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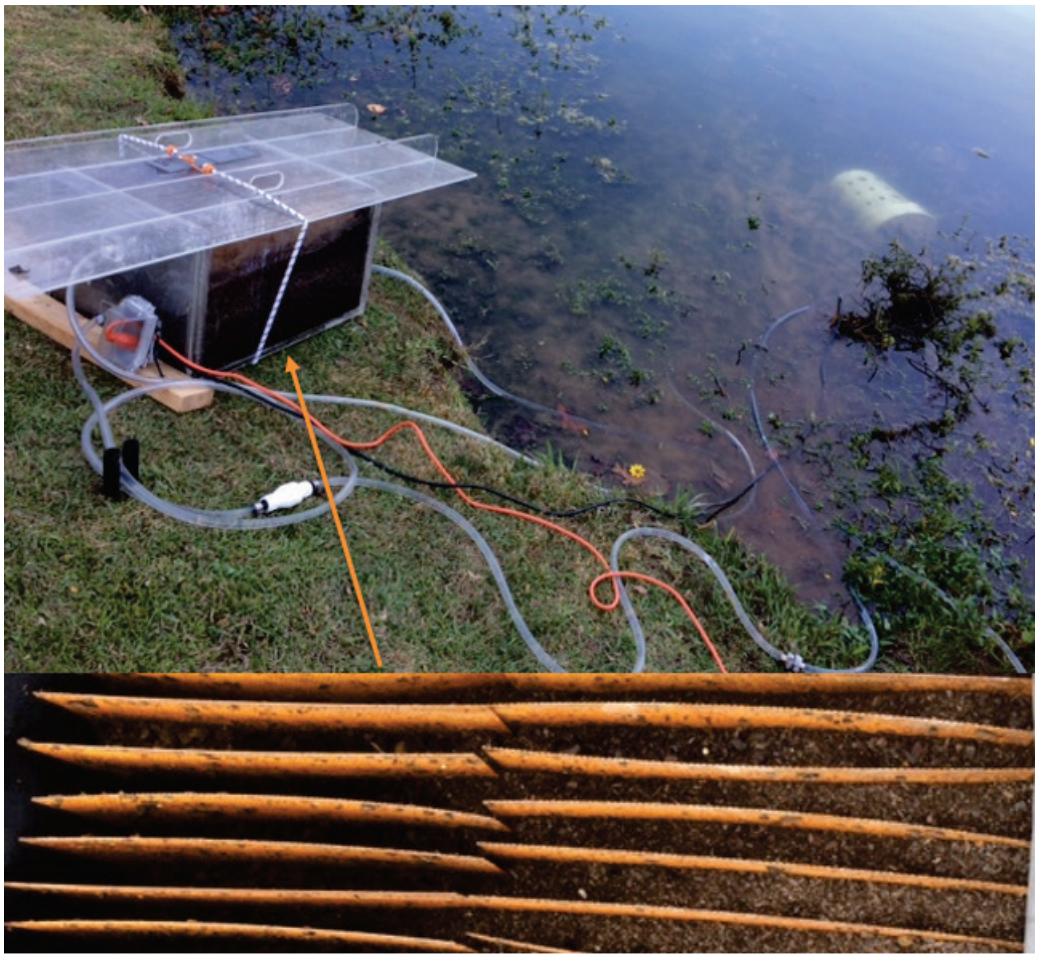
Eutrophication Management via Iron-Phosphorus Binding

Edith L. Martinez-Guerra, Luke A. Gurtowski, and Carina M. Jung

September 2020



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Edith L. Martinez-Guerra, Luke A. Gurtowski, and Carina M. Jung

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Final report

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Vicksburg, MS 39180-6199

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Abstract

The presence of phosphorus (P) in excessive quantities can lead to undesired conditions, such as cyanobacterial/algal bloom. The over-enriched hypertrophic conditions or the excess amounts of nutrients (nitrogen and P, P being the primary nutrient of concern) are the major cause of harmful cyanobacterial blooms, which can be toxic and can also lead to oxygen depletion and anoxic respiration (hypoxia) in the hypolimnion. The presence of iron compounds has been shown to bind phosphorus and diminish harmful algal blooms. Therefore, an iron-plates-packed reactor has been designed to reduce P in surface water. This cost-effective and easy-to-install system has shown promising results in phosphorus reduction.

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Preface

The work reported herein was conducted for the US Army Engineer Research and Development Center (ERDC), Aquatic Plant Control Research Program, Vicksburg, MS, under Funding Account Code 96X3122; AMSCO Code 075098. Dr. Al Cofrancesco was the Technical Director, and Dr. Linda Nelson was the Program Manager.

