FEASIBILITY OF MUCK REMOVAL IN THE IRL WATERSHED AND SUBSEQUENT FERRATE TREATMENT TO REMOVE EXCESS NUTRIENTS (Subtask 8)

Final Project Report to Brevard County Natural Resources Management Department
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DEP Grant Agreement No. S0714 – Brevard County Muck Dredging

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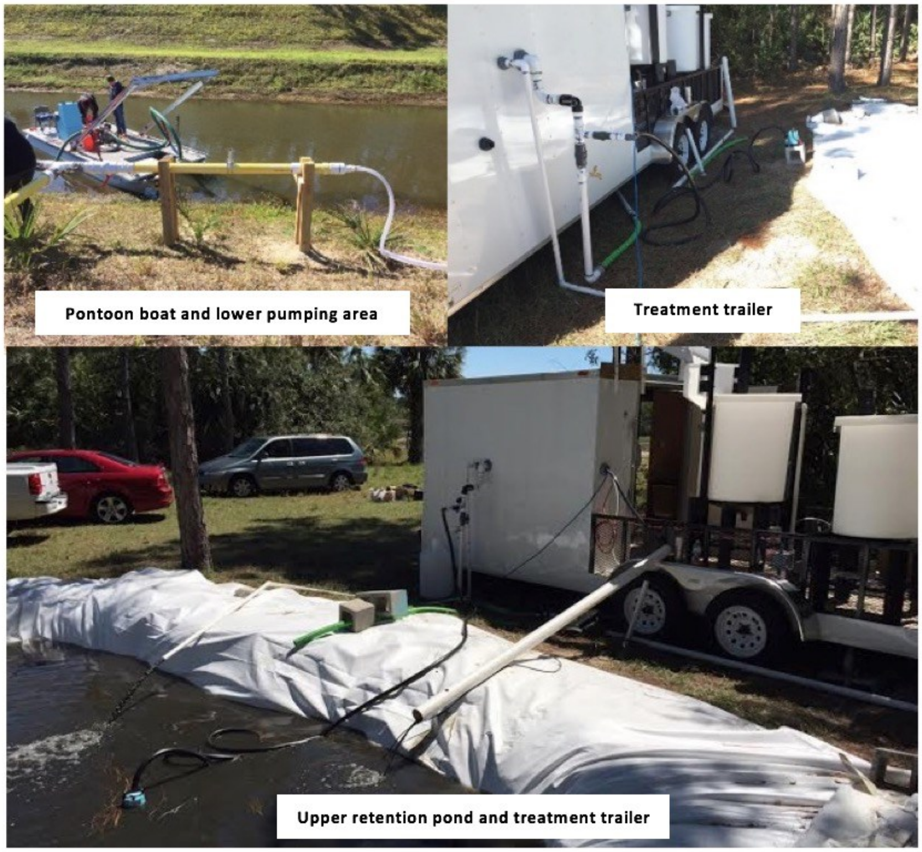

Cover image: Pilot-system test site with each component in operation.

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Acknowledgements

The PI's would like to acknowledge the Melbourne Tillman Water Control District (MTWCD) for allowing us to set-up the pilot system on the MTWCD property and use the canal for testing the pilot system. We would also like to recognize Brevard County, the IRLRI, and FIT for supporting this project. We would like to thank Brevard County Natural Resources Management Department and the Florida legislature for funding as part of DEP Grant Agreement No. S0714. We would like to thank Dr. John Trefry as well for providing muck samples and analysis.

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Summary

The focus of this project was to 1) implement the design and construction of a suction head for fine sediment dredging and 2) treat the dredged canal slurry mixture in a mobile treatment trailer system. The slurry treatment includes chemistry testing as outlined in the scope of work (SOW) below. The mobile solids removal/treatment system consists of a prototype suction head, a treatment trailer, and a deployment pontoon boat. Ferrate testing in the field confirmed the laboratory results, which showed that ferrate treatment was effective at removing the solids and nutrients.

The developed suction head has demonstrated that larger sediments can be precluded by implementing a variable intake area system, including a shroud. The ferrate chemistry has shown that ferrate was effective at removing nitrogen and phosphorous to levels below detection of the available instrumentation when the appropriate ferrate/ferric formulation was used. Greater than 64% reduction of ammonia and nitrite-nitrogen was achieved. In addition, greater than 95% of total suspended solids were removed and 90% of phosphorus was removed. Field testing of the coupled system confirms the feasibility of small scale muck sump operations along canals and rivers that flow into the IRL.

