8	1	Merit Labs
Manganese	200.8	0.005	Merit Labs
Total Solids	Hach 8271		MSU
pH	Ion Selective Electrode		MSU

*Merit Laboratories, Inc. East Lansing, MI
**Michigan State University, Department of Biosystems and Agricultural Engineering, East Lansing, MI

CHAPTER 4
RESULTS AND DISCUSSION

The first section (Phase 1 of the research) focuses on the proof-of-concept study that examines the capacity of the media and verifies that phosphorus removal was by sorption to the media and not by other means. The second part of this section is based on Phase 2 of the methods. Operational considerations including the effects of hydraulic loading and EBCT and for the mechanism of removal are discussed.

4.1 Proof-of-Concept Results

This section discusses the media sorbing capacity, effluent levels, and verifies that the phosphorus was removed by sorption to the media.

4.1.1 Phosphorus Effluent Levels

The study began with a relatively fast flow rate of 9.8 mL/min. During this period effluent phosphorus levels increased rapidly and were consistently above the desired breakthrough level of 2 mg/L, a common regulatory limit at the time (Figure 7). The flow rate was stepped down to approximately 1.6 mL/min from days 159 to 247), then again to 0.8 mL/min) for the remainder of phase one. These changes were made to enable the routine meeting of the targeted 2 mg/L breakthrough effluent phosphorus level. Thereafter, effluent phosphorus concentration levels stayed consistently below the breakthrough level until approximately day 539, (Figure 7).

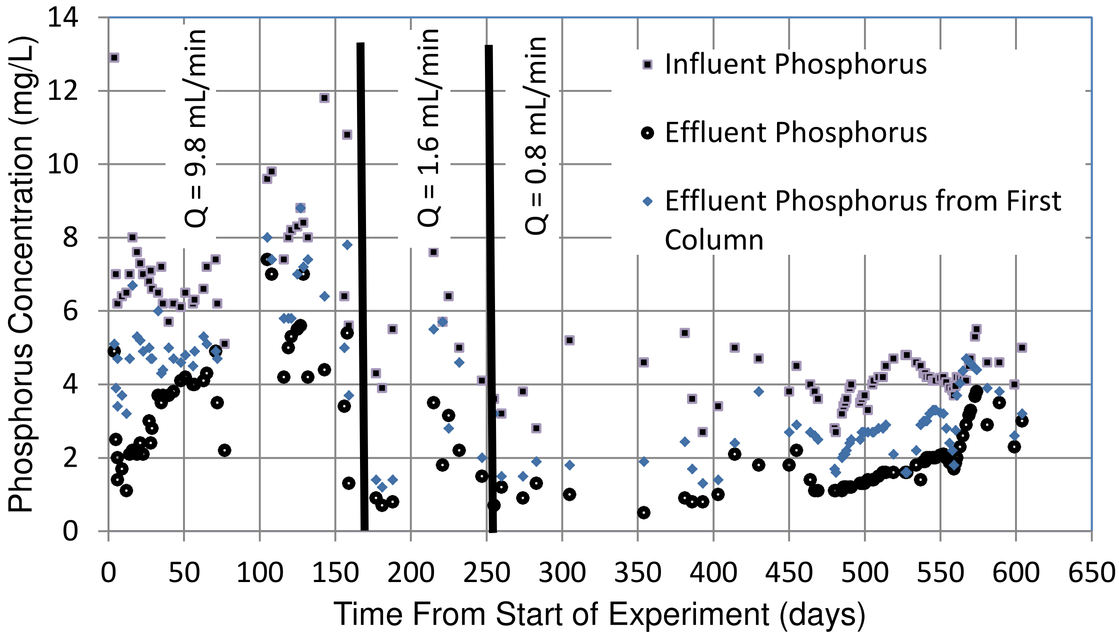


Figure 7. Phase 1 Influent and Effluent Phosphorus Concentration, Media 2083, Two Reactors in Series.

4.1.2 Media Capacity

Capacity, as calculated by the cumulative mass loading after 604 days (refer to Methods, Section 4a.) was 47 mg/g (mg phosphorus removed per g of media). This is not the ultimate capacity as the effluent phosphorus level was still lower than the influent. The amount that was analytically measured was 29 mg/g, which resulted in a percent recovery of 64%. Appendix B shows the detailed calculations. A phosphorus sorption capacity in the range of 29 to 47 mg/g is substantially higher relative to most other values found in the literature. The nano-coating appears to be critical as a previous generation of the media manufactured by MetaMateria without the nano-coating had a capacity ranging from 12 – 15 mg/g [5].

Only two other substrates were found in the literature with greater capacities: modified akaganete [45] and Fe(III) – SAMMS [44]. The reported capacities are 451.20 mg/g and 43 mg/g, respectively. Both are highly manufactured and use nano-materials. Neither were tested using actual wastewater or under different design parameters, such as EBCT and hydraulic loading, and both were batch studies. In the Fe(III)- SAMMS study, initial phosphate concentration was varied until the maximum sorption capacity was obtained, using a large molar excess of phosphate (0.02 to 18.53 mg P/L at the liquid-to solid ratio of 10,000 ml/g). Similarly the initial concentrations in the case of akaganete study varied from 10 to 300 mg P/L. Information regarding costs is unknown.

4.1.3 Verification of Phosphorus Sorption to Media

Both wastewater analysis and SEM imaging results confirm that phosphorus removal was abiotic. As well, sorption of any significant quantity of phosphorus to the pea gravel in the reactors can be shown to be highly unlikely. Each is further discussed in the proceeding subsections.

4.1.3.1 Wastewater Analysis

To rule out biological growth, influent, effluent, and the water in the headspace of each of the two columns were characterized to determine if, qualitatively, biological activity could be supported as this could lead to phosphorus uptake (Table 4).

The very low COD influent and effluent levels and lack of ammonia are not conducive for supporting microbial growth. This is not surprising as the treatment system at the retail establishment where the wastewater was collected was severely under loaded resulting in excellent treatment. Further, the reactors and tubing did not allow light penetration limiting the potential of algae growth.

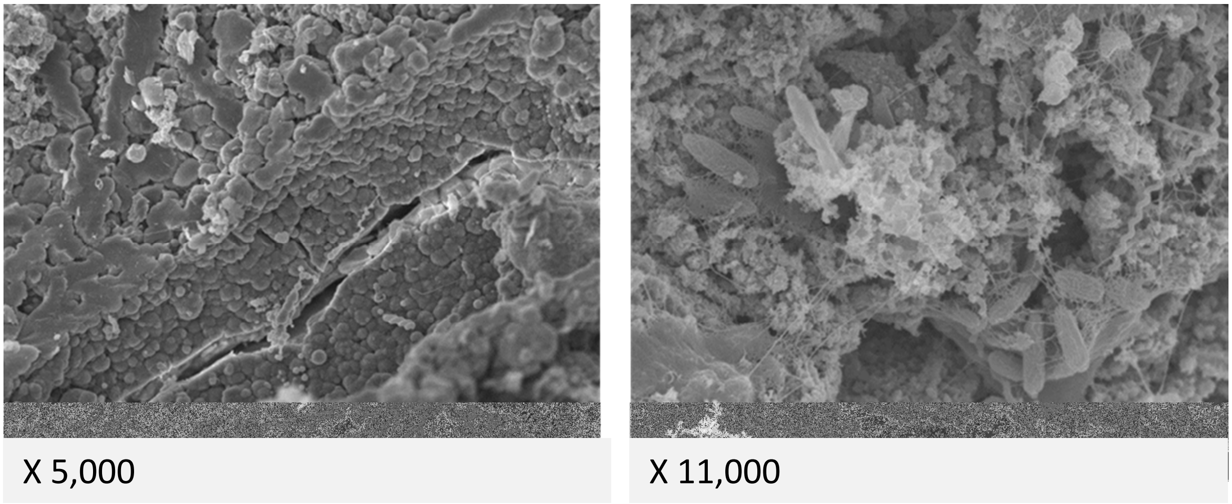
Table 4. Wastewater Characteristics at End of Phase 1.

Parameter	System Influent	Column A Headspace	Column A Effluent/Column B Influent	Column B Headspace	System Effluent
Phosphorus (mg P/L)	5		3.23		3.23
COD (mg/L)	18.8	20.2	33	23	17.5
Alkalinity (mg $CaCO_3$/L)	219	240		230	
Ammonia (mg NH_4^{3-}-N/L)	< 0.02				
Nitrate (mg NO_3^{4-}L)	33.6	35.6		35.4	
pH	8.08	7.59	7.66	7.75	7.68
DO (mg/L)	8.32	6.95		7.01	
ORP	72	82		80	

Note: Each value is an average of 3 samples. Samples collected on March 18, 2010

4.1.3.2 SEM Imaging and EDS Analysis

Qualitative analysis of SEM imaging performed in Phase 1 revealed minimal biological growth (Figure 8, left image). This conclusion was based on the examination of five representative samples for several hours at the MSU Center for Advanced Microscopy. Phase 2 media (Figure 8, right image) did show considerable growth of microorganisms to be discussed later. The lack of attached microbes in Phase 1 further qualitatively rules out of biological uptake.



X 5,000

X 11,000

Figure 8. SEM Images Taken During Phase 1 (Left) and Phase 2 (Right) Showing Differences in Attached Microbial Levels.

Surface complexation of phosphorus with the media was verified again in Phase 2 by conducting an EDS analysis of crystals found on the media's surface (Figure 9). A substantial increase in phosphorus was noted in the used media (right image) compared to the fresh media (left image).