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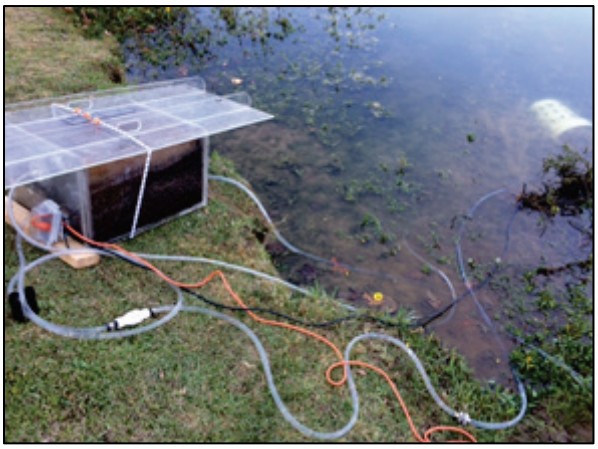
At the time of publication of this report, Dr. Brandon Lafferty was Chief of the Environmental Processes Branch; Mr. Warren P. Lorentz was Chief of the Environmental Processes and Engineering Division; Dr. Ilker Adiguzel was the Director of EL, and Dr. Jack Davis was the Deputy Director.

The Commander of ERDC was COL Teresa A. Schlosser, and the Director was Dr. David W. Pittman.

1 Introduction

The occurrence of algal blooms has increased worldwide in recent decades. Algal blooms include Eukaryotic green algae and cyanobacteria, which is commonly blue-green algae. Different technologies have been developed and implemented to physically and chemically remove algae and/or the nutrients that feed them from water bodies, including chemical treatments (e.g., copper sulfate, hydrogen peroxide), phoslock, mixing, cavitation, and modification to reservoir operation (Medina et al. 2016; Herman et al. 2017; Thomas et al. 2019). Some of these methods have successfully mitigated the blooms, but the problem often recurs (Hallegraeff 1993; Anderson et al. 2002; Miller et al. 2010; Montes et al. 2018). The purpose of this study was to provide a technique to feasibly remove phosphate (Figure 1), a key nutrient for algal production, from aqueous solutions at field scale and advance the knowledge base of management strategies for this contaminant.

Figure 1. Demonstration setup. A submergible pump was placed inside a 5 gal bucket to avoid clogging. A valve was placed in the tube to avoid back flow. The influent flowed through the pipe and the system, and it was collected at the end of the effluent tube. (See footnotes 1 and 2.)



[1] For a full list of the spelled-out forms of the units of measure used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 248-52, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

[2] For a full list of the unit conversions used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 345-7, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

1.1 Background

The presence of nutrients in excessive quantities in surface water can lead to undesirable consequences, such as algal blooms and disrupted balances within aquatic ecosystems. Excess amounts of phosphorus, typically measured as the biologically available form, orthophosphate, in water bodies is a major concern in the United States. Overly enriched, hypereutrophic conditions from excess amounts of phosphorus, nitrogen, and specific ratios of both, contribute to harmful cyanobacterial blooms (Falconer 2001; Havens 2008; Huisman et al. 2018; Malayeri et al. 2018). These blooms can be toxic or lead to oxygen depletion and anoxic respiration (hypoxia) in the hypolimnion causing serious environmental problems (Medina et al. 2018). Historically, phosphorus has been removed from wastewater and personal care products to prevent eutrophication in effluent-receiving surface waters (Jarvie et al. 2006). However, this problem has been compounded by the increase of nutrient-enriched runoff from agricultural and industrial activities (Medina et al. 2018). Some commonly used methods to remove or recover phosphate from wastewater include the following: adsorption, chemical precipitation, and biological treatment (Drenkova-Tuhtan et al. 2013; Cornel and Schaum 2009; Zhang et al. 2013; Cai et al. 2013). Similarly, these methods could be applied to remove phosphate from surface water. Unfortunately, some of these technologies may be cost prohibitive at large scale.

This report summarizes an experimental demonstration as an extension of a meso-scale experimental study focused on the removal of phosphorus from surface water through the use of iron plates (Jung et al. 2018). For decades, different forms of metal oxides have been used to sequester phosphate from aqueous solutions. The most commonly used metals are aluminum (Al^{3+}) and iron, in the form of ferrous (Fe^{2+}) and ferric (Fe^{3+}) species. Although Fe^{2+} is more economical than Fe^{3+}, the precipitate formed by oxidized Fe^{2+} in clean water is less than that from Fe^{3+} (Water Environment Federation 1998). Zero-valent iron is another form of iron used in water treatment. Although zero-valent iron use as a phosphate adsorbent has been investigated (Wu et al. 2013; Almeelbi and Bezbaruah 2012; Wu et al. 2013a; Wen et al. 2014), and it has been used to remove other water pollutants (Fu et al. 2014; Bigg and Judd 2000; Xu et al. 2017; Lu et al. 2016; Drenkova-Tuhtan et al. 2013; Hamdy et al. 2018), its research and application is not as common as divalent and trivalent iron. For this study, the plates were rusted (iron oxide) by the presence of water, air moisture, and natural organic matter placed between the plates to

enhance the effectiveness of phosphorus adsorption by forming iron oxides on the plate surface (Weng et al. 2011).

