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Prevention of Harmful Algal Blooms by the Mitigation of Phosphorus Nutrient Loading via Filtration by Steel Wool and Activated Carbon

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Honors Project:

Prevention of Harmful Algal Blooms by the Mitigation of Phosphorus Nutrient Loading via Filtration by Steel Wool and Activated Carbon

The University of Akron

Williams Honors College

26 April 2019

We affirm that this report represents work performed by only us. We assume full responsibility for originality, comprehension, and accuracy of all aspects of the report.

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Abstract

Harmful Algal Blooms (HABs) are a devastating ecological and economic consequence of the abundance of nutrient-rich agricultural runoff entering aquatic ecosystems (Baker et al. 2014). Bioavailable phosphorus from synthetic fertilizers is one of the major nutrients contributing to this global issue. Preliminary studies indicate that dissolved phosphorus can be removed from an aqueous environment when passed through a composite mixture of granular steel wool particles and activated carbon (Erickson, Gulliver, and Weiss (2007). Further research was conducted using higher quality concentration measurements to determine what grades of steel wool (0000, 000, 00) and types of activated carbon (GAC, PAC, EAC) and in what combinations are most effective at removing phosphorus, and to determine longevity of filter materials in terms of percent phosphorus removed over time, and percent iron-oxide byproducts produced over time. The feasibility of scaling up the proportions of materials was also assessed to determine the safety, health, and environmental regulations of filter implementation as well as to produce an economic analysis and design matrix. From the experimental and existing data, a prototypical filtration device was designed and analyzed with regard for materials needed, longevity, regulation, cost, and potential future implementation in two Ohio locations: the Maumee River and the Cuyahoga River.

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Executive Summary

The presence of Harmful Algal Blooms (HABs) in bodies of water such as Lake Erie is an overwhelming issue within ecosystems and steps to mitigate the growth of them have been studied for some time now. One catalyst found to proliferate these HABs is the presence of excessive nutrients such as dissolved phosphorous/phosphates and nitrogen coming from fertilizer runoff in rural areas (Baker et al, 2014). Due to their neurotoxic characteristics and aggressive nutrient uptake causing hypoxic zones HABs have become a problem for the $15.1 million tourist revenue of Lake Erie. This study aims to mitigate the nutrient loading to the HABs through the design of a filter product for point source runoff streams into larger bodies of water. More specifically, it is hypothesized that creating a filter with significant absorptive characteristics from steel wool (SW) and activated carbon (AC) will serve as a viable step and potential solution to the issues centered around HABs.

Several different materials were tested to determine the best choice for filter media and design housing, these being:

- Granular Activated Carbon (GAC)
- Extruded Activated Carbon (EAC)
- Powdered Activated Carbon (PAC)
- Steel Wool Grade 0000 (SW-0000 or 0000)
- Steel Wool Grade 000 (SW-000 or 000)
- Steel Wool Grade 00 (SW-00 or 00)
- Nylon Mesh
- Polyvinyl Chloride (PVC)
- Polylactic Acid (PLA)

Of these materials GAC, EAC, PAC, SW-0000, SW-000, and SW-00 were characterized for their absorptive capabilities in combinations of AC and SW at 1:1 weight and as they stood alone. Additionally, the use of nylon mesh to house the filter media was examined and PVC and PLA were considered and examined for use as the design housing structure. The original design of experiments for testing combinations of SW and AC can be found in **Appendix C, Table 8**. The second set of experiments took the best combination of filter media from experiment one and scaled it up, testing how larger loadings of media affected their filtering and absorptive capacities. Finally, a third experiment was run to observe the release of iron ions into the water for the determination of ecological stability of the steel wool.

It was quickly determined that PAC and EAC were not reasonable options for consideration due to their release of carbon dust into the water and unexplained increase of phosphate concentration in the samples. This information modified experiment one to consist of 10 g combinations of GAC with SW-0000, SW-000, and SW-00, along with one set of data for EAC with SW-0000. Results showed that the GAC/SW-00 mixture worked the best with an average phosphate decrease of 15.68%, followed by GAC/SW-0000 at 11.42%, GAC/SW-000 at 5.95%, and EAC/SW-0000 with an increase of 3.39%. 10 g of GAC alone showed a 31.03% decrease and SW-0000 alone showed a 13.10% decrease. Standard deviations of a population were calculated for each of the combinations, GAC/SW-00, GAC/SW-0000, GAC/SW-000, and EAC/SW-0000, and were respectively 6%, 2%, 5%, and 2%. Though the GAC/SW-00 media had the highest apparent absorption capabilities it releases a noticeably higher amount of carbon dust into the sample water, which is why GAC/SW-0000 was used for the second experiments. Similarly, GAC by itself significantly darkened the water.

The second experiment examined the effects of increasing the weight of the GAC/SW-0000 media, testing with 10 g, 20 g, and 30 g total, still at a 1:1 weight ratio. Results showed that as the amount of filter media used increased so did its absorptive capabilities, which was expected. At 10 g the average phosphate reduction was 11.42% ± 2%, at 20 g a 47.86% ± 0.7% reduction, and at 30 g a 54.29% ± 3% reduction.

Finally, the idea of putting steel wool into an aqueous environment is concerning so a study was done to see how much iron would be released into the environment. Three 2 g pads of SW were put into tap water baths and the iron content was measured with a Seachem Iron Test Kit. Initially the water had an average of 0.087 mg/L iron, at 1 hour there was 0.933 mg/L, and by 2 hours the iron was off the scale of the test kit meaning the concentration was ≥ 2 mg/L. Standard deviations for 0 hr, 1 hr, and 2 hr were 0.047 mg/L, 0.340 mg/L, and 0.00 mg/L respectively.

Throughout these experiments a nylon mesh sock was not used to house the filter media because of its inability to evenly let water through its pores. Instead specific 3D printed dispersion plates were made and used to evenly distribute water samples over the filter media. PVC and PLA test apparatuses were both used in this study and though PVC is readily accessible and already used int outdoor applications it is thought that PLA might be a more reasonable choice for design purposes.

The results of these experiments showed that there is a difference in absorptive/filtering quality of steel wool and activated carbon and that both together and alone they were able to reduce the amount of phosphate/phosphorous in an aqueous environment. GAC and SW-0000 were determined to be the best choices of filter media because of their 11.42% phosphate uptake and their ability to not stain the water. Though GAC as attractive absorptive capabilities its tendency to stain the water with carbon dust is undesirable and requires a "polishing" media in the filter with it to reduce the turbidity of the water. Additionally, as the amount of filter media increases the absorptive abilities increase as well, as expected. However, using steel wool as the "polishing" media in the filter may not be the most ideal choice due to its release of iron into the environment.

It is recommended that further studies be done to determine a replacement for steel wool within the filter. Though the experiments in this study were conducted with water solutions of approximately 0.42 mg/L phosphorus (1.26 mg/L phosphate, the concentration observed in the Maumee River [NCCOS 2017]) it will be important to run studies with actual river water samples. This would include scale up experiments as well as filter lifetime experiments. Throughout any work in this sector it is important to remember that anything having to do with the environment will be heavily regulated, especially if it concerns larger bodies of water, so it is a good idea to start any projects as early as possible and keep good communication with any regulatory agencies.

Upon the completion of this work, it appears to be a viable step if not option for beginning to mitigate the nutrient loading to HABs. An understanding of environmental engineering, biology, design, and research and development was gained throughout the duration of this project and it would be interesting to continue the work and to keep learning more about this topic. This is a topic that the group has been passionate about and believe is a real issue in our world right now, as it affects all our lives directly and/or indirectly, and if this problem can be fixed it will not only improve the quality of many bodies of water but also the quality of life of everything living around those bodies of water.