A mobile system would require that sites be identified and prepared in advance, since the current pilot system still required the use of a small detention pond. That pond could be replaced by an on-site holding tank adjacent to the sump site. In addition, an autonomous scaled-up system can be developed and installed in permanent locations in canals to manage muck removal prior to entering the Lagoon. Further improvements to the system/project can be made such as optimization of a jet ring system for more efficient sediment suspension, redesign of shroud based on sediment fall velocity analyses and flow simulation analyses, testing at multiple sites, and determining remaining sediment profile of material post dredging operations.

Scope of Work (SOW)

The outcomes from the dredging monitoring study point toward muck removal as an important method for reducing the nutrient load and improving the water quality in the IRL. There was a need to investigate muck removal and treatment systems at a variety of scales, designed for operations in a wide range of locations. This project sought to advance the understanding of the feasibility of fine sediment and muck removal and to determine an effective ferrate treatment of spoil residuals to remove nutrients from upstream sumps before it enters the IRL. In coordination with the Indian River Lagoon Research Institute (IRLRI), Melbourne-Tillman Water Control

District (MTWCD), and Brevard County, the proposed project demonstrated at pilot scale, an innovative Ferrate-based coupled dredge spoil-residuals treatment system.

Pilot scale was defined as:

- Large enough (flow) to demonstrate the collection and treatability of muck at a realistic scale, that can be reliably scaled up or down depending on ultimate design flows selected for each project.
- Small enough to be reasonably inexpensive and to be of a scale such that the ferrate required for running the plant (one day) was small enough so that the rental of a commercial Ferrator was not required (ferrate can be made daily off site, and transported to test sites).

The ferrate based system includes: muck removal, pumping, separating, spoil management, flow monitoring, mixing tank, feed chemical storage and injection system, on-line water quality monitoring systems, and sample collection capabilities, Figure 1. Past studies indicate the optimal size and flow rates for removal of muck while leaving sand in place. Systems developed for muck removal use several steps for capturing the spoil prior to treatment of the residuals. For this pilot study, we utilized the land available at the MTWCD site for a small containment pond which captured the spoil and any overflow from the treatment system. The proposed pilot system can test the sensitivity to treating the slurry at all phases of the process:

- directly treating the main line of slurry prior to the separation of the larger particles;
- treat the elutriate after the large particles have been separated;
- a combination of the two or any step in between.

One of the possible benefits of the slurry treatment was to neutralize any odors, enabling the system to be placed in close proximity to homes.

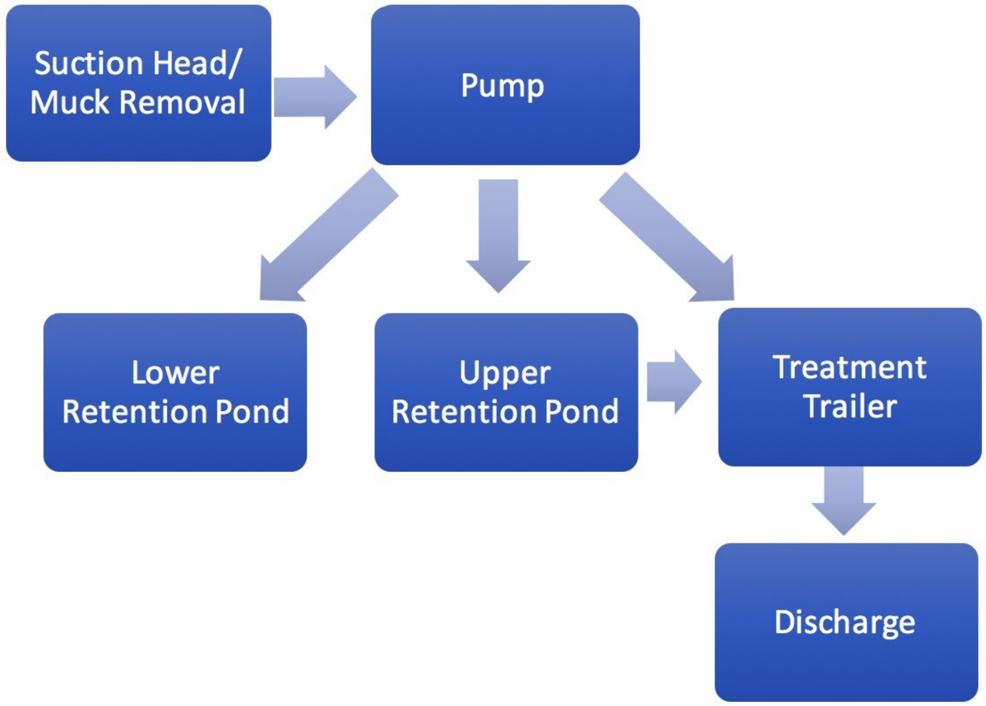


Figure 1: Components/process flow diagram

<u>Project Metrics</u>:

The success and feasibility of the system was assessed based on performance of the system, and measured by:

- Whether a dredge design can efficiently lift the muck from sites in canals, while precluding sand particles (approx. 0.2 mm and larger) from being drawn in by the suction head, under constant flow conditions
- Whether treating dredge spoils (after different separation processes) with ferrate can reduce phosphorus concentrations to very low levels, while also reducing concentrations of ammonia, TOC and suspended solids.
- Whether an efficient end use or disposal plan for the solids can be established, including the feasibility of scaling up.