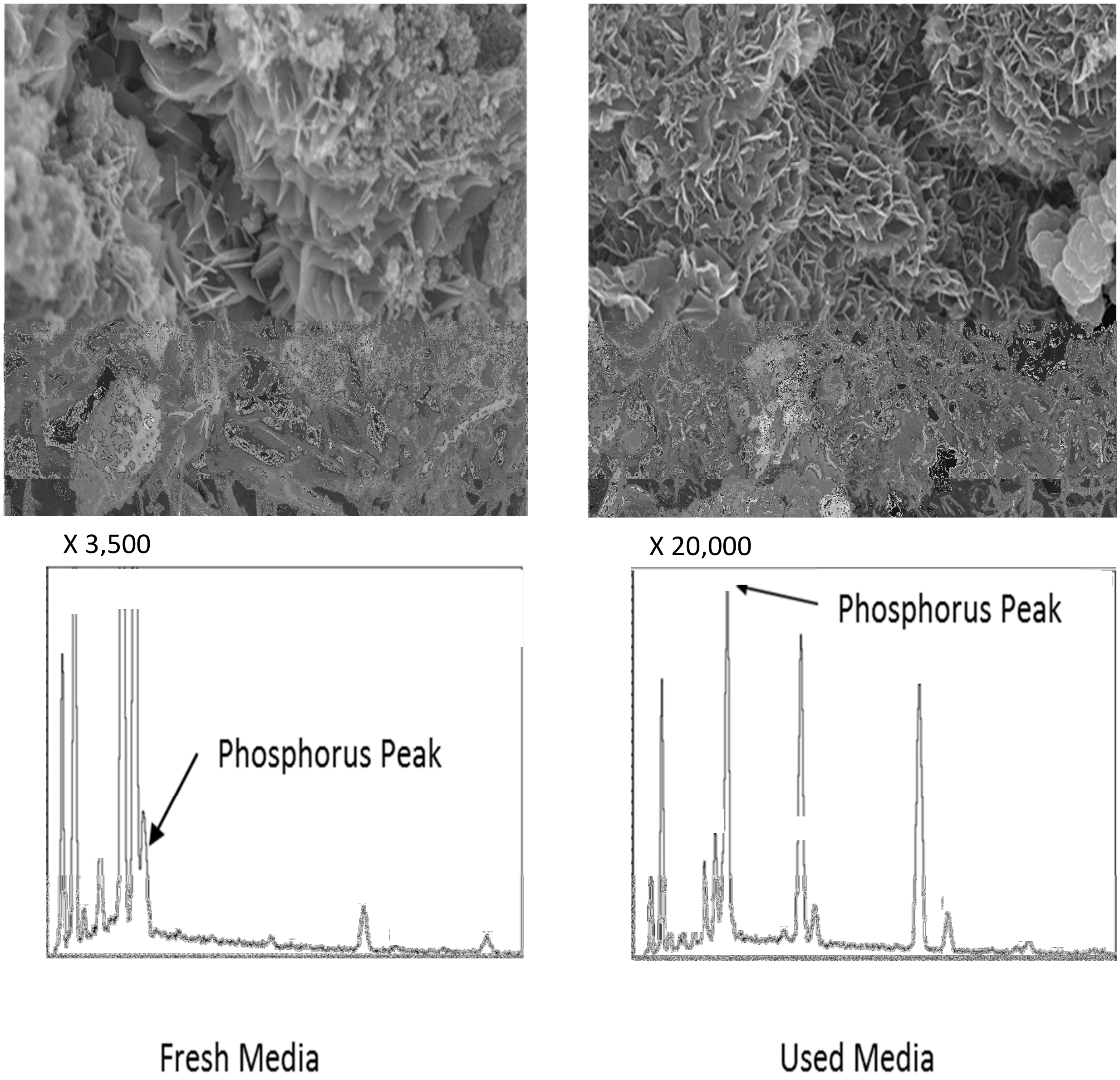


Figure 9. Phosphorus Peaks from EDS Analysis of Crystals on the Media's Surface. (Details Missing from EDS Analysis Above Can Be Found in Electronic Version).

4.1.3.3 Sorption to Pea Gravel

It is unlikely that a significant amount of phosphorus sorbed to the pea gravel used in the bottom of the reactor to keep the media in place and evenly distribute the flow of water. Using the average sorption capacity of soil (Table 1), and compensating for pore space, the mass of gravel used (285 g) could have sorbed only about 16 mg phosphorus, or 1.6 % of the phosphorus calculated to have been sorbed by the system (see Appendix C).

4.2 Impact of Empty Bed Contact Time and Hydraulic Loading on Performance

This section discusses the operational characteristics of EBCT and hydraulic loading, and uses the results to suggest a sorption mechanism.

4.2.1 Statistical Method

Statistical analyses were performed using IBM SPSS version 21.0 software. Depending on the normalcy of the data, analyses were performed using either a one-way analysis of variance, or a non-parametric test. The 0.08 level of significance was explored in addition to the more commonly used 0.05 level, with the idea that the source wastewater was natural, thus subject to slight variation in phosphorus concentration.

The independent variables were EBCT and hydraulic loading, and either phosphorus effluent concentration or fraction of phosphorus removed was the dependent variable. Whether it would be possible to control for influent soluble phosphorus concentration was uncertain due to the nature of the study: the wastewater treated was natural, thus its quality subject to change. Over the duration of Phase 2 influent soluble phosphorus (the Phase 2 primary analytic parameter) did not change significantly, and was common to all four reactors; the results can be said to be controlled for influent concentration.

However, the influent total phosphorus concentration (the Phase 1 primary analytic parameter) over the 604 day period of Phase 1 did change; the results cannot be controlled for it. (Discussion on the use of total versus soluble phosphorus as the primary analytic parameter follows in the next session, Total Versus Soluble Phosphorus as Primary Analytic Parameter, and in the Conclusion).

The days over which Phase 1 was performed were divided into three periods: 1a (days 4 through 158), 1b (days 159 through 247), and 1c (days 248 through 538). The final 65 days (days 539 through 604) of Phase 1 were not used in statistical analysis as breakthrough was occurring, which is illustrated in Figure 7, and will be discussed in part d of this section, Evidence of Mechanism.

Table 5 depicts the parameters considered in statistical blocking over each reactor: average influent P or soluble P concentration, EBCT, and hydraulic loading.

Table 5. Parameters Considered in Statistical Blocking Over Each Reactor.

Reactor Description		Ave. Influent Conc.	EBCT (hrs)	Hydro Load ($mL/min/cm^2$)
Phase 1a (days 4 - 158)	**one column**	7.49 mg total P/L	0.3	0.86
	two column	7.49 mg total P/L	0.5	0.86
Phase 1b (days 159 - 254)	**one column**	5.34 mg total P/L	1.5	0.14
	two column	5.34 mg total P/L	3.1	0.14
Phase 1c (days 255 - 538)	**one column**	3.96 mg total P/L	3.3	0.07
	two column	3.96 mg total P/L	6.7	0.07
Phase 2	**column 1**	6.78 mg soluble P/L	3.2	0.07
Phase 2	**column 2**	6.78 mg soluble P/L	1	0.22
Phase 2	**column 3**	6.78 mg soluble P/L	1	0.12
Phase 2	**column 4**	6.78 mg soluble P/L	1	0.05

4.2.2 Total versus Soluble Phosphorus as the Primary Analytic Parameter

Phase 2 conditions supported the growth of biofilm in the reactors, an unplanned occurrence, illustrated in Figure 8. Figures 10 and 11 show the total and soluble phosphorus concentrations, respectively, for all four reactors in Phase 2. Much variability is observed in the Phase 2 effluent total phosphorus concentrations, determined to be the result of periodic sloughing of biofilm. Small quantities of biofilm in an analytical sample can greatly increase the phosphorus concentrations as well as be a source of phosphorous removal from the system, to be discussed further in the Conclusions. Because continuous sampling and analyses is not practical, the contribution cannot be assessed and only the soluble phosphorus will be discussed for Phase 2 data.

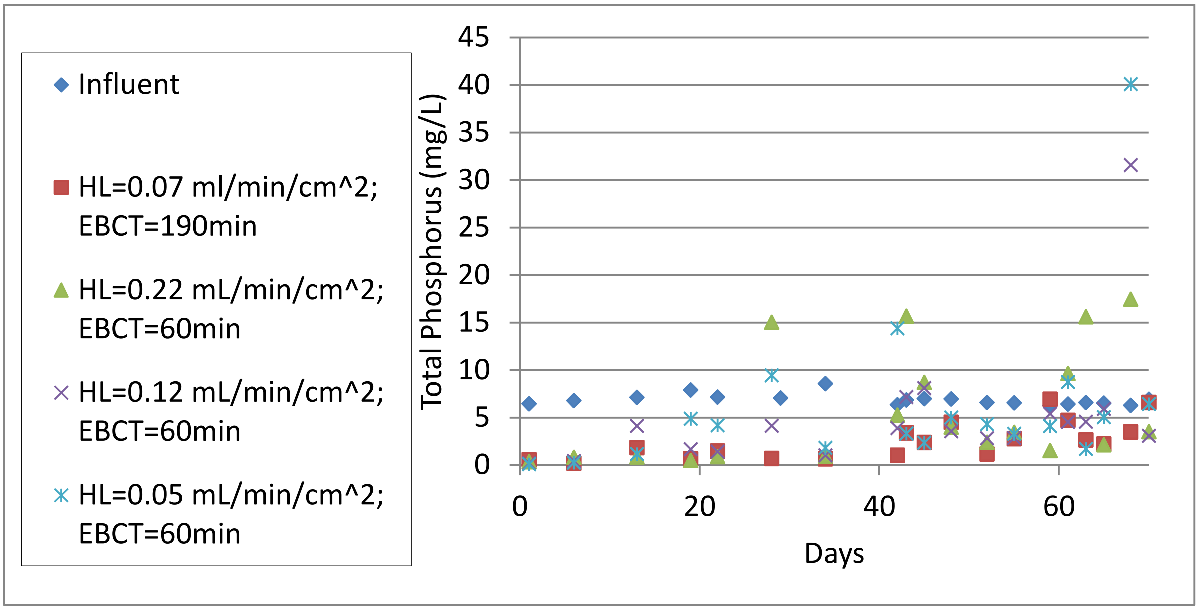


Figure 10. Influent and Effluent Total Phosphorus Concentrations, Media 5043, Single Columns, Phase 2.

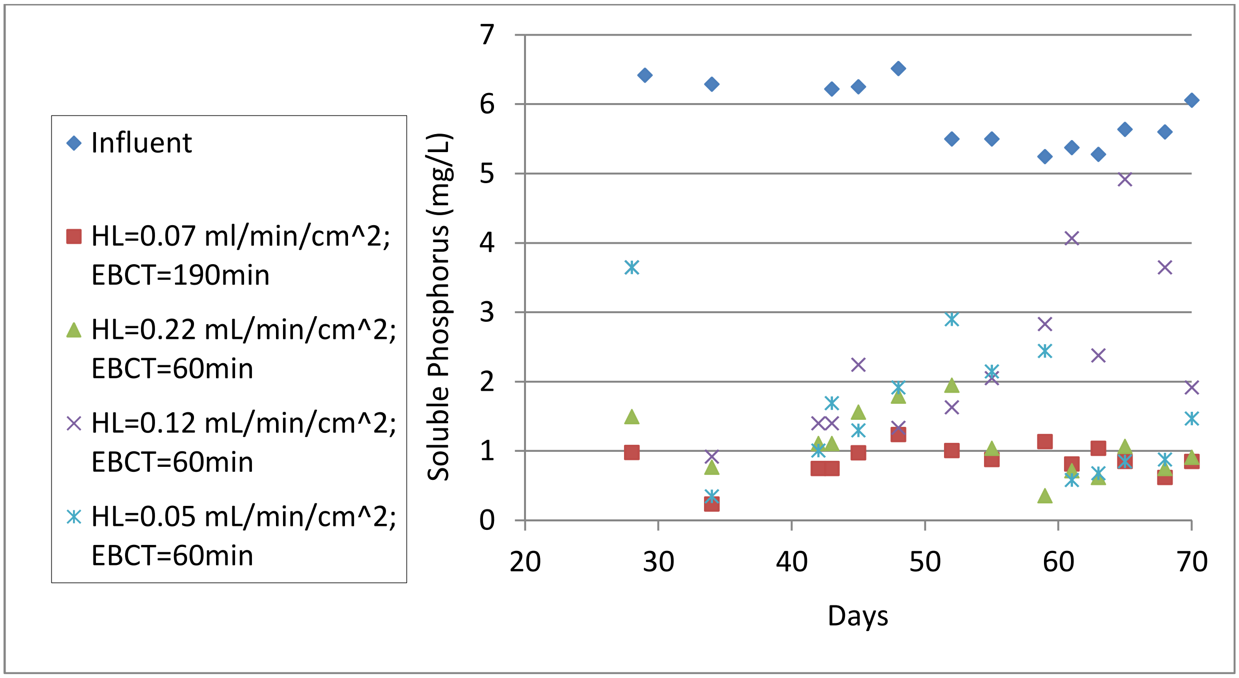


Figure 11. Influent and Effluent Soluble Phosphorus Concentrations, Media 5043, Single Columns, Phase 2.