Introduction and Background

Harmful Algal Blooms (HABs) are a devastating ecological issue partially caused by the flow of nutrient-rich agricultural runoff into large bodies of water (Baker et al, 2014). Commercial fertilizers can be classified in two groups: those of mono-ammonium phosphate (MAP), and those of diammonium phosphate (DAP), both of which contain high amounts of nitrogen and phosphorus (Vitosh et al. 1995). For clarification, phosphorous (P) and phosphate (PO_4^{-3}) can be related throughout the study since both are used by the algae. The exact relationship of their concentrations can be described as, 1 mg/L P = 3 mg/L PO_4^{-3}. These synthetic fertilizers are dumped in excess onto agricultural fields and are then carried off at point source locations into streams and rivers, like the Maumee River (Baker et al. 2014). HABs are ecologically "harmful" for two main reasons: one being their role in creating hypoxic zones in large bodies of water, and two being that they are the proliferation of cyanobacteria, a type of blue-green algae that produce neurotoxins (Baker et al. 2014). In addition to being ecologically damaging, HABs are also responsible for economic damages due to lost revenue from industries such as fishing and tourism. In 2017, Lake Erie tourism accounted for $15.1 billion in revenue and 9.0% of private employment in the lake area (Tourism Economics). Over the past fifty years, HABs in Lake Erie have increased in severity at an alarming rate, with the five worst (most intense) blooms on record occurring since 2011 (Baker et al. 2014). This is partially due to the use of artificial fertilizers as well as an increase in global temperature, which together produce the perfect conditions for algal growth. Previous studies suggest various means for controlling the more immediately manageable of these two variables: nutrient runoff. One study conducted by Erickson, Gulliver, and Weiss (2007) involved reducing dissolved phosphorus in storm drain runoff using limestone and steel wool, which reduced total dissolved phosphorus by 25 to 99%. Activated carbon is also a reliable means of controlling nutrient concentrations in aquariums and decorative ponds via filtration and absorption. Given this information, we decided to test a filter material combination of activated carbon and steel wool and then determine if our filtration mechanism could be used outside of the lab in a real-world application.

Experimental Methods

Experiment #1: Determination of Filter Materials

The purpose of the initial experiment was to determine what filter substrate types were most efficient at removing dissolved phosphorus from the aqueous environment. For this, samples of approximately 5.00 grams each of steel wool and activated carbon were prepared for 12 of the trials. Three types of steel wool (grade 0000, grade 000, and grade 00) were tested in combination with two types of activated carbon (granular activated carbon [GAC] and extruded activated carbon [EAC]). Initial plans to also include a third type of activated carbon (powder activated carbon [PAC]) were discontinued due to the realization that the powder substrate was being released into the aqueous environment through the pores in the mesh sock of the filtration system and was thus ecologically unsuitable for the final design. The three types of steel wool substrate were prepared by cutting longer spools of steel wool into granular (roughly 5-10 mm) fibers using shears. The GAC was tested as it came, in pieces of approximately 10 mm in diameter, and the EAC was prepared by chipping 1.00 cm pieces off a hollow tube of the material that came housed within a water purification filter.

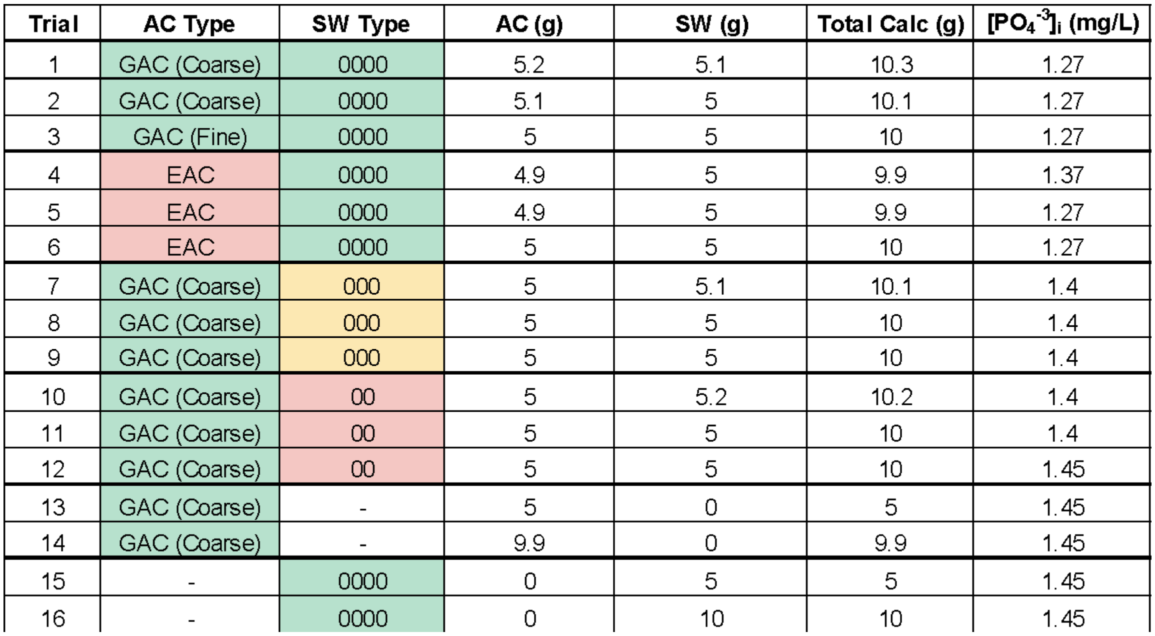
A test solution of 1.00 to 1.50 mg/L of dissolved phosphate solution (0.33 to 0.50 mg/L phosphorus) was prepared in deionized water from a 50 mg/L phosphate stock solution. This range was picked due to the calibration range of the spectrophotometer, and because the Maumee River’s present phosphorus concentration is approximately 0.42 mg/L (NCCOS 2017). 100 mL of test solution was used per trial. Two 500 mL beakers were used, one to house the test solution prior to passing through the filter, and the second to collect the test solution after passing through the filter. Phosphate concentration measurements were made using a HACH® DR1900 Spectrophotometer which was calibrated using 1.00 mg/L phosphate stock solution. The exact spectrophotometer and phosphate test procedure is shown in **Appendix D, Figures 5 and 6**.

The filter substrate was housed within a two-part 3D printed funnel that was designed specifically for this study. The top portion of the funnel was cylindrical and designed to hold up to 500 mL of an aqueous solution as well as the filter media. The filter media rested atop a circular dispersion plate with pore sizes of approximately 3.2 mm that prevented any loose material from falling through. The bottom of the funnel was conical, tapering off to a smaller opening to direct water flow into the receiving 500 mL beaker. A nylon mesh sock was secured around the bottom opening of the funnel to further prevent any loose substrate from passing through. The filter substrate was packed in layers of steel wool, activated carbon, and steel wool to allowing the mesh of the steel wool to trap particulate carbon and prevent it from being passed through the filter into the resulting test sample. The test solution was poured into the top of the cylinder funnel through a dispersion plate to help evenly disperse the water across the entire filter area.

The experimental procedure involved first securing the nylon mesh sock to the bottom of the experimental funnel housing unit and packing the filter material into the housing unit in layers. Next, 100 mL of phosphate test solution was poured through the housing unit vertically through the dispersion plate so that the water was forced to pass through the layers of filter substrate and the nylon mesh sock at the bottom of the housing unit. The test solution was collected after passing through the filter media and the resulting phosphate concentration was measured using the spectrophotometer.