Sediment cores determined the composition of the bottom sediment where the dredge was deployed. Analysis was performed to establish sediment profile, focusing on the amount of sand and larger sediments. Once pumping begins, samples are pulled out of the system prior to entering the treatment train. These samples were analyzed for sediment composition. By comparing the sediment composition of the dredge slurry to the material in the site cores, we were able to determine percent of preclusion of larger particles by the designed suction head. Success in the initial testing would be achieved if we can preclude 40% of the sand from the dredge. Subsequent testing will increase the percent of precluded sand, with an end goal of 80% preclusion.

The concentrations of both phosphorus and nitrogen compounds were measured in the raw dredge water at the test sites. These same parameters were measured after ferrate treatment under different operating conditions. The main parameter determining success of the treatment was the degree to which the macro nutrients, nitrogen and phosphorus, were removed under different treatment conditions. Chemical costs (chemicals needed to produce ferrate) can be estimated by current stock chemical costs. Based on current costs, the chemical costs for a dose of 1 mg/L of ferrate is approximately 5 cents per thousand gallons treated. Utilizing data from a study of ferrate treatment of runoff water in the Everglades, the Istokpoga Marsh Watershed Improvement District was able to show that for a background concentration of 1.3 mg/L of phosphate, ferrate at a dose of 2 mg/L could completely remove the phosphorus. Because ferrate was able to oxidize compounds and coagulate material, other materials were removed besides the phosphorus. For example, ammonia would be oxidized and organic carbon would be coagulated by the ferric hydroxide floc. In any case, removing 1.3 mg/L of phosphate with 2 mg/L of ferrate converts to a cost of about $10 per pound of phosphate removed. It is anticipated that this material containing the iron phosphate would be recycled back for use in agriculture as a soil amendment, thereby offsetting much of the treatment costs required to remove it from the water.

Future studies making use of this pilot scale system could involve testing alternate treatment systems to the proposed Ferrate system or adapting the system to be mounted on a barge allowing access from the water instead of from land. The pilot scale system also serves as a functioning template for a full-scale system.

Introduction

Removal of the legacy loading of muck has been identified as an important step in restoring the water quality in the Indian River Lagoon. The current study focuses on moving beyond monitoring and into the research and development of innovative methods of removal and remediation. This study was focused on the design of a Ferrate-based coupled mobile dredge-treatment system at a pilot scale.

To meet the criteria for a pilot scale treatment system as outlined in the SOW, a design flow for the pilot plant of 5 to 10 gallons per minute was selected. This pilot scale flow rate was chosen in an effort to keep the scale and costs manageable, with the constraint that the entire pilot treatment system needs to fit on a single trailer. The components sourced for the separation, metering, administration of the chemistry, and mixing were all selected based on this flow rate. With these pilot scale flows, the slurry could easily be managed. During actual dredging of muck from various sites in the Indian River Lagoon, or upstream in the feeding rivers and canals, design flows are highly variable. The actual flow at any site depends on the storage capacity of dredged muck around the site, the time to finish dredging a site, and the type of treatment the muck receives. This project helped define the types of treatment scenarios (utilizing ferrate) that can be used at different sites around the lagoon. The design flow for this pilot plant was set such that scaling results up or down will be easy and reliable.

The ferrate based system included: muck removal, pumping, sediment separating, spoil management, flow monitoring, mixing tanks, feed chemical storage and injection system, in-line water quality monitoring systems, and sample collection capabilities. Each of the listed components was a unique project in itself and required the PI's to start from scratch. Each sub-system has to be designed and built to meet the demands of the project. For muck removal, a custom, novel design for a variable intake area suction head was designed, constructed and tested in the field and in the lab. The suction head was designed with the goal of precluding sediments larger than 0.2 mm in diameter, fine sand and larger. In order to test the system in the field, a deployment boat was required. A custom constructed pontoon boat was built for deploying the dredging system. Upon removal of the slurry mixture with the suction head from the canal, a separating method was needed to remove and separate out any large sediments. Two methods were tested in this study: a settling pond and in-line hydrocyclones. The slurry was then pumped through the ferrate treatment system which was also custom designed for this study. Components were sized based on the pilot scale flow rates determined to be approximately 5 gallons per minute (GPM). For this project, the spoil management was relatively simple. The MTWCD allowed the team to use their property and the small volume of solids could be disposed of on site. In a prototype scale project, the larger solids separated prior to ferrate treatment would need to be contained and then shipped to a disposal site, such as a landfill, or returned to the lagoon if the solids are not contaminated. The treatment residuals, the sludge of coagulated fines precipitated out by the ferrate, were tested for reuse as a soil amendment to pepper plants.