4.2.3 Effect of EBCT

In Phase 2, reactors were operated at two EBCTs. One reactor was operated at a flow rate of 0.8 mL/min, resulting in an EBCT of 190 min (Phase 2, column 1). This condition was similar to the first column in Phase 1 during the longest EBCT (Phase 1c, single column), a design which could have provided an opportunity to see if the performances were similar. Unfortunately, differences between Phase 1 and 2 influent phosphorus concentrations did not allow for that comparison.

In Phase 2 each reactor shared a common influent, which allowed for differences in performance between two columns with similar hydraulic loading, but different EBCTs to be explored. These were reactors 1 and 4, with EBCTs of 3.2 hours and 1 hour respectively. The population was determined not to be normal; therefore a non-parametric (Independent Samples Median Test) was used rather than analysis of variance. Significance was tested at both the 0.05 and 0.08 levels, with no significant differences in performance found between the two reactors (Figure 12).

Hypothesis Test Summary

Null Hypothesis	Test	Sig.	Decision
The Medians of Effluent Sol P Concentration are the Same Across All Categories of EBCT	Independent Samples Median Test	0.434[1,2]	Retain the Null Hypothesis

Asymptotic significances are displayed. The significance level is 0.08.

1. Exact significance is displayed for this test.
2. Fisher Exact Sig.

Figure 12. Results of Independent Samples Mean Test on Effluent Concentrations of Reactors with Similar Hydraulic Loading and Varying EBCT (Phase 2 Columns 1 and 4).

However, an analysis of variance (ANOVA) test performed on the Phase 1 two-column systems over periods 1a, 1b, and 1c showed that the combination of higher EBCT, decreased hydraulic loading, and decreased influent phosphorus concentration was concomitant with higher removal efficiency. Figure 12 shows the same data as Figure 7 but as the removal efficiency. The means in removal efficiency of the three periods were tested and ANOVA results show that the systems during periods 1b and 1c had removal efficiencies that were not significantly different but were both significantly higher than the system of period 1a, illustrated in Figure 13 and Tables 6 and 7. Figure 14 illustrates the normalcy of the distribution.

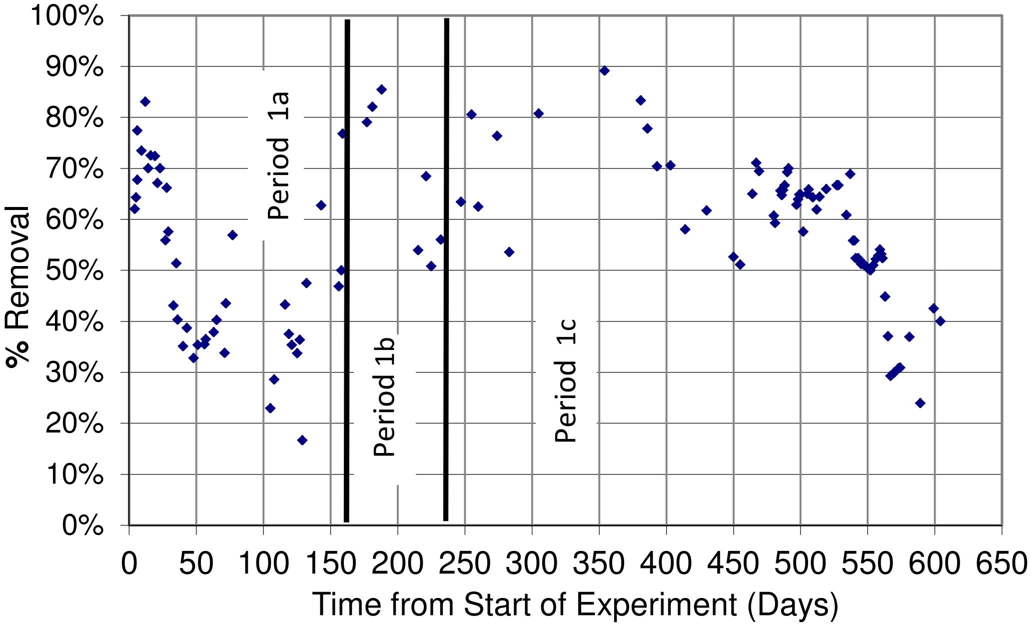


Figure 13. Phase 1, Phosphorus Removal Efficiency, Media 2083, Two Reactors in Series. Period 1a: Q = 9.8 mL/min, EBCT = 0.5 hrs, Hydraulic Loading = 0.86 mL/min/cm^2; Period 1b: Q = 1.6 mL/min, EBCT = 3.1 hrs, Hydraulic loading = .14 mL/min/cm^2; Period 1c: Q = 0.75 mL/min, EBCT = 6.7 hrs, Hydraulic loading = 0.07 mL/min/cm^2.

Table 6. ANOVA Table for the Comparison of Means of Fraction Phosphorus Removed Over Periods 1a, 1b, and 1c during Phase 1.

ANOVA

Fraction Removed

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.62	2	0.31	18.201	0
Within Groups	1.465	86	0.017		
Total	2.085	88			

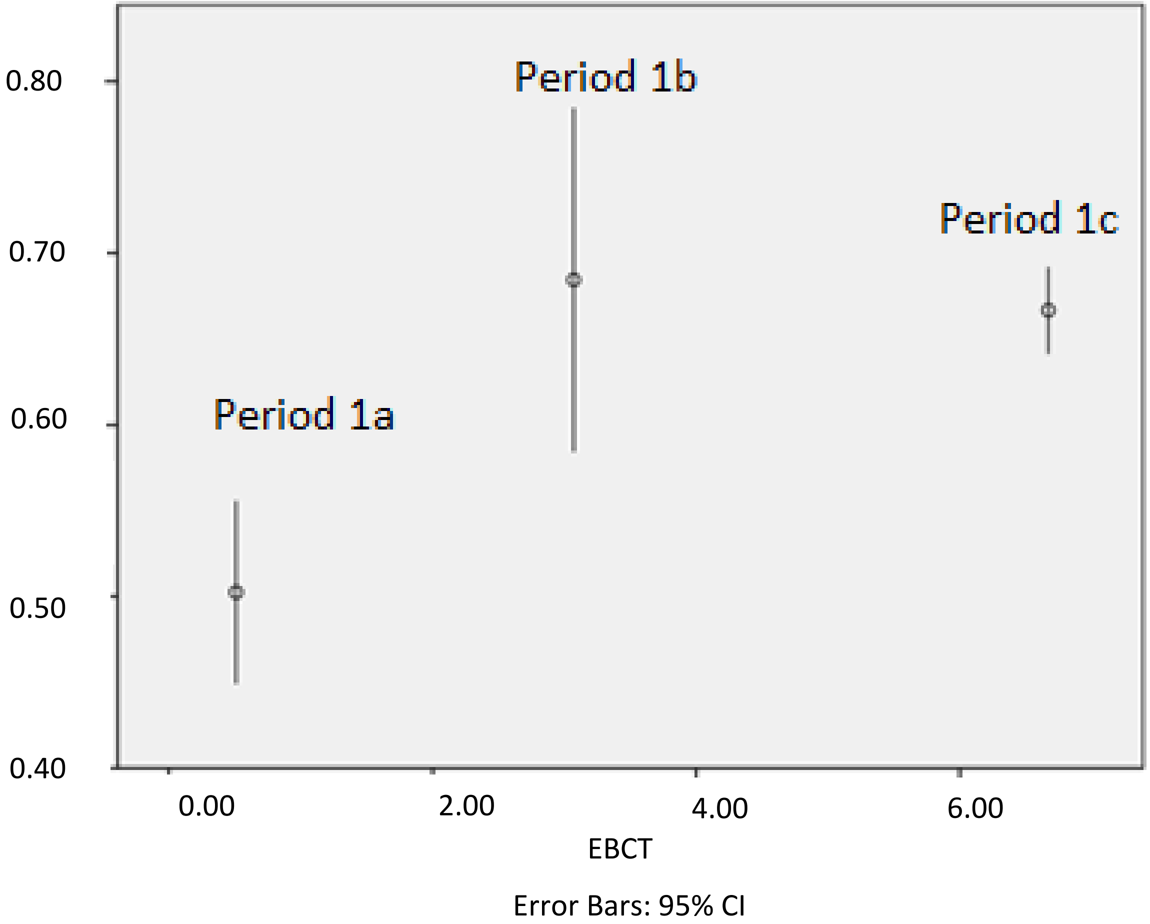


Figure 14. ANOVA Plot Comparing Means of Fraction Phosphorus Removed Over Periods 1a, 1b, and 1c During Phase 1. Y Axis Represents Mean of Fraction Removed.

Table 7. ANOVA Descriptives Table for the Comparison of Means of Fraction Phosphorus Removed Over Periods 1a, 1b, and 1c During Phase 1.

Descriptives

Fraction Removed

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
0.51	40	0.502362	0.166776	0.02637	0.449024	0.555699	0.1667	0.8308
3.07	9	0.684362	0.13035	0.04345	0.584166	0.784557	0.5078	0.8545
6.67	40	0.666578	0.079141	0.012513	0.641268	0.691888	0.5111	0.8913
Total	89	0.594571	0.153926	0.016316	0.562146	0.626996	0.1667	0.8913