According to the US Environmental Protection Agency, high iron sands have been evaluated and shown longer durations of phosphorus-removal effectiveness (EPA, TSF-41 2002). Additionally, due to the high affinity of iron oxides to orthophosphate, iron-based adsorbents have also been used to achieve low phosphorus concentrations in wastewater effluent (Genz et al. 2004). This high affinity could be due to the new functional groups created when iron is transformed into oxides, hydroxides, or oxyhydroxides. (Fink et al. 2016). Moreover, iron can be modified to increase its surface area to enhance phosphorus removal. For example, Liu et al. (2013) prepared nano-zero-valent iron by reducing natural goethite in hydrogen at 550°C to remove phosphorus as phosphate from water, while Yao et al. (2009) used iron oxide/fly ash composite adsorbent prepared with municipal solid waste fly ash and iron nitrates; Khodadadi et al. (2017) investigated the use of iron nano-magnetic particle coated with powder activated carbon. A disadvantage of using these metals is the disposal of large amounts of precipitates, but these materials can be separated to recover the phosphate and reuse it as a fertilizer (De-Bashan and Bashan 2003; Sengupta et al. 2015; Wang et al. 2015). Several of these technologies have been efficiently used; however, more research is needed to provide more cost-efficient and feasible recovery processes, which is the main intent of this study.

1.2 Objectives

For many decades, green algae and harmful algal blooms have been of major concerns during sunny summers around the world. These blooms are due to the excess amount of nutrients in water. One of the major nutrients found in surface water is phosphate, which is a non-renewable source. Therefore, the objectives of this study are to test and demonstrate the feasibility of iron plates to precipitate phosphorus from surface water. This technology could easily recover the precipitated phosphate to be reused as a fertilizer.

1.3 Approach

An acrylic reactor (2 ft width, 2.5 ft length, and 1ft depth) was designed (Figure 2) with a 1 in. tall acrylic spacer inserted in the inside-bottom of the reactor to separate the expanded metal (steel plates) used as the iron

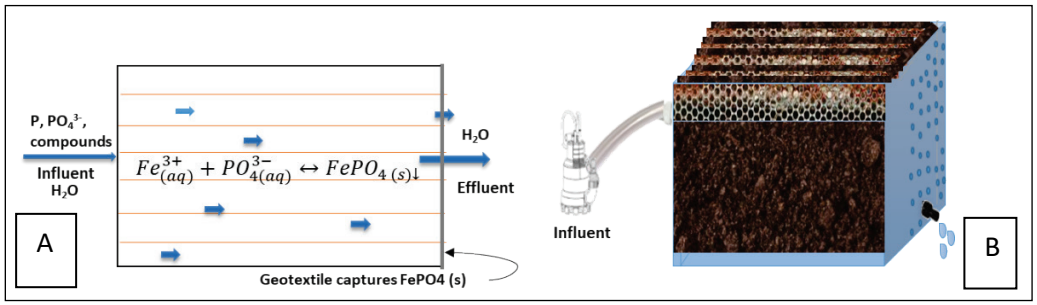
source. The plain steel sheets with Grecian pattern holes (35% open space) were purchased from McNichols, Co, Garland, TX, measuring 12 in. × 12 in. × 0.0625 in. with approximately 1.3 ft^2 surface area per plate. These iron sheets were placed 1 in. apart and parallel to each other and to the flow to increase surface area and contact time of water in the reactor. Since commercially available iron is coated with a thin layer of zinc to avoid the contact of oxygen and water with the iron, thus, avoiding corrosion, the plates were initially submerged into a citric acid solution to remove the zinc coating and speed up corrosion. Organic matter/soil was added to the reactor to keep iron reduced (natural corrosion) and to use its electric conductivity to increase corrosion of the plates.