Approach

Our approach for addressing the removal and treatment of the fine sediments termed 'muck' was to develop a purpose-designed and built suction head and connect that to a ferrate based treatment system. The ultimate goal was a self-contained dredging-treatment system for removal of fine sediments (muck) from shallow and/or environmentally sensitive regions within an estuary. For the dredging component, our approach was to design a variable intake area suction head. For hydraulic dredging, the size of the sediment entrained by the suction head is a function of the intake flow area, flow rate, and velocity, which can be controlled by the operator. Our design was focused on the preclusion of sediment grain sizes 0.2 mm and larger, as stated in the Project Metrics of Subtask 8 in the Statement of Work (SOW). In order to accomplish this, it was imperative to determine the Shields parameter (Ψ), the dimensionless critical shear stress τ_c, the Darcy-Weisbach friction coefficient f, and the drag coefficient C_D, to calculate velocity, Appendix D. Using an approximate drag coefficient of 0.44 for an imperfect sphere, a Shields parameter of 0.03, and substituting values for gravitational acceleration, diameter of sand particles, density of sand, and density of sea water, we can solve analytically for the velocity required for sediment motion.

Theory predicts sediment sizes of 0.2 mm are likely to move at current velocities of 2 cm/s or more. The goal of this project was to achieve a flow velocity of the same size by fine-tuning the intake area of the suction head which alters flow velocity, thus attaining the desired current velocity to preclude large sediments. Based on the calculated current velocity, the optimal intake area of the suction head was determined.

The volume flow rate equation, $Q = V * A$, (where Q is the volume flow rate, V is the mean current velocity, and A is the intake area) was used to find the current velocity for a given pump flow and suction head opening, Table 1. The flow rate equation was then also used to find the optimal suction head opening for a given pump flow rate and current velocity, Table 2.

Table 1: Current Velocity for Given Pump Flow and Suction Head Opening

Pump Flow (GPM)	Suction Head Opening (inches)	Velocity (cm/s)
100	0.0625	30
	2.5	7
	5	4
150	0.0625	40
	2.5	10
	5	5
200	0.0625	60
	2.5	10
	5	7

Table 2: Optimal Suction Head Opening for Given Pump Flow and Velocity

Pump Flow (GPM)	Velocity (cm/s)	Suction Head Opening (inches)
100	2	9
150	2	13
200	2	20

Operating at a flow of 100 GPM, the optimal suction head opening given by the previous theory for a desired current velocity of 2 cm/s was approximately 9 inches, Table 2.

A series of tests were completed with the variable intake suction head both on-campus at FIT and at the field site in the C-1 canal. Testing on campus was done by employing use of a 5-ft diameter by 5-ft tall plastic tank, Figure 2.

Figure 2: On-campus laboratory setup with testing tank and intake/discharge hoses

The first set of tests was performed using a 32" x 32" x 14" shroud, Figure 3, attached to the bottom of the variable intake suction head. The square shroud was designed to reduce the entrainment of ambient water. When attached to the suction head, the shroud increases the vertical distance from the bottom of the suction head to the seafloor, Figure 4.

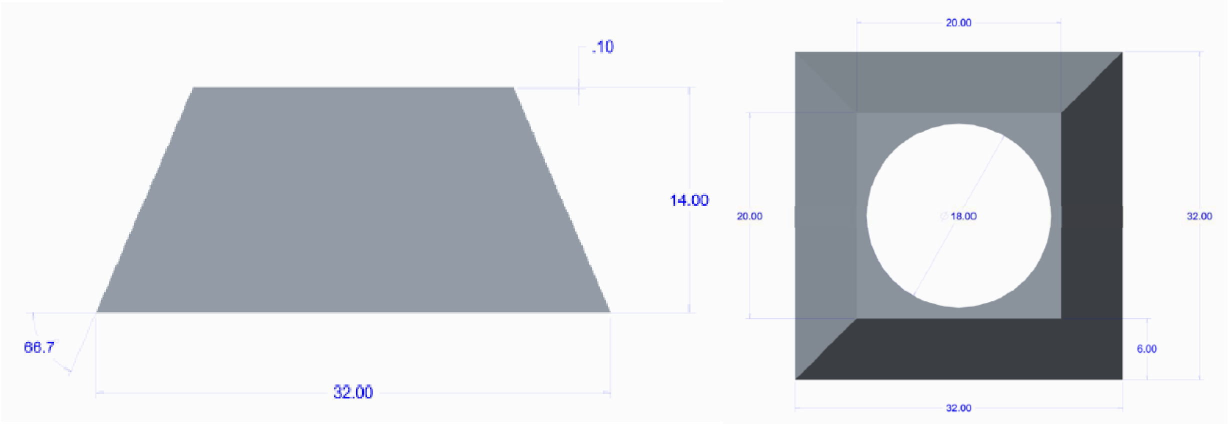


Figure 3: Rectangular Shroud Dimensions (inches)