This procedure was repeated for 14 total trials, with some adjustments to the initial experimental design made during the data collection process. For the three 0000 x GAC trials, two were conducted using coarse GAC and a third was conducted to rule out the use of fine GAC. Only three EAC trials were conducted due to unpromising initial results. Four additional trials were added to this experiment to identify whether there was a greater uptake of phosphorous from the aqueous environment when steel wool and activated carbon were used alone rather than in combination with each other. For this, two trials each of only GAC or grade 0000 steel wool in amounts of approximately 5.0g and 10.0g were done. Mass balances were also done on the volume of aqueous sample going in and coming out of the experiment. The original design of experiments can be found in **Appendix C, Figures 8**. **Table 1** below lists the exact amount of filter media used in each trial along with the initial phosphate solution concentration.

Table 1: *Summary of trials in Experiment 1 with the measured initial values.*



Trial	AC Type	SW Type	AC (g)	SW (g)	Total Calc (g)	$[PO_4^{-3}]_i$ (mg/L)
1	GAC (Coarse)	0000	5.2	5.1	10.3	1.27
2	GAC (Coarse)	0000	5.1	5	10.1	1.27
3	GAC (Fine)	0000	5	5	10	1.27
4	EAC	0000	4.9	5	9.9	1.37
5	EAC	0000	4.9	5	9.9	1.27
6	EAC	0000	5	5	10	1.27
7	GAC (Coarse)	000	5	5.1	10.1	1.4
8	GAC (Coarse)	000	5	5	10	1.4
9	GAC (Coarse)	000	5	5	10	1.4
10	GAC (Coarse)	00	5	5.2	10.2	1.4
11	GAC (Coarse)	00	5	5	10	1.4
12	GAC (Coarse)	00	5	5	10	1.45
13	GAC (Coarse)	-	5	0	5	1.45
14	GAC (Coarse)	-	9.9	0	9.9	1.45
15	-	0000	0	5	5	1.45
16	-	0000	0	10	10	1.45

Experiment #2: Confirmation of Phosphorus Uptake by Filter Materials and Scalability

The second experiment in this study was conducted to confirm the ability of the ideal filter media, determined in experiment one, to uptake phosphorus from the aqueous environment and to factor in scalability. This allowed for the determination of the feasibility of a real-world design application and later aided in cost analysis. A series of nine trials were done to ensure the collection of significant data. Tests were done by weighing out materials for each of the filters (three trials of 5 g GAC and 5 g Grade 0000 Steel Wool, three trials of 10g each, and three trials of 15g each) and preparing the test phosphate solution from the 50 mg/L phosphate stock solution. The filter materials were secured inside of the housing unit, and the same collection and analysis procedure from Experiment #1 was used to assess the percent change in dissolved phosphate from the test solution to the solution after passing through the filter materials. **Table 2** below lists the initial data for this experiment.

Table 2: *Summary of the trials in Experiment 2 with the measured initial values.*

Trial	AC Type	SW Type	AC (g)	SW (g)	Total Calc (g)	$[PO_4^{-3}]_i$ (mg/L)
1	GAC (coarse)	0000	5.2	5.1	10.3	1.27
2	GAC (coarse)	0000	5.1	5.0	10.1	1.27
3	GAC (coarse)	0000	5.0	5.0	10.0	1.4
4	GAC (coarse)	0000	10.0	10.1	20.1	1.4
5	GAC (coarse)	0000	10.1	10.0	20.1	1.4
6	GAC (coarse)	0000	10.0	10.0	20.0	1.4
7	GAC (coarse)	0000	15.0	15.0	30.0	1.4
8	GAC (coarse)	0000	15.0	15.0	30.0	1.4
9	GAC (coarse)	0000	15.0	15.0	30.0	1.4

Experiment #3: Longevity and Production of Iron Oxides

The purpose of the third experiment in this study was to determine if the steel wool filter substrate was releasing iron oxides into the aqueous environment as a byproduct over time, and to quantify this amount for determination of any potentially negative ecological impacts. For this, three 500 mL beakers were with tap water. Three sets of the ideal grade 0000 steel wool of 2 g were also prepared. The loose steel wool was placed inside each 500 mL beaker and stirred to break up any clumping material. The beakers were allowed to sit for a total of two hours, stirring once per hour to prevent settling of materials at the bottom of the beaker. At the initial time and each hour, the beaker solutions were tested for iron oxide development using a Seachem brand Multitest Iron Kit. **Table 3** lists the initial data for the experiment.

Table 3: *Summary of the initial measurements for Experiment 3.*

Trial	SW (g)	Tap Water (mL)
1	2.3	500
2	2.1	500
3	2.1	500

Results and Discussion

Experiment #1:

The most initially enticing results of experiment one was the apparent “best” results from trials of only steel wool or only activated carbon rather than a combination of the two. However, in practical application, a combination of the two filter materials is better suited for use in an ecological environment. While more phosphorus is absorbed when each is used as a sole component of the filter, each material type has its own ecological downfalls. Using only activated carbon results in water samples that stain very dark, meaning that particulate carbon is leaving the filter and entering the aquatic ecosystem. Using only steel wool results in rapid iron oxide production (as quantified by a yellow-orange color development in the resulting test sample). When the two are used in conjunction, these problems are remedied in two ways: the mesh pattern of the steel wool entraps the particulate carbon and prevents it from staining the water sample and the activated carbon works to prevent the development of iron oxides in the aqueous environment by absorbing the chloramines needed for the rust-producing reaction. For this reason, the study was continued with combined filter media.

GAC was chosen as the ideal activated carbon type simply by elimination of the other two types of activated carbon. PAC was eliminated because it stained the test sample water black, and EAC was eliminated because it reliably resulted in an increase in phosphorus concentration in the resulting water sample. Narrowing down the type of steel wool was slightly more difficult. In terms of average percent decrease in phosphate, the three types of steel wool in combination with GAC performed as follows: GAC/SW-0000 had an 11.42% decrease, GAC/SW-000 had an 8.93% decrease, and GAC/SW-00 had a 15.68% decrease. On paper, the use of grade 00 steel wool seems justified; however, the finer grade steel wool (0000) performed better in terms of trapping particulate activated carbon within its smaller mesh. All the grade 00 trials resulted in water that was stained slightly gray. For this reason, grade 0000 steel wool was chosen as the ideal steel wool grade for the rest of the study. **Table 4 and Figure 1** show the results of this experiment, where the error bars are equal to the standard deviation of each trial.