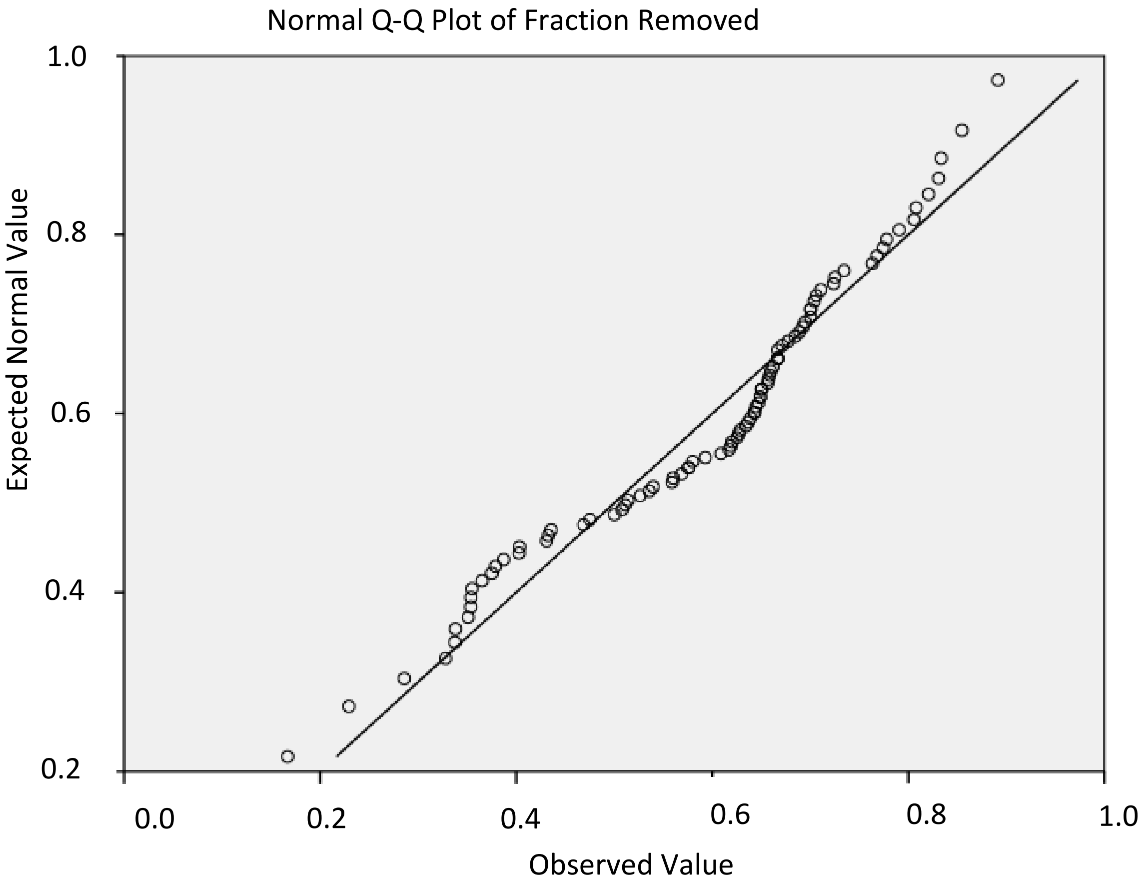
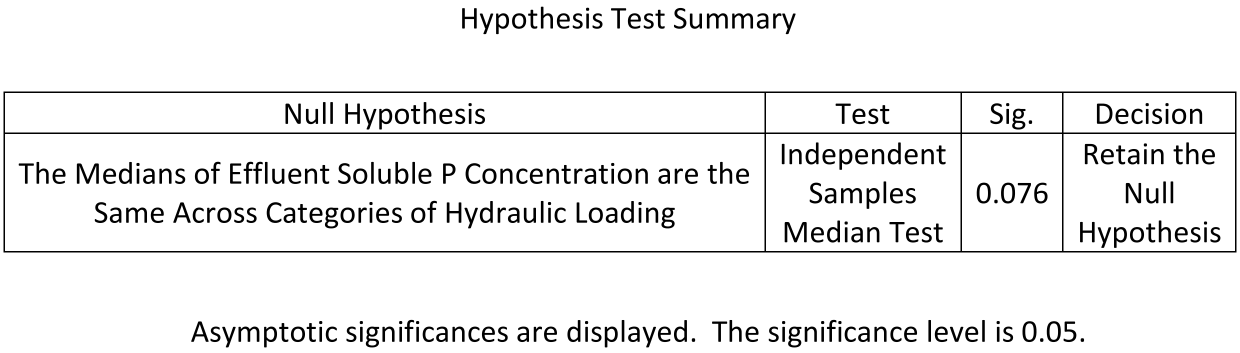


Figure 15. Illustration of Normally Distributed Population for Fraction Phosphorus Removed During Phase 1.

Brooks et. al. (2000) performed a study similar in design to the present study using wollastonite. A 15 cm in diameter, 1.5 meter long column study with a vertical up flow design using secondary treated wastewater was used. The hydraulic residence times varied from 15 to 180 hours. A direct relationship between higher residence time (which is similar to EBCT but incorporates porosity) and soluble phosphorus removal was found with removal of phosphorus was up to 96% [42].

4.2.4 Effect of Hydraulic Loading

Phase 2 reactor columns 2, 3, and 4 were operated at an EBCT of 1 hour but at different hydraulic retention times. An ANOVA was not used as the effluent phosphorus population was determined not to be normal. To examine the impact of hydraulic loading, an independent samples median non-parametric test comparing the medians in effluent concentration was performed to check for any correspondence of hydraulic loading with effluent soluble phosphorus concentrations. Non-parametric results were not conclusive. At the 0.05 significance level no difference was found (Figure 16).



Hypothesis Test Summary

Null Hypothesis	Test	Sig.	Decision
The Medians of Effluent Soluble P Concentration are the Same Across Categories of Hydraulic Loading	Independent Samples Median Test	0.076	Retain the Null Hypothesis

Asymptotic significances are displayed. The significance level is 0.05.

Figure 16. Results of Independent Samples Median Test Non-Parametric Test on Effluent Concentrations of Reactors with Constant EBCT and Varying Hydraulic Loading During Phase 2, Significance Level of 0.05.

At the less stringent 0.08 significance level a difference was found (Figure 16). Unfortunately this test does not allow for determination of where differences lie. The regret of incorrectly concluding that faster hydraulic loading is associated with decreased performance would be that (1) flow rate would either have to be decreased, or (2) surface area of media bed would have to be increased. Both scenarios pose a challenge in a field scale system in terms of expense, as slow flow rates are not practical for treating large volumes of water, and more media would be needed to have a large surface area (while retaining high EBCT). To the contrary, the regret of incorrectly determining that slower hydraulic loading is associated with decreased performance would be poorly treated wastewater, an environmental hazard.

Of the three reactors compared in the samples median test, it appears that the reactor of intermediate hydraulic loading (reactor column 3) had the least effective performance based on visual inspection of the soluble phosphorus effluent concentration graph (Figure 11). This result, in conjunction with the ANOVA of Phase 1 data (figure 13), may suggest that hydraulic loading cannot be a sole determining factor for media performance.

Hypothesis Test Summary

Null Hypothesis	Test	Sig.	Decision
The Medians of Soluble Effluent P Concentration Are the Same Across Categories of Hydraulic Loading	Independent Samples Median Test	0.076	Reject the Null Hypothesis

Asymptotic significances are displayed. The significance level is .08.

Figure 17. Results of Independent Samples Median Test Non-Parametric Test on Effluent Concentrations of Reactors with Constant EBCT and Varying Hydraulic Loading During Phase 2, Significance Level of 0.08.

4.3 Evidence for Mechanism

Figures 7 and 10 from Phase 1 show steady phosphorus removal, indicative of a high rate of sorption when the difference in phosphorus in the solute and that sorbed to the media is greatest. A breakthrough point is demonstrated with the gradual increase in effluent concentration at approximately day 539. These results are consistent with equilibrium driven complexation. The lack of strong correlation of removal efficiency with hydraulic loading is also consistent with the mechanism.

CHAPTER 5
CONCLUSION

The two hypotheses of this study were that the media can remove phosphorus long term and that complexation of phosphorus with the media is equilibrium driven.

5.1 Evidence for Hypotheses

Significant longevity was found (approximately 539 days before reaching breakthrough) and has the highest capacity (between 29 and 47 mg/g) found in the literature of any substrate tested in a column study using actual wastewater. The mechanism of phosphorus removal appears to be surface complexation (adsorption) governed by an equilibrium reaction, suggested by the shape of the effluent curve in the Phase 1 study, which is consistent with the literature. SEM analysis and EDS scans of the media show the presence of phosphate crystals, further supporting that surface complexation was the mechanism of phosphorus removal. The mechanism of equilibrium driven complexation allows for the use of commonly developed isotherm techniques such as those used for activated carbon design.

Mass transfer of a solute to a sorbing solid occurs in four steps [46].

(1) Diffusion from bulk to liquid film surrounding the solid.

(2) Diffusion through the liquid film.

(3) Diffusion into the pores of the sorbing solid.

(4) Sorption of solute to the solid.

The step that takes the longest is rate liming, controlling the overall rate of the process. A lower hydraulic loading (larger media surface area for a given flow rate) increases contact time of wastewater with any given particle of media, thus providing more time for steps two, three, and four. All are steps associated with diffusion on and into the media. Since decreasing hydraulic loading did not appear to affect the effluent phosphorus concentration, it would appear the rate limiting step is the diffusion from the bulk liquid to liquid film surrounding the solid. However, differences in EBCT in Phase 1 and in Phase 2 could not be demonstrated. Consequently which is the rate limiting step is unclear. Research by Brooks et al using wollastonite [41] indicated that hydraulic residence time (similar to EBCT) was a determining factor in phosphorus removal, and the present research showed similar trends though not statistically significant.

5.2 Role of Biological and Nutritional Content in the Source Wastewater

An unplanned, though critical lesson learned in this study, is if the organic and nutritional content of onsite produced wastewater can be high enough to cause bacterial growth in the reactor, the media will not be effective. In Phase 2 initially only total phosphorus was measured, and showed high variability. This variability was determined to be the result of microbial flocks sloughing off the media. Consequently, the measurement of soluble phosphorus was initiated as the sloughed biomass was filtered out before analyzing.

In Phase 1 the primary analytical parameter was total phosphorus, and its concentration was stable. The wastewater characteristics in Phase 1 and did not support biological growth (Table 5). In Phase 2 this was not the case. The average

COD level was substantially higher (Table 5) and spikes in total phosphorus concentration along with the appearance of cloudy brownish material in the effluent were determined to be the result of sloughing biofilm. As well, SEM images of media taken from the tops of the reactors verified the presence of microbial growth.

Table 8. Influent Wastewater Characterization.

Parameter	**Phase 1**	**Phase 2**
	Average Concentration (mg/L)	**Average Concentration (mg/L)**
Nitrate-N	33.6	Not Detected
Silica	NA	19.0
Sulfate	NA	5.4
$TBOD_5$	NA	22
TKN	NA	53
Ammonia-N	ND	53.3^{+}
Alkalinity (as $CaCO_3$)	219	103^{**+}
Arsenic	NA	0.005
Calcium	NA	38.2
Iron	NA	3.14
Magnesium	NA	11.8
Manganese	NA	0.23
Total Solids	NA	765**
pH	8.08	7.5**
Tot. COD	19	55**
Sol. COD	NA	42**
Tot. Phosphorus	5	6.81**
Sol. Phosphorus	NA	5.89**

Notes: In Phase 1, each value is an average of 3 samples. Samples collected on March 18, 2010. In Phase 2, all samples collected on April 5, 2011 and analyzed in duplicate unless noted otherwise.

**Samples collected 6/29/2011

$^{+}$Analyzed in Triplicate

ND: Not Detected

NA: Not Available

Further evidence for the growth and sloughing of biofilm flocks is in the significant variation of total and soluble effluent COD and its correlation with increases in total phosphorus effluent concentration. Effluent containing bacteria would have a high COD level. To provide evidence that increased levels of total phosphorus in the effluent was indicative of the sloughing of bacterial growth, total effluent phosphorus was compared to total effluent COD for all four columns. The resulting R^2 value was 0.6722, a relatively strong correlation (Appendix E). Correlation of soluble P with total COD in the effluent was also examined. The correlation coefficient comparing these was R^2 = 0.006 (Appendix E). This very low correlation supports the notion that bacterial sloughing did not affect the sorption of soluble P to the media and the use of soluble phosphorus as the primary analytical parameter in determining media efficiency.

Standard deviations in total phosphorus to soluble phosphorus ratios give an idea of the degree to which total effluent phosphorus spikes occurred. Notice that the influent ratio is steady, but variability is high in the effluent (Table 9).

Table 9. Average Soluble Phosphorus Concentrations and Ratios of Total to Soluble Phosphorus Concentrations for Source Wastewater and the Effluent of Each Reactor, with Standard Deviations.