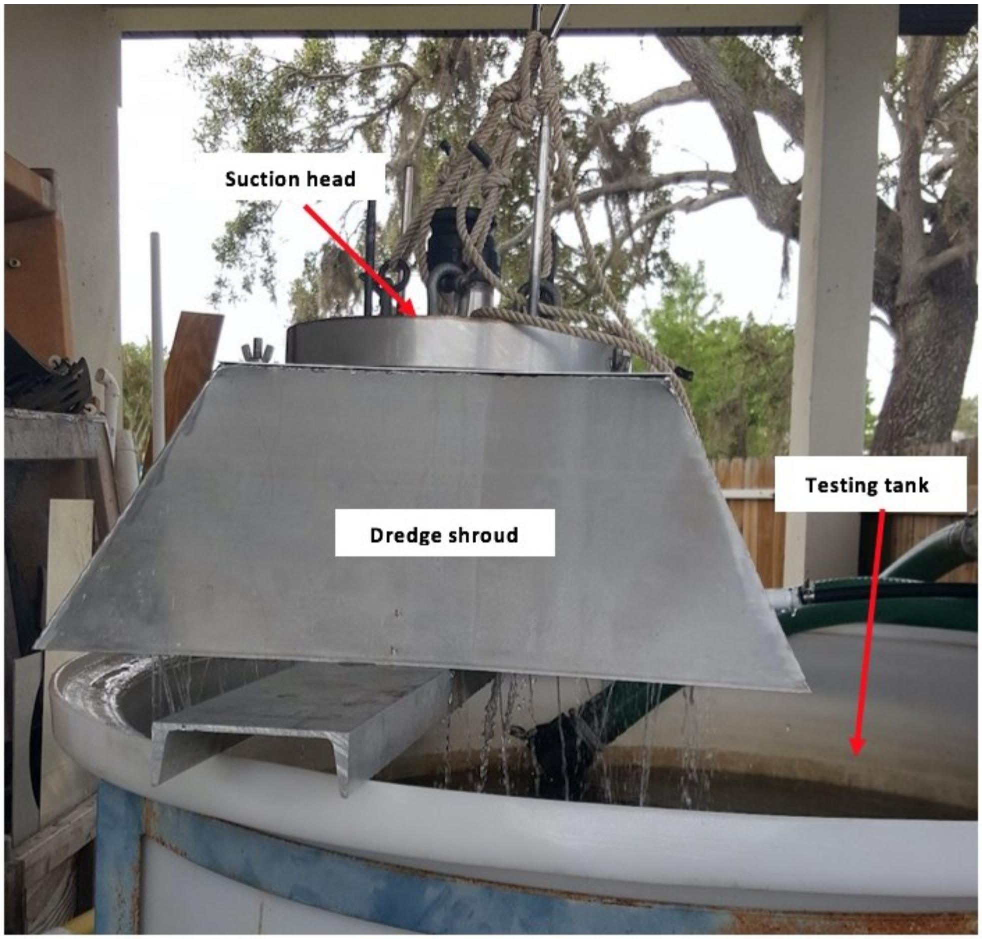


Figure 4: Rectangular Shroud Attached to Suction Head

Tests were completed using two different types of active jet systems. The purpose of the active jets was to mobilize and suspend sediment into the suction head intake area. With both types of active jet systems, the shroud was utilized and remained attached to the suction head. The first set of tests was performed on June 5th, June 6th, and June 8th using a pressure washer to act as an active jet. A 2-inch diameter hole was cut out of the rectangular shroud for the pressure washer to be inserted and pointed towards the bottom sediment.

The second set of active jet testing was executed on June 12th, June 14th, and June 15th. A one-inch diameter flexible irrigation hose with 1/8" holes drilled approximately an inch apart was connected to the bottom of the rectangular shroud with pipe straps, Figure 5. The hose was then connected to a PVC tee with hose shanks and hose clamps. A one-inch diameter hole was cut out of the shroud for the intake of the PVC tee to connect to the pumping source. A pool pump rated at 40 GPM was used to pump water through the irrigation hose to suspend sediment.