***Table 4:** Average results of filter media from Experiment 1. Standard deviation is calculated for the population.*

Exp. 1: Determination of Filter Media

	Avg Mass (g)	Avg. % d[PO_4^{-3}]	Std. Dev
GAC/0000	10.13	11.42%	1.97%
EAC/0000	9.93	-3.39%	1.99%
GAC/000	10.03	5.95%	4.68%
GAC/00	10.07	15.68%	6.11%
GAC	9.90	31.03%	
0000	10.00	13.10%	

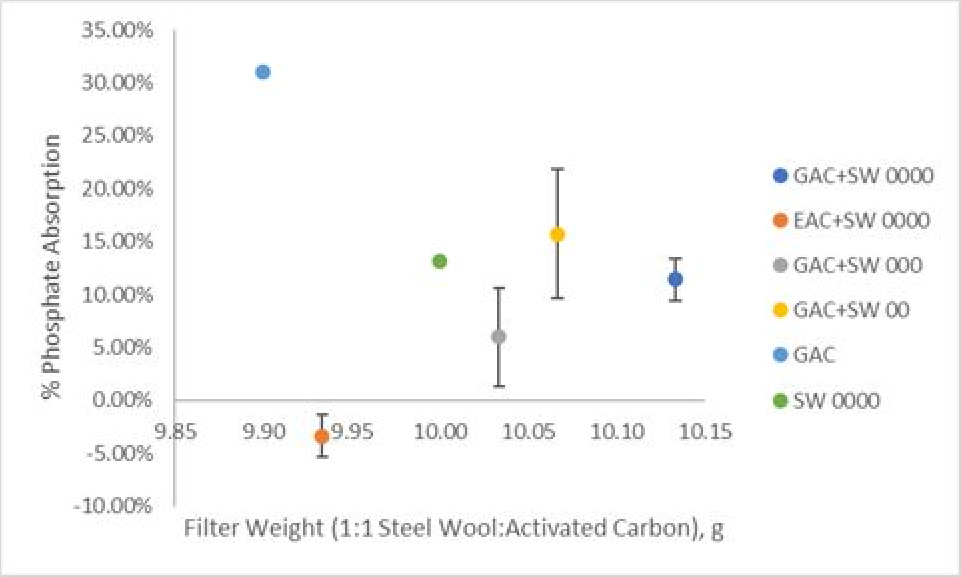


***Figure 1:** Plot of the performance of each combination of filter media in Experiment 1. Error bars are equal to the standard deviation of the data sets.*

The resulting "best" combination of steel wool and activated carbon as determined by experiment one was SW-0000 and GAC.

Experiment #2:

The results of experiment two were promising in that they demonstrated how scaling up the filter materials could potentially allow for the removal of the target percentage of phosphorus from the aqueous environment. Exact numbers have changed throughout the years, but the Ohio Phosphorus Task Force has generally recommended a 40% - 46% decrease in phosphorus loading into the Western basin of Lake Erie each year since 2001 to reduce the area of hypoxic zones and decrease HABs severity (Scavia et al. 2014). **Table 5** shows the measured data, but it can be seen in **Figure 2** how the slight increase in filter media greatly affected the absorption abilities of the system.

Table 5: *Average data from scale-up in Experiment 2. Standard deviation is calculated for the population of the data.*

Exp. 2: Scale Up Data			
AC:SW	**Avg Mass (g)**	**Avg. % d[PO_4^{-3}]**	**Std. Dev**
1:1	10.13	11.42%	1.97%
1:1	20.07	47.86%	0.71%
1:1	30.00	54.29%	2.67%

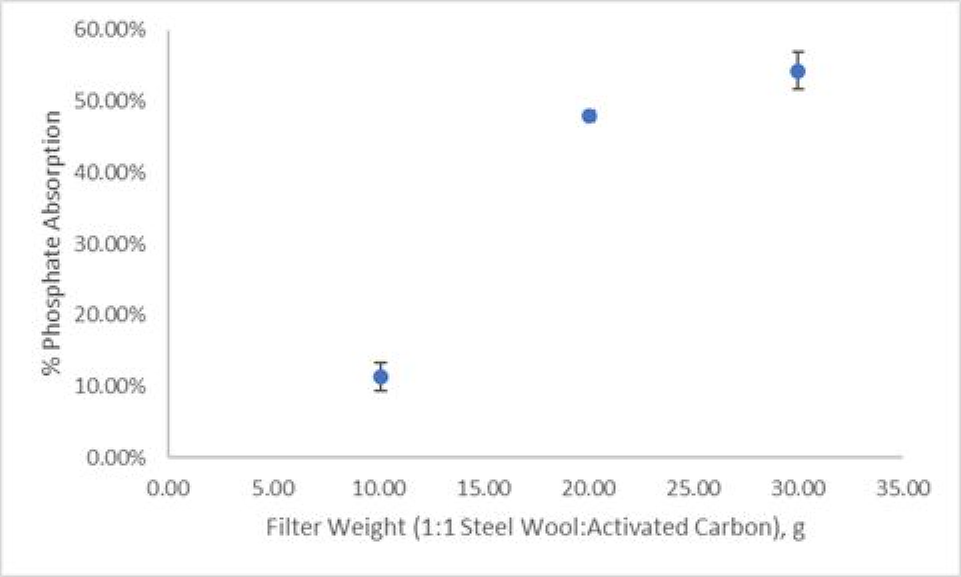


Figure 2: *Plot of the scale-up data from Experiment 2. Error bars are equal to the standard deviation of the data set.*

By scaling up slightly the range of 40% - 46% decrease was able to be achieved, this was seen by just doubling the amount of filter media used from the first experiment. The data seemed to follow the trend of a radical function, moving towards a horizontal asymptote (leveling off), as the media weight increased, so one might assume that you do not need to continue to increase the amount of filter media to achieve desired results. Additionally, it should be noted that phosphorus is still needed to create a healthy environment, so taking out too much could pose a whole new set of environmental struggles. With that in mind it will be important to select the proper amount of filter media in the final design.

Experiment #3:

The results of experiment three demonstrated more fully how quickly iron oxides can be produced from the steel wool when used without activated carbon as a chloramine neutralizer.

For this experiment, the trials had to be run without activated carbon in the beakers because the Seachem Brand Multitest Iron Kit quantified total iron by color gradient, the results of which may have been altered if the activated carbon darkened the water sample. Because of this, the steel wool particles produced iron oxides at a faster rate than would be expected of a filter of combined steel wool and activated carbon. After only two hours, the iron oxides levels produced by the steel wool maxed out the gradient chart included with the test kit (2.0 mg/L). There is clearly a wide range of iron levels in aquatic ecosystems that is considered ecologically dangerous, and the commercial steel wool used in this study, unfortunately, falls within that range. **Table 6** and **Figure 3** summarize the results from this experiment.

Table 6: *Summary of the iron oxide data in Experiment 3. Standard deviation was calculated for the population.*

Exp. 3: Iron Oxide Analysis					
t (hr)	**Trial 1 (mg/L)**	**Trial 2 (mg/L)**	**Trial 3 (mg/L)**	**Trial Avg. (mg/L)**	**Std. Dev.**
0	0.12	0.02	0.12	0.087	0.047
1	0.8	1.4	0.6	0.933	0.340
2	2	2	2	2.000	0.000

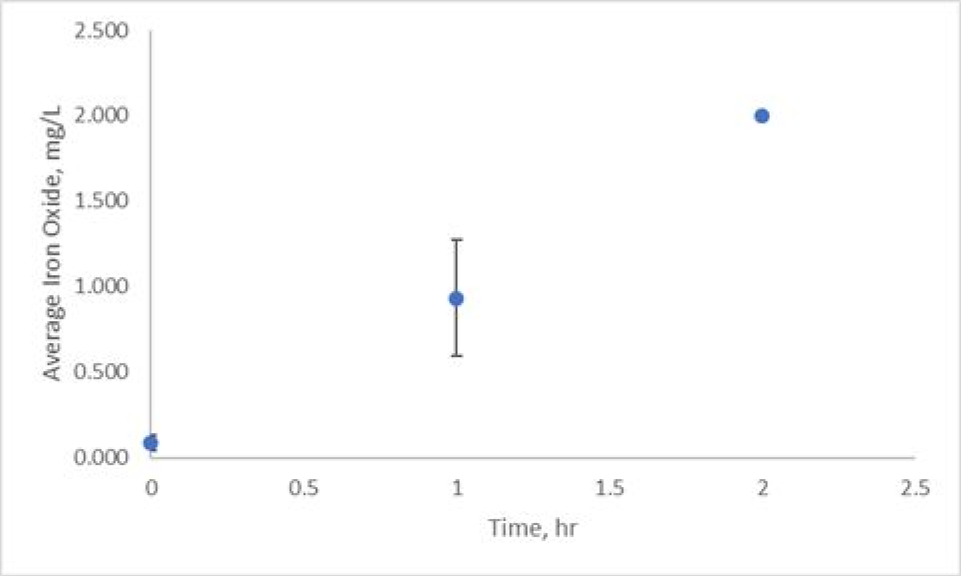


Figure 3: *Plot of the change in iron oxide concentration over 2 hours. Error bars are equal to the standard deviation.*

However, experiment one demonstrated the necessity of using steel wool as a means of containing particulate carbon from the GAC that would otherwise taint the aqueous environment. These conflicting realizations led to the consideration of room for future work involving designing a polymer mesh that could still encapsulate the particulate activated carbon without producing iron oxides as a byproduct.