The reactor was installed at the end of October 2017. After several trials to find an adequate height to avoid head-loss in the pump, the target flow rate was set to 0.8 L/min, and the actual flow rate fluctuated between 0.6 and 0.8 L/min. Upon the completion of the trial period, sample collection started on 16 November 2017 and continued to the end of April 2018. During the first two months (November and December), the samples were collected twice daily. Then, samples were collected once daily (January to the end of April 2018). For each sample period, one 500 mL aliquot was collected from the lake and reactor outlet to evaluate the influent and effluent conditions. Samples were immediately taken to the US Army Engineer Research and Development Center laboratory facilities for analysis via LaMotte Series 1200 Multi-wavelength Colorimeter (LaMotte Company, Chesterton, MD). LaMotte Multi-wavelength Colorimeter was used following the ascorbic acid method, which utilizes ammonium molybdate and antimony potassium tartrate (LaMotte Method 78, phosphate-low range). Each sample was filtered with a 0.45 μm nylon syringe filter (Fisher Scientific) before analysis.

The performance demonstration of this project was done during the fall and winter season. Historically, winter seasons are temperate in Mississippi, but low temperatures during the months of December 2017 and January 2018 interfered with sample collection due to freezing of the tube. Additionally, the concentration of phosphorus during these cold days was extremely low and undetectable with the aforementioned methods. Moreover, the cold season was followed by storm events in the months of March and April (2018). During one storm event in April, the water level in the lake increased, and it submerged the tank. Although the tank was covered at all times during the demonstration, the high water level flooded

the reactor. Following this event, the reactor operation was stopped for a few days to allow the water level to drop and reactor to dry.

Figure 2. A) Schematic of flow path and B) iron-plates-packed reactor.



1.4 Study area

The study was carried out at Brown Lake (Figures 3 and 4) at the US Army Engineer Research and Development Center, Waterways Experiment Station, in Vicksburg, MS. Brown Lake was developed primarily to supply water to hydraulic model operations. From 1929 to 1966, silts accumulated in this lake, and dredging became necessary; 278,000 yd^3 of silt were removed in 1966 (Tiffany 1968). The second and most recent dredging activity was done in 2000. The original lake was 24 acres, but its size has been reduced due to silt buildup over the years. The current lake's area is 20.5 acres with a volume of approximately 333,333 ft^3 according to Figure 4 and Table 1. This location was selected due to its proximity to the laboratory and known algal problems during the summer.

Figure 3. Aerial view of Brown Lake.

Figure 4. Map of Brown Lake featuring overlaying dimensions for approximate volume calculations (Google Maps [2018]).

Table 1. Approximate dimensions for Brown Lake's volume calculations assuming a trapezoid surface area and a uniform depth.

Dimension	Approximate Value	Unit
Base	930	ft
Height	1920	ft
Depth	10	ft
Volume	8,928,000	ft^3

2 Results

2.1 Water analysis

As shown in Figure 5, the phosphate removal percentage varied throughout the entire demonstration period, but the fluctuation was higher during the colder months. This could be due to extremely low phosphate concentrations that were often difficult to detect, which is shown as a data gap from day 48 through day 65. It resulted on a removal of approximately 53% with a standard deviation of 8%. Figure 6 shows that during the first month, the average influent concentration was 0.14 mg/L, which dropped to 0.07 mg/L during the month of December and to 0.01 mg/L in January. The concentrations started to increase after March, for an average concentration of 0.27 mg/L at the end of the experiment and a yearly average concentration of approximately 0.5 mg/L. The effluent and influent graphs are shown in Figures 6 and 7, respectively.

Figure 5. Phosphate removal percentage. The box plots and whisker outside the graphs indicate averages of the data.