Figure 5: Active Jet Setup with Pool Pump and Irrigation Hose

A passive jet system was designed to eliminate the need for an additional power source to supply power to an active jet pump. Four passive jets were 3D printed with acrylonitrile butadiene styrene (ABS), an oil-based thermoplastic that has high strength, flexibility, and durability. The design consists of a 4-inch diameter cone that tapers to a 1-inch diameter by 4-inch-long cylinder which further tapers to an approximately ¼ inch diameter hole. A 3D printed nut holds the cone in place from underneath the shroud, Figure 6.

Figure 6: 3D Printed Passive Jet

A test was also completed using only the shroud with an extension attached, Figure 7. An additional foot long piece of stainless steel was attached to the end of the shroud which can be easily removed as needed. The purpose of the extension was to justify the need for a variable intake area to control the amount of sand greater than 0.2 mm in diameter that was precluded. When testing with the extension, the gear system that controls the intake area was removed and only the suction hose was attached to the top of the shroud.

Figure 7: Rectangular Shroud with Extension Attached

The variable intake area suction head also underwent testing at the pilot site (Site 3 at C-59 and C-1). Altogether, the dredging and treatment operated as a combined system through the treatment trailer. At the field site, dredged slurry was pumped from the suction head on the pontoon boat, Figure 8, through 3-inch diameter pipe where it passes through a tee, Figure 9. At the tee, flow was diverted to a discharge pipe into a lower retention pond or into 1.5-inch pipe that led to the top of the hill into the trailer where it was treated directly as it was being pumped, Figure 10.

The primary goal of the field test was to perform a full system operation to test the use of hydrocyclones, devices used to separate suspended particles in a liquid solution, in the treatment trailer. Samples of the slurry mixture were collected with the suction head operating only at the fully open setting of 5 inches because best results were seen in lab testing with the shroud at the open setting. Samples were taken at 3 different locations, the bottom of the hill from the 3-inch discharge pipe, the top of the hill from the 1.5-inch pipe before entering the trailer, and after entering the trailer and being filtered by the hydrocyclones.