Wastewater	Average Soluble P (mg/L)	Standard Deviation (ave sol P)	Average tot P/sol P	Standard Deviation (ave tot P/sol P)
Influent	5.84	0.46	1.17	0.08
Effluent for:				
0.07/mL/min/cm^2; EBCT= 190 min	0.86	0.25	3.80	1.99
0.05 mL/min/cm^2; EBCT= 60 min	1.40	0.78	7.98	12.19
0.12 mL/min/cm^2; EBCT= 60 min	2.37	1.20	2.68	2.13
0.22 mL/min/cm^2; EBCT= 60 min	1.06	0.46	8.04	8.29

The growth of biofilm was a clear disadvantage. Besides decreasing the performance of the media, the practicality of removing biofilm from the media for media re-use is questionable. Measures to remedy this are needed for the media to be effective and flexible enough for use in less treated onsite wastewater treatment. Resulting spikes of effluent total phosphorus are an environmental issue and total phosphorus is the parameter that is regulated if there is a phosphorus limit imposed.

Besides decreasing the performance of the media, the practicality of removing biofilm from the media for media re-use is questionable. One possible treatment method for the removal of biofilm from the media is the use of enzymes such as those used in the removal of biofilms from medical equipment and contact lenses. These enzymes are species specific [47], and determining what the needed enzymes would be for the particular microbial strains growing on the media would require study. Additionally the effectiveness of such enzymes to remove a biofilm on this particular media, and whether the media would retain its performance ability is unknown, so would also require study.

If the treatment of wastewater were improved before it enters the reactor (as it was in Phase 1) the growth of biofilm on the media would be avoided. Another option (which was preliminarily explored, though not conclusively at the end of Phase 2) is to add media with disinfecting qualities. A more conventional treatment approach could be to disinfect the reactor influent using chlorine or UV light or to filter the sloughed biofilm from the effluent.

5.3 Future Needs

Each hypothesis was proven. However, further studies to allow for practical implementation are required as presented below.

- Based on literature and trends from this research hydraulic loading appears not to be a determining factor in phosphorus removal efficiency; further study is warranted to rule out the effect of hydraulic loading greater than 0.22 mL/min/cm^2
- It is necessary to determine what the minimum EBCT is in a controlled study to meet treatment goals, as to minimize the amount of media needed for field-scale systems. This will reduce capital costs although it will also reduce the capacity of the media. In this study, the rate at which influent flowed into the system was slow; for a larger volume of wastewater, the rate would have to be faster to be practical.
- Phase 1 used two reactors in series. This made possible the use of remaining capacity in a reactor which had lost its ability to remove phosphorus to the desired effluent limit by moving it to the first position. A future study could look at optimal rotating of reactors to conserve media.
- A complete cost analysis is needed for: the use of the media in treating wastewater, including an estimation of the revenue potential for regenerating the media and harvesting the phosphorus.
- Further study is needed to determine the best course of action in terms of safety and cost for preventing or treating microbial growth on the media.

- Further study is warranted to determine what effect, if any, there is on the release of the media particles into the environment.

There is promise for the use of this media in other applications including the following:

- Constructed wetland, treatment of agricultural runoff.
- Tile drain runoff.
- Manure management strategies.
- Food processing wastewater treatment

The incorporation of the media into tile drain could be a valuable technology, allowing for phosphorus removal wherever tile drain can be used. Prevention of the release of media particles would have to be considered, as well as effects of changing ground water levels and different soil types.

In conclusion, not only is there the need to keep excess phosphorus from entering the environment, a demonstrable health and safety concern, there is a need to use both freshwater and phosphorus conservatively. Onsite wastewater treatment allows water to be returned to the aquifer where it came from. The use of filter media such as the one used in this study allows for the recovery of phosphorus and deliberate reuse of a non-renewable resource where it is needed.

APPENDICES

APPENDIX A:

Spreadsheet Used in Calculation of Phase 1 Cumulative Loading

Table 10. Phase One, Two Column System, 7/09/2008 - 9/10/2008, Cumulative Loading Spreadsheet Part A.

Date	Day	Time Measured	Time to Next (hours)	Beginning Flow (ml/min)	Adjusted Flow (ml/min)	Average Flow (ml/min)	Influent (mg P/L)	Effluent (mg P/L)
7/9/2008	0	12.00		10	10	5	7.20	3.70
7/13/2008	4	15.00	99.00	10	10	10	12.90	4.90
7/14/2008	5	14.00	11.00	10	10	10	7.00	2.50
7/15/2008	6	9.00	31.00	10	10	10	6.20	1.40
7/15/2008	6	14.00	5.00	10	10	10	6.20	2.00
7/18/2008	9	14.00	72.00	10	10	10	6.40	1.70
7/21/2008	12	12.30	70.30	10	10	10	6.50	1.10
7/23/2008	14	12.00	47.70	10	10	10	7.00	2.10
7/25/2008	16	12.00	48.00	10	10	10	8.00	2.20
7/28/2008	19	12.00	72.00	10	10	10	7.60	2.10
7/30/2008	21	16.00	52.00	10	10	10	7.30	2.40
8/1/2008	23	8.00	40.00	10	10	10	7.00	2.10
8/5/2008	27	14.00	102.00	10	10	10	6.80	3.00
8/6/2008	28	16.00	26.00	10	10	10	7.10	2.40
8/7/2008	29	14.00	22.00	10	10	10	6.60	2.80
8/11/2008	33	12.00	94.00	10	10	10	6.50	3.70
8/13/2008	35	12.00	48.00	10	10	10	7.20	3.50
8/14/2008	36	12.00	24.00	10	10	10	6.20	3.70
8/18/2008	40	12.00	96.00	10	10	10	5.70	3.70
8/21/2008	43	12.00	72.00	10	10	10	6.20	3.80
8/26/2008	48	12.00	120.00	10	10	10	6.10	4.10
8/29/2008	51	12.00	72.00	10	10	10	6.50	4.20
9/3/2008	56	12.00	120.00	10	10	10	6.20	4.00
9/4/2008	57	12.00	24.00	10	10	10	6.30	4.00
9/10/2008	63	12.00	144.00	10	10	10	6.60	4.10

Table 11. Phase One, Two Column System, 9/12/2008 - 3/17/2008, Cumulative Loading Spreadsheet Part A.

Date	Day	Time Measured	Time to Next (hours)	Beginning Flow (ml/min)	Adjusted Flow (ml/min)	Average Flow (ml/min)	Influent (mg/L P)	Effluent (mg/L P)
9/12/2008	65	12.00	48.00	10	10	10	7.20	4.30
9/18/2008	71	12.00	144.00	10	10	10	7.40	4.90
9/19/2008	72	12.00	24.00	10	10	10	6.20	3.50
9/24/2008	77	12.00	120.00	10	10	10	5.10	2.20
10/24/2008	105	12.00	672.00	10	10	10	9.60	7.40
10/27/2008	108	12.00	72.00	10	10	10	9.80	7.00
11/3/2008	116	12.00	192.00	10	10	10	7.40	4.20
11/6/2008	119	12.00	72.00	10	10	10	8.00	5.00
11/9/2008	121	12.00	48.00	10	0	10	8.20	5.30
11/12/2008	125	12.00	144.00	0	10	0	8.30	5.50
11/14/2008	127	12.00	192.00	10	10	10	8.80	5.60
11/18/2008	129	12.00	48.00	10	10	10	8.40	7.00
11/21/2008	132	12.00	72.00	10	10	10	8.00	4.20
12/2/2008	143	12.00	264.00	10	10	10	11.80	4.40
12/15/2008	156	12.00	312.00	10	10	10	6.40	3.40
12/17/2008	158	12.00	48.00	10	10	10	10.80	5.40
12/18/2008	159	12.00	24.00	1.08	1.10	5.54	5.60	1.30
1/5/2009	177	12.00	432.00	1.08	1.10	1.09	4.30	0.90
1/9/2009	181	13.00	97.00	1.08	1.10	1.09	3.90	0.70
1/16/2009	188	11.00	166.00	1.22	1.20	1.16	5.50	0.80
2/13/2009	215	18.00	655.00	1.18	1.20	1.19	7.60	3.50
2/19/2009	221	10.00	136.00	1.20	1.20	1.20	5.70	1.80
2/23/2009	225	12.00	98.00	1.18	1.20	1.19	6.40	3.15
3/2/2009	232	12.00	168.00	1.19	1.20	1.19	5.00	2.20
3/17/2009	247	12.00	360.00	0.82	0.82	1.01	4.10	1.50

Table 12. Phase One, Two Column System, 3/25/2009 -11/16/2009, Cumulative Loading Spreadsheet Part A.

Date	Day	Time Measured	Time to Next (hours)	Beginning Flow (ml/min)	Adjusted Flow (ml/min)	Average Flow (ml/min)	Influent (mg/L P)	Effluent (mg/L P)
3/25/2009	255	12.00	192.00	0.82	0.80	0.82	3.60	0.70
3/30/2009	260	12.00	120.00	0.82	0.82	0.81	3.20	1.20
4/13/2009	274	12.00	336.00	0.80	0.80	0.81	3.80	0.90
4/22/2009	283	13.00	205.00	0.79	0.79	0.80	2.80	1.30
5/14/2009	305	12.00	539.00	0.78	0.78	0.79	5.20	1.00
7/2/2009	354	9.00	1173.00	1.90	0.80	1.34	4.60	0.50
7/29/2009	381	7.45	646.45	1.60	0.80	1.20	5.40	0.90
8/3/2009	386	11.00	123.55	0.80	0.80	0.80	3.60	0.80
8/10/2009	393	12.30	169.30	0.80	0.80	0.80	2.70	0.80
8/20/2009	403	10.30	238.00	0.80	0.80	0.80	3.40	1.00
8/31/2009	414	13.00	254.70	0.80	0.80	0.80	5.00	2.10
9/16/2009	430	10.00	393.00	0.80	0.80	0.80	4.70	1.80
10/6/2009	450	9.00	479.00	0.80	0.80	0.80	3.80	1.80
10/11/2009	455	15.00	114.00	1.30	0.82	1.05	4.50	2.20
10/20/2009	464	15.00	216.00	0.80	0.80	0.81	4.00	1.40
10/23/2009	467	15.00	72.00	0.20	0.60	0.50	3.80	1.10
10/25/2009	469	15.00	48.00	0.40	0.90	0.50	3.60	1.10
11/5/2009	480	10.00	319.00	1.20	0.90	1.05	2.80	1.10
11/6/2009	481	10.00	295.00	0.70	0.80	0.80	2.70	1.10
11/10/2009	485	10.00	96.00	0.80	0.00	0.80	3.20	1.10
11/11/2009	486	10.00	24.00	0.00	0.80	0.00	3.40	1.20
11/12/2009	487	10.00	24.00	0.80	0.80	0.80	3.50	1.20
11/13/2009	488	10.00	24.00	0.80	0.80	0.80	3.60	1.20
11/15/2009	490	10.00	48.00	0.80	0.80	0.80	3.90	1.20
11/16/2009	491	10.00	24.00	0.80	0.80	0.80	4.00	1.20

Table 13. Phase One, Two Column System, 11/22/2009 - 1/16/2010, Cumulative Loading Spreadsheet Part A.