Safety, Health, and Environmental Regulations

By taking on the challenge of mitigating nutrient loading into Lake Erie and other bodies of water it is important to take into consideration the environmental impact that the designed solution is going to have. The main concern of this study is the production of iron oxide from the steel wool in the filters into the environment, however it is important to also consider the impact of activated carbon residue and PLA. Ultimately, the environmental impacts will drive the design of a product to mitigate phosphorus loading.

In terms of iron release into the environment, some literature suggests that iron levels as low as 0.1 mg/L can be damaging to fish gills because the free radicals produced by the iron oxides can cause oxidation of the gill tissue and lead to secondary infections (Dryden Aqua, n.d.). More wide scale damage has also been documented in an aquatic ecosystem downstream from a quarry, where iron levels of 86 mg/L led to widespread fish die off (Slaninova et al. 2014). With this being said, a more in-depth analysis should be done on the target area for mitigation to determine if the release of iron will be detrimental. Additionally, this opens the door for the research of a different media besides steel wool to act as a replacement.

Based on the SDS for Activated Carbon, it appears that there are no critical environmental concerns. Any ecological and toxicological concerns appear to be at large concentrations such as 1000 mg/L and 8000 mg/kg bodyweight (Fischer Scientific, 2015). However, experiments showed that the activated carbon can release dust into the water tinting it black, which could skew results, but this can be fixed by rinsing the carbon before use.

PLA was the material used for the testing apparatus and is a viable option for the products design due to its, versatility, use in 3D printing, and eco-friendly nature. Additionally, PLA is biocompatible, biosourced, and biodegradable. A concerning characteristic of PLA though is its tendency to degrade and undergo hydrolysis in the presence of water molecules, including water vapor and liquid water (Roca-Smith et al., 2017). This degradation process produces lactic acid and its oligomers which raises some questions about PLA's environmental impact. L-lactic acid was originally registered with the Environmental Protection Agency (EPA) as a pesticide in 1988, however it is not currently being used as an end use pesticide. Though this byproduct is a known ingredient in some pesticides, the EPA has stated that "L-lactic acid will have "no effect" on endangered or threatened terrestrial or aquatic species, or their designated critical habitats, as listed by the U.S. Fish and Wildlife Service (USFWS) and the National Oceanic and Atmospheric Administration (NOAA)" (U.S. Environmental Protection Agency, 2009). Outside of the realm of endangered and threatened species it has also been said that in general, birds, fish, aquatic invertebrates, and honey bees are safe because L-lactic acid is virtually non-toxic to them (U.S. Environmental Protection Agency, 2009). This information indicates that PLA is still a viable material option, however the degradation of the material may cause unnecessary maintenance requirements.

Prior to development approval will need to be sought out from both the EPA and the Ohio Department of National Resources (ODNR), which both have regulations on allowable materials in contaminants within water sources, especially those leading to larger bodies of water such as the Lake Erie basin and Ohio River basin. The best course of action would be to get in direct contact and work directly with these organizations to finalize an approved design.

The intent of the final product design is for it to be easily environmentally friendly, useable, simple, and safe. There are not many, if any, moving parts to this product which will reduce the risk of injury when maintaining it. Lastly, the filter media used in the product should be relatively harmless and require minimum maintenance.

Prototype Design

For this project there were multiple design elements that were considered. First and foremost, two different testing apparatuses were designed and built to conduct experiments. The first was made from PVC pipe and was split into two parts that allowed a filter to be inserted and screwed into the center part of the pipe. At the bottom of the pipe there was ball valve to allow the flow of water out of the apparatus. Testing was done with this by unscrewing the two halves of the pipe and putting a filter, made with the appropriate media in a nylon mesh sock, in and screwing the two halves back together. The phosphate solution sample could then be poured through the pipe with the ball valve open, first passing through the filter media and then out the end into a beaker or other appropriate container. This apparatus can be seen in **Appendix D, Figure 8**. Upon experimenting with this prototype, it was discovered that water did not pass very well through the nylon mesh sock if it had other, less resistive, paths to take. It was seen that typically all the water would only pass through a small portion of the sock and filter, leaving the rest dry.

This discovery led to the design of a new testing apparatus, which was designed in SolidWorks and 3D printed in PLA with 100% infill. The apparatus is loosely based off the concept of the first PVC design, but more tailored to the needs of the experiments and can be seen in **Figure 4 (Left)**. There are two halves to it, with the top half having a capacity of 500 mL and the bottom coming to a taper to act as a funnel into a beaker. The top and bottom of the design fit together in such a way so that water does not flow out of the chamber as it travels through and there are flanges to lock the orientation of the fit. Two circular dispersion plates were designed and printed with 3.2 mm pores. These plates fit into tracks in both the top and bottom of the assembly and are offset by 90°. This design is meant to diminish the need for the filter media to be held inside of a mesh sock, so it is built in such a way that one dispersion plate is fit into the bottom half below the filter media and another in the top half above the filter media. As aforementioned, the plates are offset by 90°, which was intentional to make sure that when the water hit and was dispersed by the first plate it did not travel straight down through a hole in the second plate that was lined up with the first, but rather it would travel through the media and be stopped by the second plate, being dispersed again, before flowing through the rest of the apparatus. Ultimately, this increased the residence time of contact between the water sample and the filter media. Additionally, the plates are removable not only to allow for the replacement of the filter, but also so different dispersion plates could be designed and inserted based on the needs of the experiment. When experiments began it was determined that a nylon mesh sock should be placed over the very end of the apparatus to catch any residue from the filter before the water sample entered the beaker. **Figure 4 (Right)** shows the final printed product assembled during testing. More pictures of the assembly can be found in **Appendix D.**

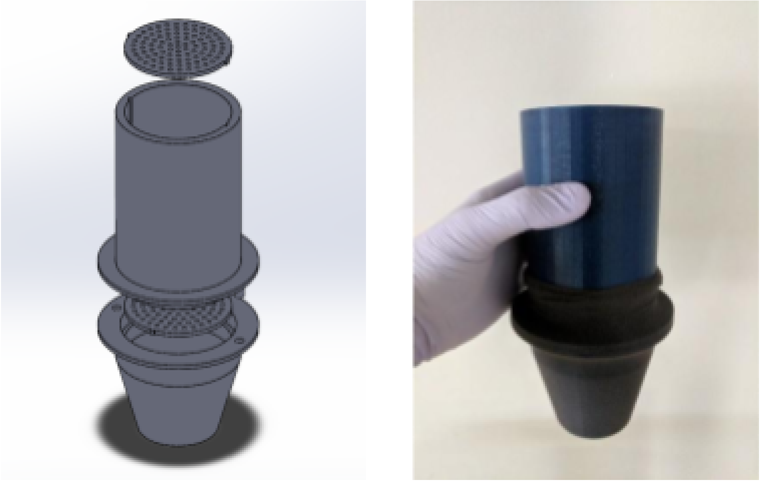


Figure 4: The testing apparatus designed for this study. Left - The model in SolidWorks, Right - The 3D printed fully assembled apparatus.