Figure 8: Pontoon Boat with Suction Head Deployed

Figure 9: Tee with Discharge Flow

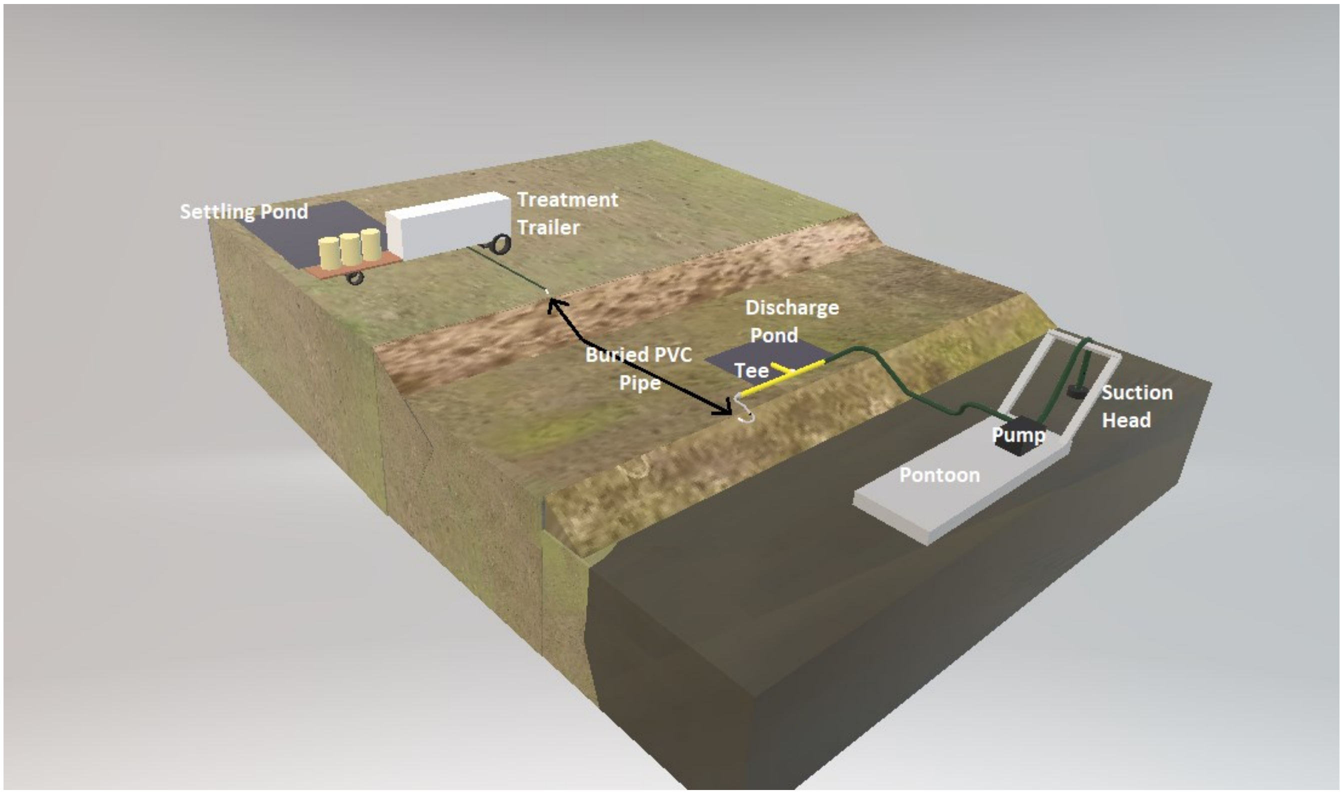


Figure 10: Model Diagram of Dredging System on Site

At the trailer, the flow rate could also be adjusted as it was pumped through the system and was typically kept between 3 and 10 GPM. The slurry was sent through two hydrocyclones to rapidly separate the heavier particles, Figure 11. Various combinations of hydrocyclones were used during initial testing with mesh sizes ASTM No. 100, 60, 40, and 30, see Appendix C. For the final field test, two combinations were tested, sizes 40 and 60 meshes and sizes 40 and 30 meshes. The size 30 mesh has the capability to filter sediment larger than 0.545 mm, while size 40 mesh can filter larger than 0.42 mm and size 60 mesh can filter larger than 0.25 mm.

Figure 11: Dredge Slurry Actively Pumped Through Hydrocyclones

Following filtering through the hydrocyclones, the remaining slurry was pumped through a series of chemical treatment containers. The first container dosed the slurry with ferrate while the tank was stirred with a motorized mixer, Figure 12. As the first tank filled, the slurry flowed into the secondary tank where the pH was lowered and also continuously stirred with a motorized mixer. The treated water then flowed into the third tank where the flocculated material and water separated (see Treatment Section). The first reaction vessel (right) contained the oxidation process of ferrate, and the second reactor (middle) contained the coagulation reactions. The third reactor (left) was the clarifier. The detention time through the pilot plant was 40 minutes, when running at 3 GPM. This process is discussed further in the sub-section Design and Fabrication of the Pilot Treatment System.

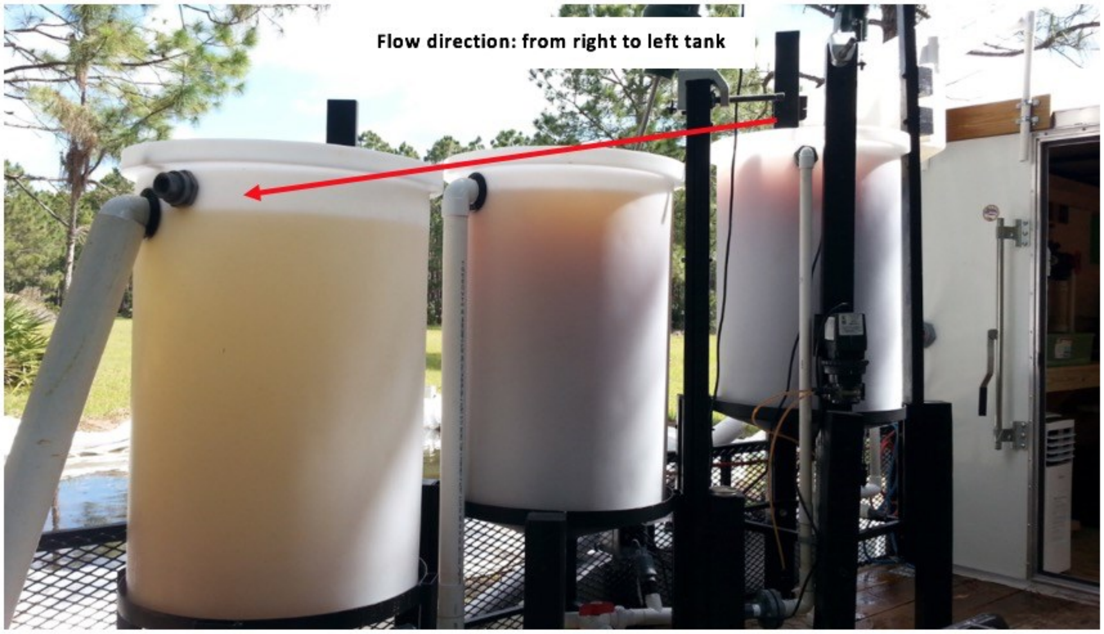


Figure 12: Ferrate Pilot Plant Treating Muck Dredge Water at Tillman Canal Site

Each test, with the exception of the extended shroud test, was performed with the suction head opened at 3 settings: ⅝ inch, 2.5 inches, and 5 inches, Figure 13.