Date	Day	Time Measured	Time to Next (hours)	Beginning Flow (ml/min)	Adjusted Flow (ml/min)	Average Flow (ml/min)	Influent (mg/L P)	Effluent (mg/L P)
11/22/2009	497	10.00	144.00	0.80	0.00	0.80	3.50	1.30
11/23/2009	498	10.00	24.00	0.00	0.80	0.00	3.60	1.30
11/24/2009	499	12.00	26.00	0.80	0.80	0.80	3.70	1.30
11/25/2009	500	12.00	24.00	0.80	0.80	0.80	3.70	1.30
11/27/2009	502	12.00	48.00	0.80	0.80	0.80	3.30	1.40
11/30/2009	505	12.00	72.00	0.60	0.60	0.70	4.00	1.40
12/1/2009	506	12.00	24.00	0.70	0.70	0.65	4.10	1.40
12/4/2009	509	12.00	72.00	0.80	0.80	0.75	4.20	1.50
12/7/2009	512	12.00	72.00	0.80	0.80	0.80	4.20	1.60
12/9/2009	514	11.00	47.00	0.90	0.60	0.85	4.50	1.60
12/14/2009	519	12.00	121.00	0.60	0.00	0.60	4.70	1.60
12/22/2009	527	18.50	186.50	0.00	1.10	0.00	4.80	1.60
12/22/2009	527	20.50	14.00	1.10	0.60	1.10	4.80	1.60
12/23/2009	528	12.00	15.50	0.60	0.60	0.60	4.80	1.60
12/29/2009	534	22.50	154.50	1.20	1.20	0.90	4.60	1.80
1/1/2010	537	19.00	68.50	0.50	0.50	0.85	4.50	1.40
1/4/2010	539	10.00	39.00	0.10	2.00	0.30	4.30	1.90
1/5/2010	540	14.50	28.50	1.80	1.80	1.90	4.30	1.90
1/6/2010	541	12.00	21.50	2.90	1.80	2.35	4.20	2.00
1/8/2010	543	14.75	50.75	1.50	1.50	1.65	4.20	2.00
1/9/2010	545	17.50	50.75	1.20	1.80	1.35	4.10	2.00
1/10/2010	546	13.50	20.00	0.80	0.80	1.30	4.10	2.00
1/11/2010	547	16.00	26.50	0.70	0.70	0.75	4.10	2.00
1/14/2010	550	9.50	65.50	0.00	1.20	0.35	4.17	2.07
1/16/2010	552	18.00	56.50	1.00	0.80	1.10	4.20	2.10

Table 14. Phase One, Two Column System, 1/18/2010 – 3/08/2010, Cumulative Loading Spreadsheet Part A.

Date	Day	Time Measured	Time to Next (hours)	Beginning Flow (ml/min)	Adjusted Flow (ml/min)	Average Flow (ml/min)	Influent (mg P/L)	Effluent (mg P/L)
1/18/2010	554	11.00	41.00	1.00	1.00	0.90	4.06	1.99
1/20/2010	556	11.00	48.00	1.20	1.20	1.10	3.91	1.87
1/22/2010	558	11.00	48.00	1.00	1.00	1.10	3.84	1.81
1/23/2010	559	16.00	29.00	0.80	0.80	0.90	3.70	1.70
1/24/2010	560	13.00	21.00	1.10	1.10	0.95	3.95	1.85
1/25/2010	561	13.50	24.50	0.10	0.60	0.60	4.20	2.00
1/27/2010	563	11.00	45.50	0.10	1.60	0.35	4.17	2.30
1/29/2010	565	14.50	51.50	0.90	0.90	1.25	4.13	2.60
1/31/2010	567	18.00	51.50	1.00	1.00	0.95	4.10	2.90
2/2/2010	569	12.00	42.00	1.90	0.80	1.45	4.50	3.16
2/3/2010	570	17.00	29.00	0.70	0.70	0.75	4.70	3.29
2/6/2010	573	13.00	68.00	0.70	0.70	0.70	5.30	3.67
2/7/2010	574	14.50	25.50	1.20	1.20	0.95	5.50	3.80
2/14/2010	581	18.50	172.00	1.30	1.30	1.25	4.60	2.90
2/21/2010	589	16.00	189.50	1.50	0.80	1.40	4.60	3.50
3/3/2010	599	17.00	241.00	0.90	0.90	0.85	4.00	2.30
3/8/2010	604	11.00	114.00	0.90	0.90	0.90	5.00	3.00

Table 15. Phase One, Two Column System, 7/9/2008 – 9/10/2008, Cumulative Loading Spreadsheet Part B.

Date	Day	Diff. (mg P/L)	Immed. Vol. (L)	Total Vol (L)	Mass P removed (mg)	Cum. Mass P Removed (mg)	Cum. Mass P Removed (g)	Mass P Influent (mg)
7/9/2008	0		7.2	3.6		0	0	
7/13/2008	4	8.00	52.2	52.2	417.60	417.60	0.42	673.38
7/14/2008	5	4.50	13.8	13.8	62.10	479.70	0.48	96.60
7/15/2008	6	4.80	18.6	18.6	89.28	568.98	0.57	115.32
7/15/2008	6	4.20	3.0	3.0	12.60	581.58	0.58	18.60
7/18/2008	9	4.70	43.2	43.2	203.04	784.62	0.78	276.48
7/21/2008	12	5.40	42.2	42.2	227.77	1012.39	1.01	274.17
7/23/2008	14	4.90	28.6	28.6	140.24	1152.63	1.15	200.34
7/25/2008	16	5.80	28.8	28.8	167.04	1319.67	1.32	230.40
7/28/2008	19	5.50	43.2	43.2	237.60	1557.27	1.56	328.32
7/30/2008	21	4.90	31.2	31.2	152.88	1710.15	1.71	227.76
8/1/2008	23	4.90	24.0	24.0	117.60	1827.75	1.83	168.00
8/5/2008	27	3.80	61.2	61.2	232.56	2060.31	2.06	416.16
8/6/2008	28	4.70	15.6	15.6	73.32	2133.63	2.13	110.76
8/7/2008	29	3.80	13.2	13.2	50.16	2183.79	2.18	87.12
8/11/2008	33	2.80	56.4	56.4	157.92	2341.71	2.34	366.60
8/13/2008	35	3.70	28.8	28.8	106.56	2448.27	2.45	207.36
8/14/2008	36	2.50	14.4	14.4	36.00	2484.27	2.48	89.28
8/18/2008	40	2.00	57.6	57.6	115.20	2599.47	2.60	328.32
8/21/2008	43	2.40	43.2	43.2	103.68	2703.15	2.70	267.84
8/26/2008	48	2.00	72.0	72.0	144.00	2847.15	2.85	439.20
8/29/2008	51	2.30	43.2	43.2	99.36	2946.51	2.95	280.80
9/3/2008	56	2.20	72.0	72.0	158.40	3104.91	3.10	446.40
9/4/2008	57	2.30	14.4	14.4	33.12	3138.03	3.14	90.72
9/10/2008	63	2.50	86.4	86.4	216.00	3354.03	3.35	570.24

Table 16. Phase One, Two Column System, 9/12/2008 – 3/17/2009, Cumulative Loading Spreadsheet Part B.

Date	Day	Diff. (mg P/L)	Immed. Vol. (L)	Total Vol (L)	Mass P removed (mg)	Cum. Mass P Removed (mg)	Cum. Mass P Removed (g)	Mass P Influent (mg)
9/12/2008	65	2.90	28.8	28.8	83.52	3437.55	3.44	207.36
9/18/2008	71	2.50	86.4	86.4	216.00	3653.55	3.65	639.36
9/19/2008	72	2.70	14.4	14.4	38.88	3692.43	3.69	89.28
9/24/2008	77	2.90	72.0	72.0	208.80	3901.23	3.90	367.20
10/24/2008	105	2.20	403.2	403.2	887.04	4788.27	4.79	3870.72
10/27/2008	108	2.80	43.2	43.2	120.96	4909.23	4.91	423.36
11/3/2008	116	3.20	115.2	115.2	368.64	5277.87	5.28	852.48
11/6/2008	119	3.00	43.2	43.2	129.60	5407.47	5.41	345.60
11/9/2008	121	2.90	28.8	28.8	83.52	5490.99	5.49	236.16
11/12/2008	125	2.80	43.2	0.0	0.00	5490.99	5.49	0.00
11/14/2008	127	5.60	115.2	115.2	645.12	6136.11	6.14	1013.76
11/18/2008	129	1.40	28.8	28.8	40.32	6176.43	6.18	241.92
11/21/2008	132	3.80	21.6	43.2	164.16	6340.59	6.34	345.60
12/2/2008	143	7.40	158.4	158.4	1172.16	7512.75	7.51	1869.12
12/15/2008	156	3.00	187.2	187.2	561.60	8074.35	8.07	1198.08
12/17/2008	158	5.40	28.8	28.8	155.52	8229.87	8.23	311.04
12/18/2008	159	4.30	8.0	8.0	34.29	8264.16	8.26	44.66
1/5/2009	177	3.40	143.5	28.2	95.88	8360.04	8.36	121.26
1/9/2009	181	3.20	32.2	6.3	20.26	8380.31	8.38	24.70
1/16/2009	188	4.70	55.9	11.6	54.30	8434.61	8.43	63.54
2/13/2009	215	4.10	44.8	46.8	191.74	8626.35	8.63	355.43
2/19/2009	221	3.90	9.4	9.8	38.19	8664.54	8.66	55.81
2/23/2009	225	3.25	6.7	7.0	22.74	8687.28	8.69	44.78
3/2/2009	232	2.80	12.0	12.0	33.68	8720.96	8.72	60.14
3/17/2009	247	2.60	21.8	21.8	56.61	8777.57	8.78	89.27

Table 17. Phase One, Two Column System 3/25/2009 – 11/16/2009, Cumulative Loading Spreadsheet Part B.

Date	Day	Diff. (mg P/L)	Immed. Vol. (L)	Total Vol (L)	Mass P removed (mg)	Cum. Mass P Removed (mg)	Cum. Mass P Removed (g)	Mass P Influent (mg)
3/25/2009	255	2.90	11.6	9.4	645.12	6136.11	6.14	1013.76
3/30/2009	260	2.00	7.3	5.8	40.32	6176.43	6.18	241.92
4/13/2009	274	2.90	20.2	16.3	164.16	6340.59	6.34	345.60
4/22/2009	283	1.50	9.9	9.8	1172.16	7512.75	7.51	1869.12
5/14/2009	305	4.20	25.6	25.5	561.60	8074.35	8.07	1198.08
7/2/2009	354	4.10	95.7	94.5	155.52	8229.87	8.23	311.04
7/29/2009	381	4.50	46.5	46.5	34.29	8264.16	8.26	44.66
8/3/2009	386	2.80	5.9	5.9	95.88	8360.04	8.36	121.26
8/10/2009	393	1.90	8.0	8.1	20.26	8380.31	8.38	24.70
8/20/2009	403	2.40	11.4	11.4	54.30	8434.61	8.43	63.54
8/31/2009	414	2.90	12.2	12.2	191.74	8626.35	8.63	355.43
9/16/2009	430	2.90	18.9	18.9	38.19	8664.54	8.66	55.81
10/6/2009	450	2.00	23.0	23.0	22.74	8687.28	8.69	44.78
10/11/2009	455	2.30	7.2	7.2	33.68	8720.96	8.72	60.14
10/20/2009	464	2.60	10.4	10.5	56.61	8777.57	8.78	89.27
10/23/2009	467	2.70	2.2	2.2	645.12	6136.11	6.14	1013.76
10/25/2009	469	2.50	1.7	1.4	40.32	6176.43	6.18	241.92
11/5/2009	480	1.70	19.4	20.1	164.16	6340.59	6.34	345.60
11/6/2009	481	1.60	13.5	14.2	1172.16	7512.75	7.51	1869.12
11/10/2009	485	2.10	4.6	4.6	561.60	8074.35	8.07	1198.08
11/11/2009	486	2.20	0.4	0.0	0.00	9897.76	9.90	0.00
11/12/2009	487	2.30	1.2	1.2	2.65	9900.41	9.90	4.03
11/13/2009	488	2.40	1.2	1.2	2.76	9903.18	9.90	4.15
11/15/2009	490	2.70	1.2	2.3	6.22	9909.40	9.91	8.99
11/16/2009	491	2.80	1.2	1.2	3.23	9912.62	9.91	4.61

Table 18. Phase One, Two Column System 11/22/2009 – 1/16/2010, Cumulative Loading Spreadsheet Part B.