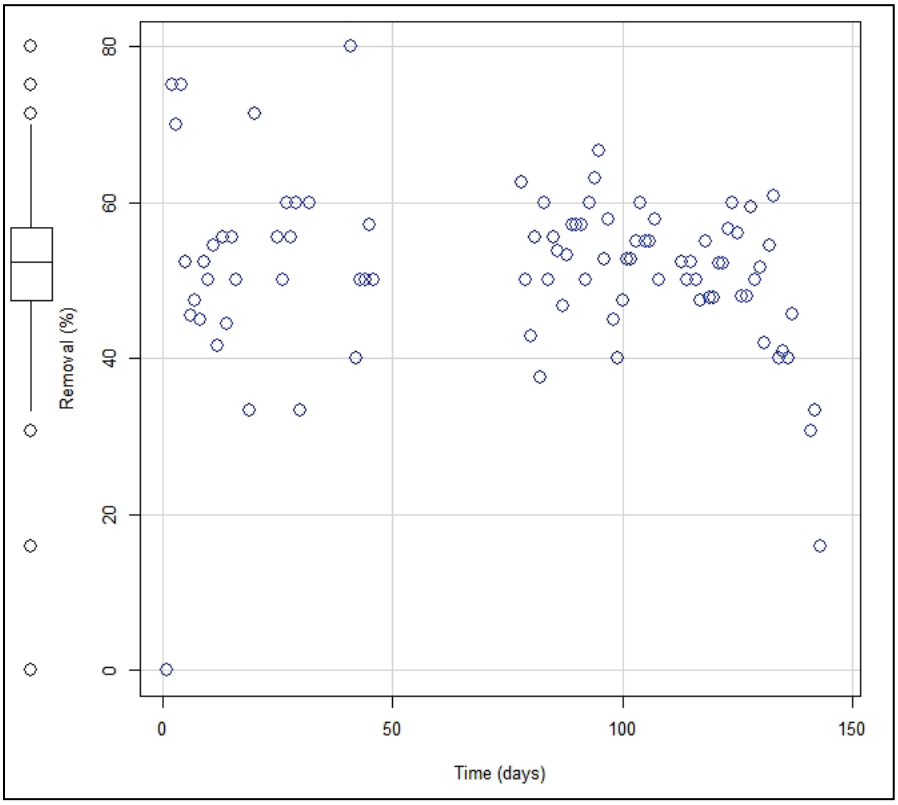


Figure 6. Phosphate concentrations in the influent.

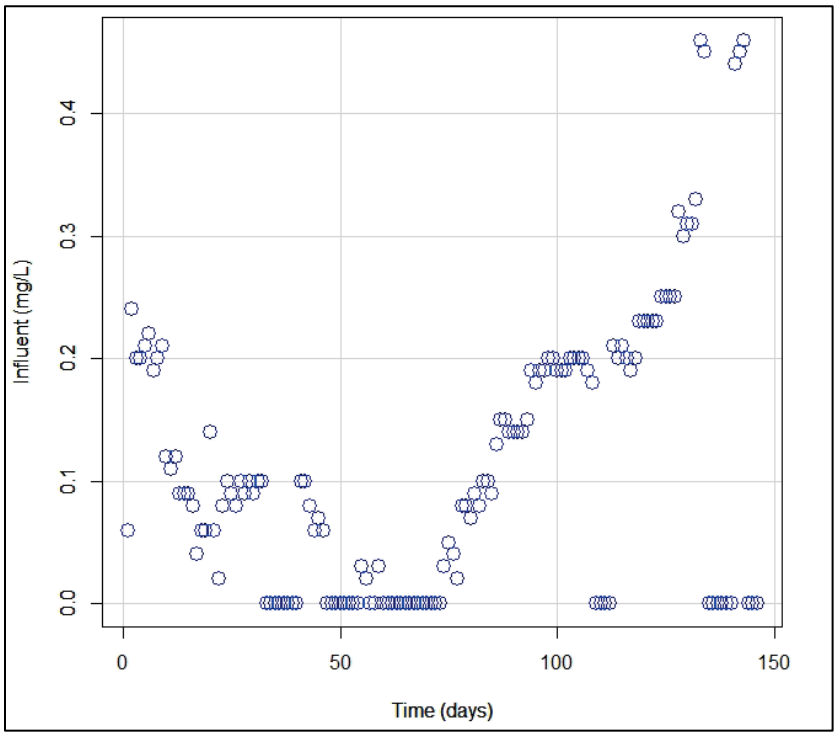
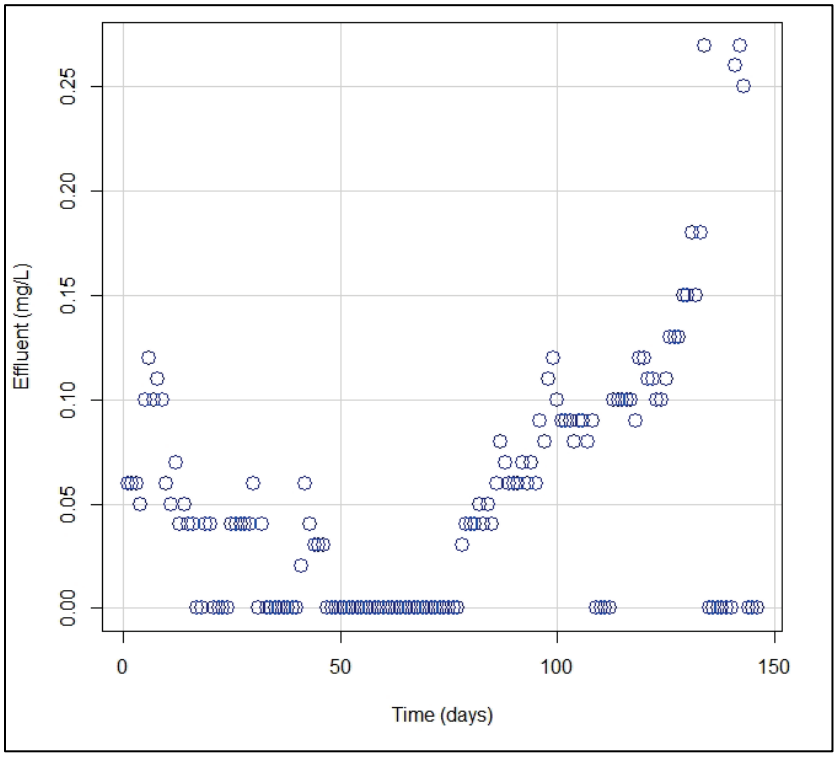