Looking forward at the final product design several concepts were considered. The concepts were narrowed down to four which consisted of:

1. **Point Source Filter:** A filtration/absorption device that would be put into point source inlets into rivers, such as runoff streams coming from farms.
2. **River Mouth Break:** A filtration/absorption device set into rivers that would help mitigate the wakes generated by maritime traffic disturbing aquatic ecosystems.
3. **Absorption Tower:** Towers filled with filter media that would be located closer to the river banks, with lights atop of them to steer boats away.
4. **Bed Interceptor Filters:** A filter modeled after a bedload interceptor that would be in the bed of the river or used with a bedload interceptor.

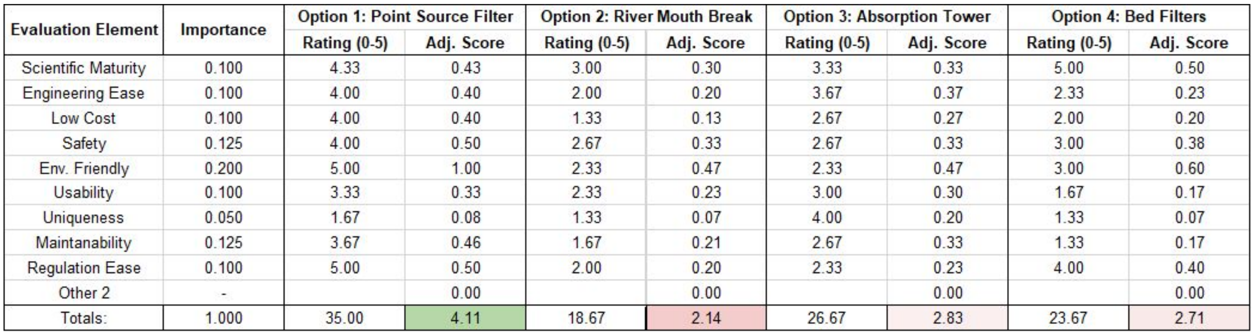
Each of these were considered for a variety of different reasons, but to standardize and compare the ideas properly a design matrix was created, considering the following aspects:

- Scientific Maturity
- Engineering Ease
- Low Cost
- Safety
- Environmental Friendliness
- Usability

- Uniqueness
- Maintainability
- Regulation Ease

The purpose of defining these aspects was to look at what is important for the design of this product. Each characteristic was then given an "importance rating" and raking was performed on a scale of 0-5 by each team member. These values were averaged together to give the final design matrix summarized in **Table 7**.

Table 7: *Summary of the design matrix for product development moving forward.*



Evaluation Element	Importance	Option 1: Point Source Filter		Option 2: River Mouth Break		Option 3: Absorption Tower		Option 4: Bed Filters	
		Rating (0-5)	Adj. Score	Rating (0-5)	Adj. Score	Rating (0-5)	Adj. Score	Rating (0-5)	Adj. Score
Scientific Maturity	0.100	4.33	0.43	3.00	0.30	3.33	0.33	5.00	0.50
Engineering Ease	0.100	4.00	0.40	2.00	0.20	3.67	0.37	2.33	0.23
Low Cost	0.100	4.00	0.40	1.33	0.13	2.67	0.27	2.00	0.20
Safety	0.125	4.00	0.50	2.67	0.33	2.67	0.33	3.00	0.38
Env. Friendly	0.200	5.00	1.00	2.33	0.47	2.33	0.47	3.00	0.60
Usability	0.100	3.33	0.33	2.33	0.23	3.00	0.30	1.67	0.17
Uniqueness	0.050	1.67	0.08	1.33	0.07	4.00	0.20	1.33	0.07
Maintanability	0.125	3.67	0.46	1.67	0.21	2.67	0.33	1.33	0.17
Regulation Ease	0.100	5.00	0.50	2.00	0.20	2.33	0.23	4.00	0.40
Other 2	-		0.00		0.00		0.00		0.00
Totals:	1.000	35.00	4.11	18.67	2.14	26.67	2.83	23.67	2.71

As shown, the Point Source Filter was evaluated to be the most promising design and steps were taken in the consideration of how that prototype would be designed. The design would consist of a housing unit that could be semi-permanent in the point source and minimally disrupt flow. PLA is a front running option because of its eco-friendly nature and versatility, regardless of its tendency to degrade. Though the housing unit would be semi-permanent, the filter media would need to be replaced regularly, however the actual time frame is not known at this time. Some benefits to this design would be that it could be adapted to whatever point source stream it is in with PLA being able to be 3D printed and if proven necessary the filter media could be varied to filter/absorb a variety of pollutants found in the water source.

Economic Analysis

Economics is another driving force in the development of this product. The materials used in this experiment are relatively cheap and easily accessible. To give a reference of how cheap materials were the Steel Wool Grade 0000 cost $14.99 for 225 g which came out to be $0.07/gram and the Granular Activated Carbon cost $12.99 for 1134 g, making it $0.01/gram. This made the most expensive filter of our experiments $1.17 for a 30 g filter (1:1 weight ratio of SW to AC). The costs given are for relatively finite amounts of each material, however, it is expected that the cost can be decreased by buying the materials in bulk.

It is expected that the product needs to remove approximately 40% of phosphorus present in the water to bring the levels down to an acceptable amount, which means that a 30 g filter could suffice, as demonstrated in experiment two. It is uncertain how long a filter will last, but it is assumed that the design of this product requires that the filter media be replaced on a regular basis. This would incur costs for the owner of the product, however even with accounting for profit margins the replacement filter media would not cost very much (i.e: 50% margin would result in a $2.34 filter cost). The actual product housing is not expected to need to be replaced very often however at some point that will become a factor. Overall, it is thought that this product could be made and sold affordably, especially once material prices decrease from buying in bulk.

Conclusion and Recommendations

As tenants of the blue planet, the health of our aquatic and marine ecosystems should be at the forefront of our awareness as both laypeople and as members of the scientific community.

The mitigation of phosphorus nutrient loading into aquatic ecosystems is a crucial step in reducing the severity of Harmful Algal Blooms, which greatly threaten the health of these ecosystems. The greatest outcome of this study is its contribution to the body of knowledge of ways to manage and prevent ecologically devastating Harmful Algal Blooms.

This study showed that phosphorus can be reduced by a mixture of 15 g SW-0000 and 15g GAC by 54.29%. Until a better material option is found, PLA will work for the housing of the prototype because of its versatility and biocompatibility. The Point Source Filter is meant to be installed in the outlet streams from properties with high phosphorus output, such as farms using excess amounts of fertilizer, rather than a river or larger body of water itself. By tackling the point source runoff streams rather than a larger body of water or river it is thought that the mitigation of nutrient loading will be more manageable and more effective. There will be less red tape to cross and the product can be marketed at a much more manageable size. It is thought that if the phosphorus loading to Lake Erie from the Maumee is reduced by 40% - 46% a significant impact will be made on the amount of HABs that are present in Lake Erie. The results from this study surpass that reduction rate but can easily be scaled back to whatever reduction amount is desired.