Date	Day	Diff. (mg P/L)	Immed. Vol. (L)	Total Vol (L)	Mass P removed (mg)	Cum. Mass P Removed (mg)	Cum. Mass P Removed (g)	Mass P Influent (mg)
11/22/2009	497	2.20	6.9	6.9	15.21	9927.83	9.93	24.19
11/23/2009	498	2.30	0.6	0.0	0.00	9927.83	9.93	0.00
11/24/2009	499	2.40	1.2	1.2	3.00	9930.83	9.93	4.62
11/25/2009	500	2.40	1.2	1.2	2.76	9933.59	9.93	4.26
11/27/2009	502	1.90	1.2	2.3	4.38	9937.97	9.94	7.60
11/30/2009	505	2.60	3.0	3.0	7.86	9945.83	9.95	12.10
12/1/2009	506	2.70	1.1	0.9	2.53	9948.36	9.95	3.84
12/4/2009	509	2.70	3.5	3.2	8.75	9957.11	9.96	13.61
12/7/2009	512	2.60	3.5	3.5	8.99	9966.09	9.97	14.52
12/9/2009	514	2.90	2.1	2.4	6.95	9973.04	9.97	10.79
12/14/2009	519	3.10	4.7	4.4	13.50	9986.55	9.99	20.47
12/22/2009	527	3.20	4.5	0.0	0.00	9986.55	9.99	0.00
12/22/2009	527	3.20	0.8	0.9	2.96	9989.50	9.99	4.44
12/23/2009	528	3.20	0.6	0.6	1.79	9991.29	9.99	2.68
12/29/2009	534	2.80	5.6	8.3	23.36	10014.65	10.01	38.38
1/1/2010	537	3.10	3.3	3.5	10.83	10025.48	10.03	15.72
1/4/2010	539	2.40	0.8	0.7	1.68	10027.16	10.03	3.02
1/5/2010	540	2.40	2.1	3.2	7.80	10034.96	10.03	13.97
1/6/2010	541	2.20	2.6	3.0	6.67	10041.63	10.04	12.73
1/8/2010	543	2.20	3.0	5.0	11.05	10052.68	10.05	21.10
1/9/2010	545	2.10	4.9	4.1	8.63	10061.32	10.06	16.85
1/10/2010	546	2.10	1.6	1.6	3.28	10064.59	10.06	6.40
1/11/2010	547	2.10	2.0	1.2	2.50	10067.10	10.07	4.89
1/14/2010	550	2.10	2.9	1.4	2.89	10069.98	10.07	5.74
1/16/2010	552	2.10	4.7	3.7	7.83	10077.82	10.08	15.66

Table 19. Phase One, Two Column System 1/18/2010 – 3/8/2010, Cumulative Loading Spreadsheet Part B.

Date	Day	Diff. (mg P/L)	Immed. Vol. (L)	Total Vol (L)	Mass P removed (mg)	Cum. Mass P Removed (mg)	Cum. Mass P Removed (g)	Mass P Influent (mg)
1/18/2010	554	2.07	2.2	2.2	4.58	10082.40	10.08	8.99
1/20/2010	556	2.04	2.7	3.2	6.46	10088.86	10.09	12.39
1/22/2010	558	2.03	3.2	3.2	6.43	10095.29	10.10	12.17
1/23/2010	559	2.00	1.4	1.6	3.13	10098.42	10.10	5.79
1/24/2010	560	2.10	1.3	1.2	2.51	10100.94	10.10	4.73
1/25/2010	561	2.20	1.0	0.9	1.94	10102.88	10.10	3.70
1/27/2010	563	1.87	1.5	1.0	1.79	10104.67	10.10	3.98
1/29/2010	565	1.53	2.6	3.9	5.91	10110.57	10.11	15.95
1/31/2010	567	1.20	3.2	2.9	3.52	10114.10	10.11	12.04
2/2/2010	569	1.34	3.2	3.7	4.90	10118.99	10.12	16.44
2/3/2010	570	1.41	2.0	1.3	1.84	10120.83	10.12	6.13
2/6/2010	573	1.63	3.3	2.9	4.66	10125.49	10.13	15.14
2/7/2010	574	1.70	1.7	1.5	2.47	10127.96	10.13	7.99
2/14/2010	581	1.70	10.8	12.9	21.93	10149.89	10.15	59.34
2/21/2010	589	1.10	12.5	15.9	17.51	10167.40	10.17	73.22
3/3/2010	599	1.70	11.6	12.3	20.89	10188.29	10.19	49.16
3/8/2010	604	2.00	7.2	6.2	12.31	10200.61	10.20	30.78

Table 20. Phase One, Two Column System 7/9/2008 – 9/10/2008, Cumulative Loading Spreadsheet Part C.

Date	Day	Cum. Mass P Influent (mg)	Cum. Mass P Influent (g)	% Removal	Notes
7/9/2008	0	0.00	0.00	0.0%	
7/13/2008	4	673.38	0.67	62.0%	
7/14/2008	5	769.98	0.77	64.3%	
7/15/2008	6	885.30	0.89	77.4%	Analyzed by MSU PSS Lab.
7/15/2008	6	903.90	0.90	67.7%	
7/18/2008	9	1180.38	1.18	73.4%	
7/21/2008	12	1454.55	1.45	83.1%	
7/23/2008	14	1654.89	1.65	70.0%	
7/25/2008	16	1885.29	1.89	72.5%	
7/28/2008	19	2213.61	2.21	72.4%	
7/30/2008	21	2441.37	2.44	67.1%	
8/1/2008	23	2609.37	2.61	70.0%	
8/5/2008	27	3025.53	3.03	55.9%	
8/6/2008	28	3136.29	3.14	66.2%	
8/7/2008	29	3223.41	3.22	57.6%	
8/11/2008	33	3590.01	3.59	43.1%	
8/13/2008	35	3797.37	3.80	51.4%	
8/14/2008	36	3886.65	3.89	40.3%	
8/18/2008	40	4214.97	4.21	35.1%	
8/21/2008	43	4482.81	4.48	38.7%	
8/26/2008	48	4922.01	4.92	32.8%	
8/29/2008	51	5202.81	5.20	35.4%	
9/3/2008	56	5649.21	5.65	35.5%	
9/4/2008	57	5739.93	5.74	36.5%	
9/10/2008	63	6310.17	6.31	37.9%	

Table 21. Phase One, Two Column System 9/12/2008 – 3/17/2009, Cumulative Loading Spreadsheet Part C.

Date	Day	Cum. Mass P Influent (mg)	Cum. Mass P Influent (g)	% Removal	Notes
9/12/2008	65	6517.53	6.52	40.3%	
9/18/2008	71	7156.89	7.16	33.8%	
9/19/2008	72	7246.17	7.25	43.5%	
9/24/2008	77	7613.37	7.61	56.9%	
10/24/2008	105	11484.09	11.48	22.9%	Second column tubing was clogged and fixed.
10/27/2008	108	11907.45	11.91	28.6%	
11/3/2008	116	12759.93	12.76	43.2%	
11/6/2008	119	13105.53	13.11	37.5%	
11/9/2008	121	13341.69	13.34	35.4%	11/9/2008 date was artificially inserted as zero flow spotted on 11/4/2008.
11/12/2008	125	13341.69	13.34	33.7%	
11/14/2008	127	14355.45	14.36	63.6%	
11/18/2008	129	14597.37	14.60	16.7%	
11/21/2008	132	14942.97	14.94	47.5%	
12/2/2008	143	16812.09	16.81	62.7%	
12/15/2008	156	18010.17	18.01	46.9%	
12/17/2008	158	18321.21	18.32	50.0%	
12/18/2008	159	18365.87	18.37	76.8%	Q adjusted.
1/5/2009	177	18487.13	18.49	79.1%	
1/9/2009	181	18511.83	18.51	82.1%	
1/16/2009	188	18575.37	18.58	85.5%	
2/13/2009	215	18930.80	18.93	53.9%	
2/19/2009	221	18986.62	18.99	68.4%	
2/23/2009	225	19031.40	19.03	50.8%	
3/2/2009	232	19091.54	19.09	56.0%	
3/17/2009	247	19180.81	19.18	63.4%	

Table 22. Phase One, Two Column System 3/25/2009 – 11/16/2009, Cumulative Loading Spreadsheet Part C.

Date	Day	Cum. Mass P Influent (mg)	Cum. Mass P Influent (g)	% Removal	Notes
3/25/2009	255	19214.74	19.21	80.6%	
3/30/2009	260	19233.44	19.23	62.5%	
4/13/2009	274	19295.50	19.30	76.3%	
4/22/2009	283	19322.91	19.32	53.6%	
5/14/2009	305	19455.43	19.46	80.8%	
7/2/2009	354	19889.90	19.89	89.1%	
7/29/2009	381	20141.24	20.14	83.3%	
8/3/2009	386	20162.59	20.16	77.8%	
8/10/2009	393	20184.53	20.18	70.4%	
8/20/2009	403	20223.37	20.22	70.6%	
8/31/2009	414	20284.50	20.28	58.0%	
9/16/2009	430	20373.16	20.37	61.7%	
10/6/2009	450	20460.53	20.46	52.6%	
10/11/2009	455	20492.85	20.49	51.1%	
10/20/2009	464	20534.91	20.53	65.0%	Only Q measured. The rest of data is averaged.
10/23/2009	467	20543.12	20.54	71.1%	
10/25/2009	469	20548.31	20.55	69.4%	Only Q measured. The rest of data is averaged.
11/5/2009	480	20604.58	20.60	60.7%	Only Q measured. The rest of data is averaged.
11/6/2009	481	20586.54	20.59	59.3%	
11/10/2009	485	20601.28	20.60	65.6%	WW Inf. tank not empty. All values averaged.
11/11/2009	486	20601.28	20.60	64.7%	11/11/2009 in AM Inf. tank was found empty.
11/12/2009	487	20605.32	20.61	65.7%	Only Q measured. The rest of data is averaged.
11/13/2009	488	20609.46	20.61	66.7%	Only Q measured. The rest of data is averaged.
11/15/2009	490	20618.45	20.62	69.2%	Only Q measured. The rest of data is averaged.
11/16/2009	491	20623.06	20.62	70.0%	

Table 23. Phase One, Two Column System 11/22/2009 – 1/16/2010, Cumulative Loading Spreadsheet Part C.