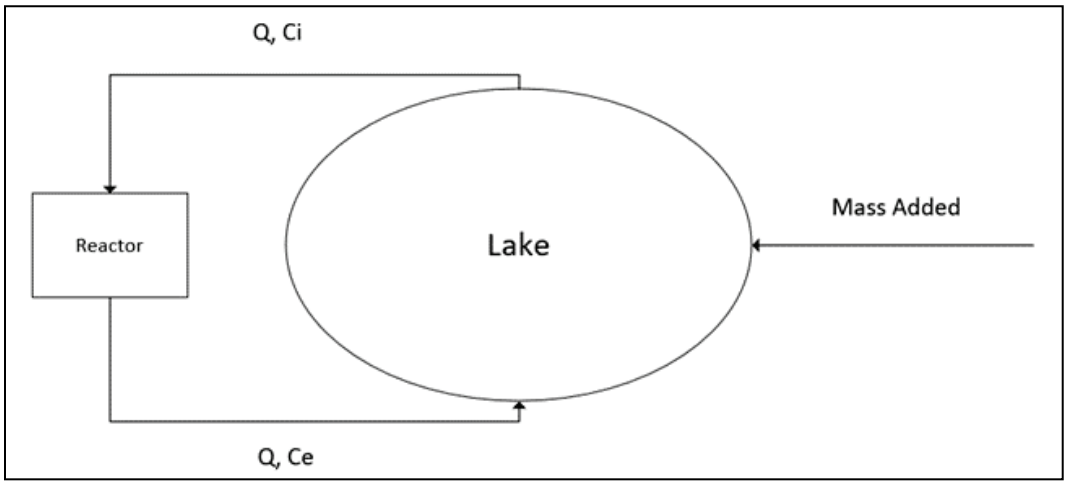
Figure 7. Phosphate concentrations in the effluent.



2.2 Data modeling

Phosphate removal results can be used to model the management system and further evaluate its performance. The appropriate model based on these results will approximate the concentration within Brown Lake at a given time after the reactor is introduced (Equation 1). The management system utilized in this study is shown in Figure 8. The overall mass balance when applying this reactor to the Brown Lake is defined by Equation 3.

Figure 8. Schematic (not to scale) of mass balance for phosphate removal system.