Moving forward it will be necessary to study the longevity of the filter and filter media in an aqueous environment to determine how often it needs to be replaced. This will have a significant impact on the product being designed. Additionally, more targeted research on regulations in this sector needs to be conducted and a replacement for steel wool should be considered to aid in navigating through the regulatory world.

For now, it has been shown that a viable filter can be designed with a PLA housing unit, adjustable based on need, packed with replaceable GAC/SW-0000 filter media. This product will target point source runoffs and significantly reduce the amount of nutrient loading into bodies of water. Though the main target of this product is to mitigate phosphorus nutrient loading other contaminants can be tackled as well since the filter media is replaceable. It is the hope and goal that this will aid in taking a big step towards the cleanup of HABs in bodies of water such as Lake Erie.

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Appendices

Appendix A: Definitions

GAC – Granulated Activated Carbon
EAC – Extruded Activated Carbon
PAC – Powdered Activated Carbon
SW – Steel Wool
PLA – Polylactic Acid
PVC – Polyvinyl Chloride

To be finished

Appendix B: Sample Calculations

Phosphate to Phosphorus Relationship
Standard Solution Dilution
% Change Phosphate Concentration
Averages
Standard Deviation

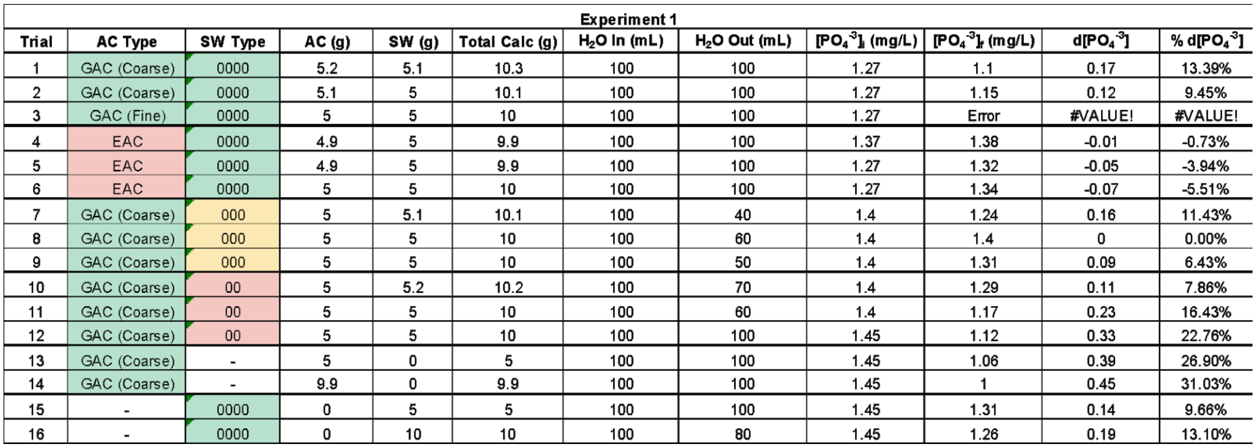
To be finished

Appendix C: Raw Experimental Data

Table 8: *The original design of experiments for Experiment 1.*

Trial	AC Type	SW Type
1	GAC	0000
2	GAC	0000
3	GAC	0000
4	PAC	0000
5	PAC	0000
6	PAC	0000
7	EAC	0000
8	EAC	0000
9	EAC	0000
10	GAC	000
11	GAC	000
12	GAC	000
13	PAC	000
14	PAC	000
15	PAC	000
16	EAC	000
17	EAC	000
18	EAC	000
19	GAC	00
20	GAC	00
21	GAC	00
22	PAC	00
23	PAC	00
24	PAC	00
25	EAC	00
26	EAC	00
27	EAC	00

Table 9: *Complete data set for Experiment 1.*

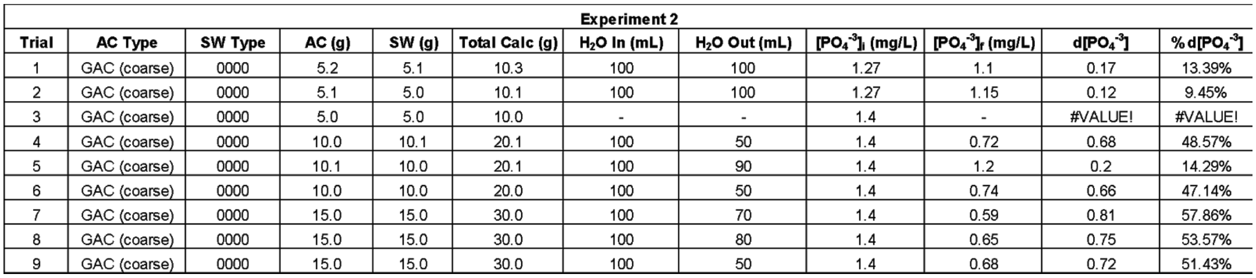


Experiment 1											
Trial	AC Type	SW Type	AC (g)	SW (g)	Total Calc (g)	H_2O In (mL)	H_2O Out (mL)	$[PO_4^{-3}]_i$ (mg/L)	$[PO_4^{-3}]_f$ (mg/L)	$d[PO_4^{-3}]$	% $d[PO_4^{-3}]$
1	GAC (Coarse)	0000	5.2	5.1	10.3	100	100	1.27	1.1	0.17	13.39%
2	GAC (Coarse)	0000	5.1	5	10.1	100	100	1.27	1.15	0.12	9.45%
3	GAC (Fine)	0000	5	5	10	100	100	1.27	Error	#VALUE!	#VALUE!
4	EAC	0000	4.9	5	9.9	100	100	1.37	1.38	-0.01	-0.73%
5	EAC	0000	4.9	5	9.9	100	100	1.27	1.32	-0.05	-3.94%
6	EAC	0000	5	5	10	100	100	1.27	1.34	-0.07	-5.51%
7	GAC (Coarse)	000	5	5.1	10.1	100	40	1.4	1.24	0.16	11.43%
8	GAC (Coarse)	000	5	5	10	100	60	1.4	1.4	0	0.00%
9	GAC (Coarse)	000	5	5	10	100	50	1.4	1.31	0.09	6.43%
10	GAC (Coarse)	00	5	5.2	10.2	100	70	1.4	1.29	0.11	7.86%
11	GAC (Coarse)	00	5	5	10	100	60	1.4	1.17	0.23	16.43%
12	GAC (Coarse)	00	5	5	10	100	100	1.45	1.12	0.33	22.76%
13	GAC (Coarse)	-	5	0	5	100	100	1.45	1.06	0.39	26.90%
14	GAC (Coarse)	-	9.9	0	9.9	100	100	1.45	1	0.45	31.03%
15	-	0000	0	5	5	100	100	1.45	1.31	0.14	9.66%
16	-	0000	0	10	10	100	80	1.45	1.26	0.19	13.10%

Trial 4 in Table 9 showed an error in phosphate reading due to the fine GAC instead of course and causing and excessive amount of carbon dust to be released into the water, tinting it dark gray and not measurable by the spectrophotometer. From this instance fine GAC was not used for any more experiments.