Date	Day	Cum. Mass P Influent (mg)	Cum. Mass P Influent (g)	% Removal	Notes
11/22/2009	497	20647.25	20.65	62.9%	All values averaged.
11/23/2009	498	20647.25	20.65	63.9%	Pump speed was found on "zero".
11/24/2009	499	20651.87	20.65	64.9%	Only Q measured. The rest of data is averaged.
11/25/2009	500	20656.13	20.66	64.9%	Only Q measured. The rest of data is averaged.
11/27/2009	502	20663.73	20.66	57.6%	Only Q measured. The rest of data is averaged.
11/30/2009	505	20675.83	20.68	65.0%	
12/1/2009	506	20679.67	20.68	65.9%	Only Q measured. The rest of data is averaged.
12/4/2009	509	20693.27	20.69	64.3%	Only Q measured. The rest of data is averaged.
12/7/2009	512	20707.79	20.71	61.9%	Only Q measured. The rest of data is averaged.
12/9/2009	514	20718.58	20.72	64.4%	12/14/2009 artificially inserted to account for Q = 0 spotted on 12/16/2009. Unclogged 12/22/2009 6:30 am; Q regained. NOTE: system was clogged some time after 12/14/2009 until 12/22/2009.
12/14/2009	519	20739.05	20.74	66.0%	
12/22/2009	527	20739.05	20.74	66.7%	
12/22/2009	527	20743.48	20.74	66.7%	
12/23/2009	528	20746.16	20.75	66.7%	Only Q measured. The rest of data is averaged.
12/29/2009	534	20784.54	20.78	60.9%	Only Q measured. The rest of data is averaged.
1/1/2010	537	20800.26	20.80	68.9%	
1/4/2010	539	20803.28	20.80	55.8%	Only Q measured. The rest of data is averaged.
1/5/2010	540	20817.25	20.82	55.8%	Only Q measured. The rest of data is averaged.
1/6/2010	541	20829.98	20.83	52.4%	Only Q measured. The rest of data is averaged.
1/8/2010	543	20851.08	20.85	52.4%	Only Q measured. The rest of data is averaged.
1/9/2010	545	20867.94	20.87	51.2%	
1/10/2010	546	20874.33	20.87	51.2%	Inf/Eff data used was from 1/9/2010.
1/11/2010	547	20879.22	20.88	51.2%	Inf/Eff data used was from 1/9/2010.
1/14/2010	550	20884.96	20.88	50.4%	No flow spotted on 1/14/2010. Replaced tubing and probed Eff hose barb of second column.
1/16/2010	552	20900.62	20.90	50.0%	

Table 24. Phase One, Two Column System 1/08/2010 – 3/08/2010, Cumulative Loading Spreadsheet Part C.

Date	Day	Cum. Mass P Influent (mg)	Cum. Mass P Influent (g)	% Removal	Notes
1/18/2010	554	20909.61	20.91	51.0%	Q = 29.5mL/30min. Inf/Eff data is averaged.
1/20/2010	556	20922.00	20.92	52.2%	Q = 42mL/35 min. Inf/Eff data is averaged.
1/22/2010	558	20934.16	20.93	52.9%	Q = 72mL/74min. Inf/Eff data is averaged.
1/23/2010	559	20939.96	20.94	54.1%	Q = 73mL/90min.
1/24/2010	560	20944.68	20.94	53.2%	Q = 75mL/69min. Inf/Eff data is averaged.
1/25/2010	561	20948.39	20.95	52.4%	
1/27/2010	563	20952.37	20.95	44.8%	Q adjusted over 5 hours; Q final = 28mL/18min.
1/29/2010	565	20968.33	20.97	37.0%	Q = 4.5mL/5min. Inf/Eff data is averaged.
1/31/2010	567	20980.36	20.98	29.3%	Q = 385mL/351min.
2/2/2010	569	20996.80	21.00	29.8%	Q adjusted over 2 hours. Q final = 18mL/24min.
2/3/2010	570	21002.94	21.00	30.0%	Q = 7mL/10min. Inf/Eff data is averaged.
2/6/2010	573	21018.07	21.02	30.8%	Q = 7mL/10min. Inf/Eff data is averaged.
2/7/2010	574	21026.07	21.03	30.9%	Q = 98mL/79min.
2/14/2010	581	21085.41	21.09	37.0%	Q = 1060mL/821min.
2/21/2010	589	21158.63	21.16	23.9%	
3/3/2010	599	21207.80	21.21	42.5%	
3/8/2010	604	21238.58	21.24	40.0%	Final Day, Phase 1.

APPENDIX B:

Calculations for Determination of Capacity in Phase 1

Calculations for Determination of Capacity in Phase 1

Table 25. Capacity Calculations from Cumulative Mass Loading.

Calculated from Cumulative Mass Loading			
	Phosphorus Recovered (mg)	Dry Weight of Media (g)	capacity (mg/g)
First Column		111.58	
Second Column		106.34	
Both Columns in Series	10,201	217.92	46.81

Table 26. Capacity Calculations from Digestion Analysis.

Calculated from Digestion Analysis			
Sample Description	Sample Date	Result (mg/kg)	Corrected for New(mg/kg)
First Column (a) -Mixture of All Locations	3/18/2010	46,720.84	
First Column (b)- Mixture of All Locations	3/18/2010	47,093.25	
Average of First Column		46,907.05	30,361.07
Second Column - Top	3/18/2010	36,408.44	
Second Column - Middle	3/18/2010	45,134.99	
Second Column - Bottom	3/18/2010	49,363.98	
Average of Second Column		43,635.80	27,089.82
Unused Media	3/18/2010	16,545.98	
Average Recovery of Phosphorus Over Both Columns (Capacity): 28.73 mg/g			

APPENDIX C:

Calculations for Determination of Phosphorus Sorption to Pea Gravel in Phase 1

Table 27. Calculations for Determination of Phosphorus Sorption to Pea Gravel in Phase 1.

	Mass of Gravel (g)	Approximate Volume of Gravel (mL)
First Column	143.4	100
Second Column	141.8	100
Both Columns in Series	285.2	200

0.2852 kg gravel	113 mg P (from Table 1)	0.5 porosity
	kg soil	

= 16.11 mg (Phosphorus Potentially Sorbed to Gravel)

Total Mass P Removed = 10,201 mg (from Appendix A)

Phosphorus Potentially Sorbed to Gravel as Percentage of Total Mass Removed: (16.11 mg/10,201mg x 100%)

= **1.6 %**

APPENDIX D:

Correlations between Total P and Soluble P Concentration with Total COD Concentration

Phase 2 Correlations between Effluent Total P and Soluble P Concentration with Effluent Total COD Concentration

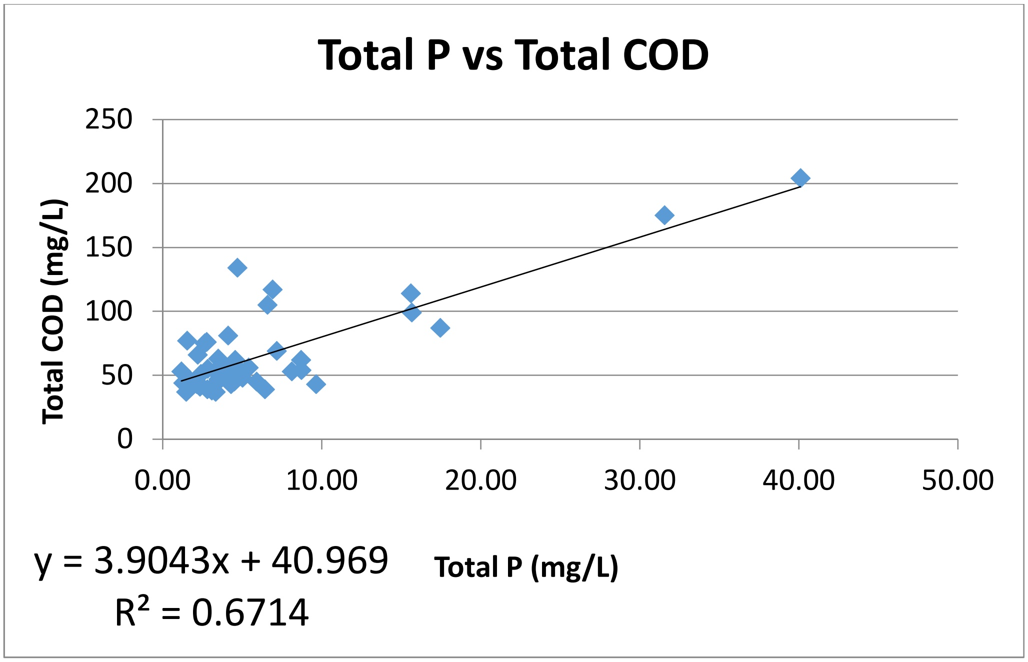


Figure 18: Effluent Total Phosphorus vs. Effluent Total COD.

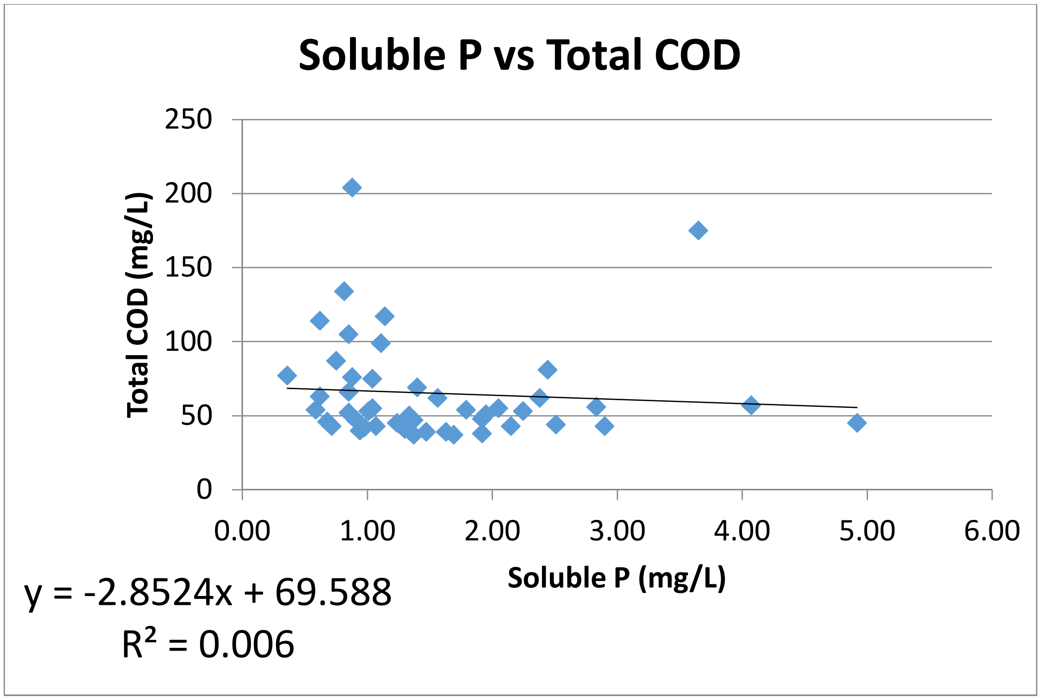


Figure 19: Effluent Soluble Phosphorus vs. Effluent Total COD.

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