$$\frac{dM}{dt} = V\frac{dC}{dt} = QC_e - QCi + W \quad (1)$$

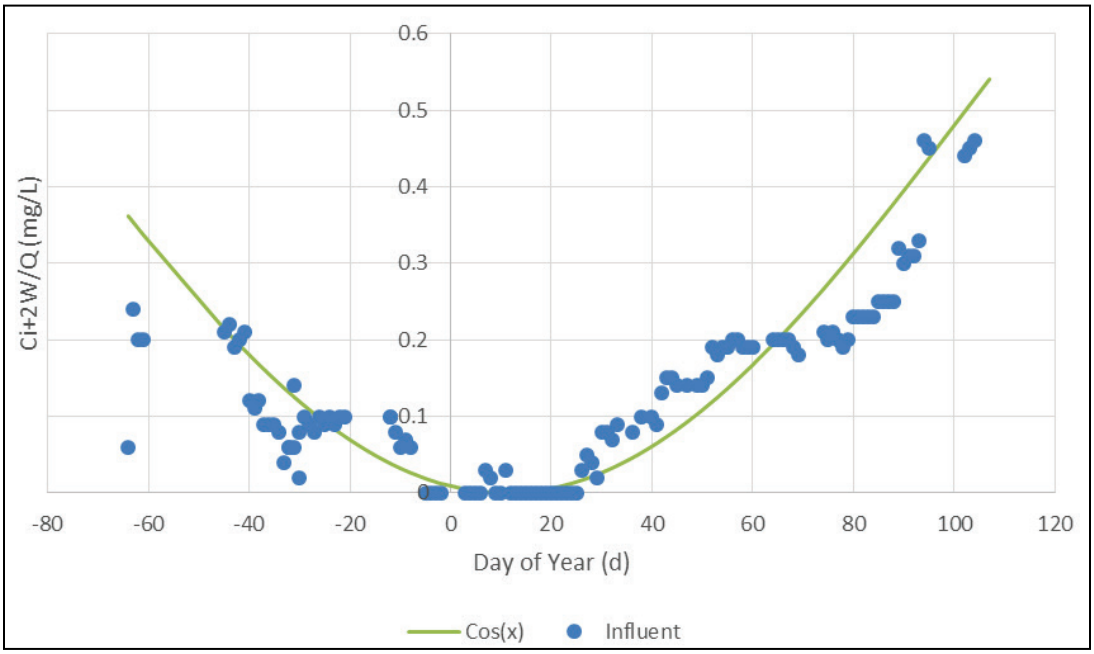
where

M = mass of contaminant
V = volume of water body
Q = flow rate for reactor
C = aqueous concentration of phosphate
Ci = influent phosphate concentration for reactor
C_e = effluent phosphate concentration for reactor
W = phosphate load from external sources.

$$\frac{dC}{dt} = -\frac{Q}{2V}\left(C_i - \frac{2W}{Q}\right) \quad (2)$$

For this study, the influent concentration followed a sinusoidal pattern associated with fluctuation related to seasonal inputs. Accordingly, the phosphate concentration at the beginning of the year (winter) was much lower than that observed during warmer seasons. As shown in Figure 9, the influent data were compared against a sinusoidal approximation to model the variable phosphate concentration in the lake throughout the study. In this figure, the days of the year are listed such that January 1 is labeled "day 1." The model fitting the data for the influent concentration and loading term in Equation 2 is derived from Equation 3 and defined by Equation 4. Assuming 50% removal of influent phosphate as indicated from the experimental results, the mass balance can be reduced to Equation 4. This simplified mass balance can be used for any water body using this reactor for phosphate removal.

Figure 9. Sinusoidal model for Brown Lake phosphate concentration during valuation.



$$C_i + \frac{2W}{Q} = \frac{C_{max}+C_{min}}{2} + \frac{C_{max}-C_{min}}{2}\cos\left(\frac{t-(t_{min}+182.5)}{182.5}\pi\right) \quad (3)$$

$$C_i + \frac{2W}{Q} = 0.5 + 0.5\cos\left(\frac{t-193.5}{182.5}\pi\right) \quad (4)$$

where

C_{max} = maximum annual concentration observed in lake (mg/L) – 1.0 mg/L for this study
C_{min} = minimum annual concentration observed in lake (mg/L) – 0.0 mg/L for this study
t = time since start of the year (d)
t_{min} = day of year in which the concentration reaches its minimum (d) – 11 d in this study.

Sinusoidal concentration fluctuations can be expected for lakes in which nutrient loads change seasonally through runoff into their watersheds. For all water bodies exhibiting these conditions such that other loads are negligible, Equations 2 and 3 can be combined to provide the mass balance of phosphate for the system when the evaluated reactor is applied; this approximation is shown in Equation 5. This mass balance can be integrated to further model the concentration of phosphate within the water body throughout the operating duration of the reactor, as shown in Equation 6. The indefinite integral of the final model for this study involving Brown Lake is shown in Equation 7.

$$\frac{dC}{dt} = -\frac{Q}{2V}\left(\frac{C_{max}+C_{min}}{2} + \frac{C_{max}-C_{min}}{2}\cos\left(\frac{t-(t_{min}+182.5)}{182.5}\pi\right)\right) \quad (5)$$

$$C = \frac{Q}{8V\pi}\left(365(C_{min}-C_{max})\sin\left(\frac{\pi(2t-2t_{min}-365)}{365}\right) - 2\pi(C_{min}+C_{max})t\right) + Constant \quad (6)$$

$$C = -\frac{Q}{8V\pi}\left(365\sin\left(\frac{\pi(2t-387)}{365}\right) + 2\pi t\right) + Constant \quad (7)$$

Equation 2 could also be modified to model the change in concentration for ponds in which the system is isolated from external loading throughout the process. Thus, Equation 8 would be used to model the performance of the reactor. In this case, phosphate would be added via batch either through seasonal runoff or other sources primary to the use of the reactor. No additional phosphate would be assumed while the reactor is in operation. Equation 9 shows the anticipated concentration as a function of time under these conditions:

$$\frac{dC}{dt} = -\frac{Q}{2V}C_i \quad (8)$$

$$C = C_i = C_{i,0}e^{\frac{-Q(t-t_0)}{2V}} \quad (9)$$

where

$C_{I,o}$ = initial influent concentration from water body (mg/L)
t_o = initial time since start of the year (d).