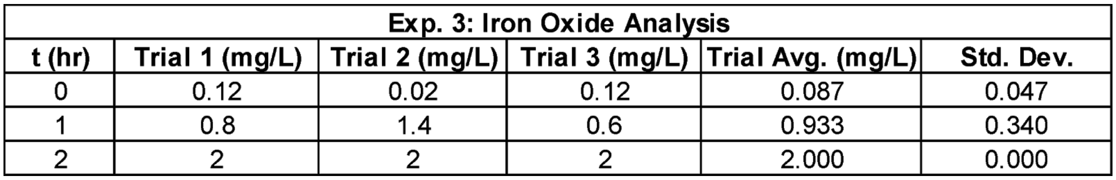
Trials 4 – 6 in Table 9 was the EAC/SW-0000 media and showed a consistent increase in phosphate concentration when measured so EAC was ruled out as a possible filter media.

Table 10: *Complete data set for Experiment 2.*



Experiment 2											
Trial	AC Type	SW Type	AC (g)	SW (g)	Total Calc (g)	H_2O In (mL)	H_2O Out (mL)	$[PO_4^{-3}]_i$ (mg/L)	$[PO_4^{-3}]_f$ (mg/L)	$d[PO_4^{-3}]$	% $d[PO_4^{-3}]$
1	GAC (coarse)	0000	5.2	5.1	10.3	100	100	1.27	1.1	0.17	13.39%
2	GAC (coarse)	0000	5.1	5.0	10.1	100	100	1.27	1.15	0.12	9.45%
3	GAC (coarse)	0000	5.0	5.0	10.0	-	-	1.4	-	#VALUE!	#VALUE!
4	GAC (coarse)	0000	10.0	10.1	20.1	100	50	1.4	0.72	0.68	48.57%
5	GAC (coarse)	0000	10.1	10.0	20.1	100	90	1.4	1.2	0.2	14.29%
6	GAC (coarse)	0000	10.0	10.0	20.0	100	50	1.4	0.74	0.66	47.14%
7	GAC (coarse)	0000	15.0	15.0	30.0	100	70	1.4	0.59	0.81	57.86%
8	GAC (coarse)	0000	15.0	15.0	30.0	100	80	1.4	0.65	0.75	53.57%
9	GAC (coarse)	0000	15.0	15.0	30.0	100	50	1.4	0.68	0.72	51.43%

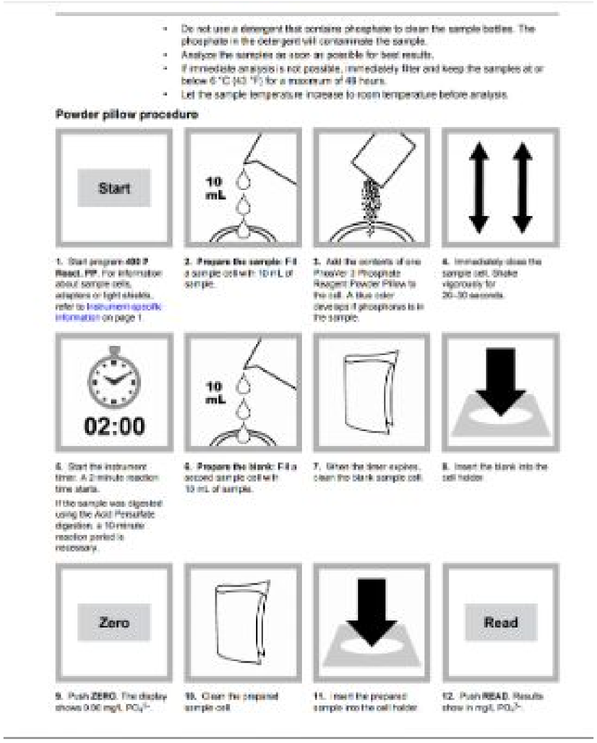
Table 11: *Complete data set for Experiment 3.*



Exp. 3: Iron Oxide Analysis					
t (hr)	Trial 1 (mg/L)	Trial 2 (mg/L)	Trial 3 (mg/L)	Trial Avg. (mg/L)	Std. Dev.
0	0.12	0.02	0.12	0.087	0.047
1	0.8	1.4	0.6	0.933	0.340
2	2	2	2	2.000	0.000

Appendix D: Supporting Documentation

Figure 5: *Hach DR 1900 used in the experiments.*



- Do not use a detergent that contains phosphate to clean the sample bottles. The phosphate in the detergent will contaminate the sample.
- Analyze the samples as soon as possible for best results.
- If immediate analysis is not possible, immediately filter and keep the samples at or below 6 °C (43 °F) for a maximum of 48 hours.
- Let the sample temperature increase to room temperature before analysis.

Powder pillow procedure

1. Start program **490 P React. PP**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

2. **Prepare the sample:** Fill a sample cell with 10 mL of sample.

3. **Add the contents of one** PhosVer 3 Phosphate Reagent Powder Pillow to the cell. A blue color develops if phosphorus is in the sample.

4. Immediately close the sample cell. Shake vigorously for 20–30 seconds.

5. Start the instrument timer. A 2-minute reaction time starts.

If the sample was digested using the Acid Persulfate digestion, a 10-minute reaction period is necessary.

6. **Prepare the blank:** Fill a second sample cell with 10 mL of sample.

7. When the timer expires, clean the blank sample cell.

8. Insert the blank into the cell holder.

9. Push **ZERO**. The display shows 0.00 mg/L PO_4^{3-}.

10. Clean the prepared sample cell.

11. Insert the prepared sample into the cell holder.

12. Push **READ**. Results show in mg/L PO_4^{3-}.

Figure 6: *Procedure used with the Hach for measuring phosphate concentration in a sample.*

Figure 7: *The Seachem Iron Test Kit used in Experiment 3.*

Figure 8: *The original test apparatus used in the experiments.*

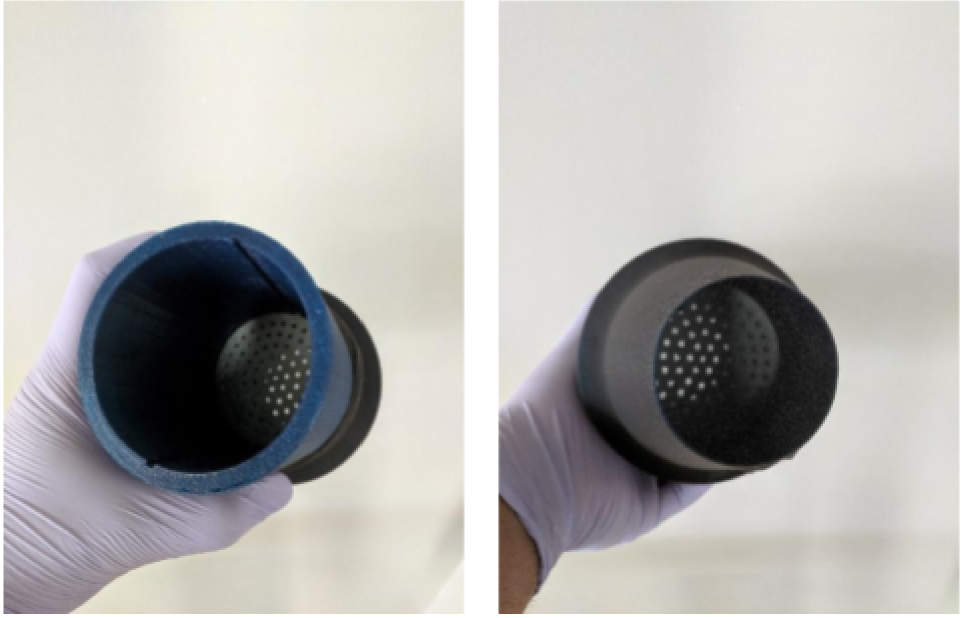


__Figure 9:__ Other views of the fully assembled 3D printed test apparatus.