Equation 9 can be further modified to show the time required to provide a target concentration. This model is shown in Equation 10:

$$t = \frac{2V}{Q} \ln\left(\frac{C_{i,0}}{C_i}\right) \quad (10)$$

Both models defined by Equations 7 and 10 can be used to determine the approximate time expected for phosphate reduction to target concentrations within a water body of a given volume. Conditions including the volume, concentration, and phosphate loading trends should be investigated to determine the applicability of these models for other cases in Brown Lake and other water bodies.

3 Conclusions and Recommendations

The influent data showed that the concentration of phosphate in Brown Lake was approximately ten times higher than that recommended in a water body, which is preferred to be between 0.01 and 0.075 mg/L (EPA 2002). One factor in the high P concentration is that Brown Lake maintains a year-round population of Canada geese, and their droppings can contribute to the phosphorus balance (Dressborn et al. 2016). Another contributing factor could be dredging activities, which have been conducted in the lake several times over the years. However, as shown under results, these concentrations varied as the seasons changed. Although complete saturation of the plates was not reached during the demonstration period, periodic maintenance was performed to ensure the optimal performance of the system. Every month, the geotextile used at the end of the reactor to intercept the solids was replaced to ensure the retention of iron phosphate. During the last 2 months of the demonstration, the geotextile material was completely removed, and an activated carbon filter was added prior to the effluent collection. Additionally, removal of phosphate was reduced in the final samples collected in this study. This reduction indicates that initial saturation of the iron plates could have occurred.

As mentioned under the Results section, the tested reactor (5 ft^3) with a total iron surface area of 3 m^2 was capable of removing 53% phosphate. A scaled-up reactor for these same conditions (8,928,000 ft^3) with a phosphate design concentration of 0.8 mg/L will require a reactor of 199 ft^3 and a flow rate of 9 gpm, with an iron surface area of 67,125 ft^2. The lake has a water body load of 276 lb of phosphate and with the iron-plates capacity being 1 oz. Such system will require continuous maintenance of the iron plates, which will affect maintenance cost. The plates must be changed weekly (52 times per year) to remove any iron-phosphate binding on the surface and/or any biofilm problems. However, this can be overcome with the addition of less labor-intensive iron source; for example, pure-iron bars or thinner iron plates could be embedded in the soil and allowed to rust until they are completely consumed, thus reducing maintenance time/cost and increasing iron surface area. Additional maintenance will include monthly replacement of the geotextile prior to the effluent and pump clean up. The geotextile could be replaced with other technologies, such as the addition of a clarifier to collect the solids

coming out of the system, but the particles are too small that a chemical may have to be added to flocculate the particles.

EPA (2002) only provides recommended levels for phosphate, which are not required to be met; therefore, any removal will enhance surface water quality. For example, this system could drastically reduce its cost if the removal percentage is lowered to 10%, the reactor size will be reduced to 39.8 ft^3 and a flow rate of 1.7 gpm. In this case, the iron surface area will be 13,425 ft^2. Although the average removal percentage achieved proved that iron plates can be used to easily bind to phosphate for its reduction in aqueous solutions, further research is required to enhance the iron-surface-area binding capacity to make it cost effective. It should be considered to add a thin layer of granular activated carbon before the geotextile, prior to discharge back to the lake. The reduction of the distance between the plates would increase the metal surface area and enhance phosphate removal. The contact time can be also increased to improve iron-phosphate binding. This can be done by increasing the size of the system while maintaining the same flow. As previously mentioned, the used plates were treated with acid to remove the corrosion resistant layer; however, corrosion resistivity may still exist. It is suggested to use pure iron to avoid any binding interference. Moreover, corrosion of the plates can be accelerated by removing the organic matter from between the plates and adding electric current through the plates. The reported data could be used as a baseline to expand this type of research.

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14. ABSTRACT

The presence of phosphorus (P) in excessive quantities can lead to undesired conditions, such as cyanobacterial/algal bloom. The over-enriched hypertrophic conditions or the excess amounts of nutrients (nitrogen and P, P being the primary nutrient of concern) are the major cause of harmful cyanobacterial blooms, which can be toxic and can also lead to oxygen depletion and anoxic respiration (hypoxia) in the hypolimnion. The presence of iron compounds has been shown to bind phosphorus and diminish harmful algal blooms. Therefore, an iron-plates-packed reactor has been designed to reduce P in surface water. This cost-effective and easy-to-install system has shown promising results in phosphorus reduction.

15. SUBJECT TERMS

Algal blooms, Eutrophication, Iron compounds, Nutrient pollution of water, Phosphorus, Water—Purification, Water quality

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