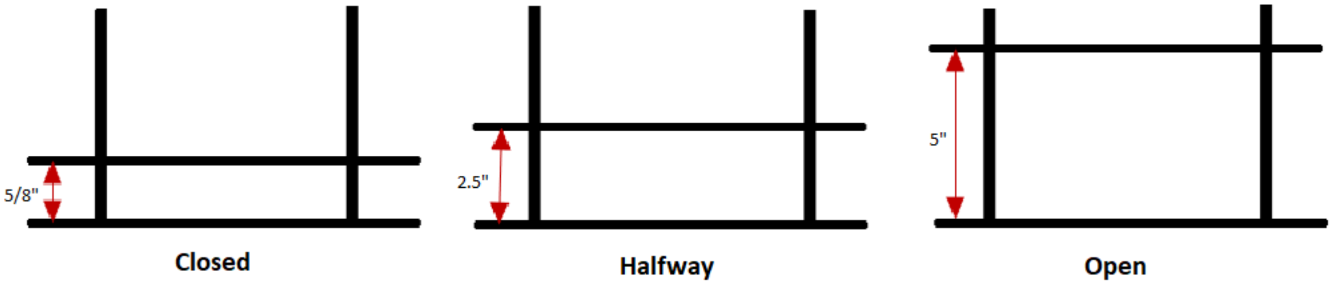


Figure 13: Diagram of Suction Head Openings

Three samples of each were taken with the addition of a control taken from the 3-inch diameter intake hose without the suction head attached for a total of 12 samples. When testing with the extension, the suction head and gear system was removed and samples were collected with only the intake hose, shroud, and extension. A total of 12 samples were collected for each test, and in between sample sets of 3, the shroud was raised and the slurry mixture was stirred. All samples were then analyzed using the developed ASTM sediment analysis procedure (ASTM D6913/D6913M-17) and then averaged together. From a total of 17 lab tests, the average error associated with the developed sediment analysis procedure was 4%. The procedure used for sediment analysis can be found in Appendix A.

After completing sediment analysis, each set of results was summarized graphically with a cumulative distribution chart produced in MATLAB, from which a significant amount of information can be obtained. The most important measure of sediment samples for our purposes was d50, or median sand size. The d50 value can be taken directly from the cumulative distribution curve, as it is the size for which half the sample is coarser by weight and half the sample is finer. The percent reduction in d50 revealed how much the median sediment size was reduced in each sample set as compared to the control. For instance, percent reduction in d50 for an open sample can be found using the equation:

$$\frac{control - open}{control} * 100\%$$

By calculating the percent reductions, inferences were made about the effectiveness of the particular setup used for testing.

Design and Fabrication of the Pilot Scale Ferrate Treatment System

The design parameters (reaction detention times, mixing intensity, ferrate dose etc.) were determined by bench scale testing of muck samples collected from around the IRL. The test results from this work are included in Appendix F and background information of Ferrate(VI) is included in Appendix E. The pilot ferrate treatment system was designed considering:

1) Portability: The system had to be transportable to move the pilot treatment system out to various sites where experiments could be run. The design included on board power capabilities (gasoline powered electric generator) and all plumbing required for connection to various size pipes bringing water to be treated into the trailer. The trailer was also air-conditioned, and temperature controlled reactors were added to maintain the ferrate feed stock during testing. The trailer could be easily hauled by University vans, and could be quickly leveled and set up in the field. The trailer was instrumented with all monitors required to assure correct operation of the treatment system. Portable analytical equipment was included (pH electrode, and UV/Viz. spectrophotometer) to allow operators to adjust chemical feed streams for optimal treatment of muck discharge water for removal of N, P, and suspended solids. Treatment of aqueous streams with ferrate required a determination of the ferrate dose, total iron content, and pH, and these parameters are adjustable at the treatment site. The operator of the pilot system adjusted these parameters by regulation of flow rates for both the ferrate and ferric feed solutions.

2) Reactor design to accommodate ferrate chemistry to efficiently and reliably generate a ferrate feedstock for treatability studies. This design included determination of optimal temperature regimes required for generating high purity ferrate solutions, and the determination of time required at different temperatures in order to ensure a reliable generation of the ferrate product. The ferrate solutions generated were then tested to determine stability with time, in order to optimize storage conditions on site for the feed solution. Lastly, the reactor design and

operational temperature scenarios were optimized in order to generate a ferrate solution as rapidly as possible.

The trailer-mounted pilot plant system was comprised of three reactor vessels. In order to save money, and make fabrication easier, all reactors were the same size (approx. 40 gallons). The pilot plant was designed to operate by gravity (tanks open to the atmosphere). The system was designed to operate at between 3–5 GPM giving detention times through the treatment system of between 40 and 24 min. The reactor volumes (and therefore detention times) were adjusted by lowering the reactor discharges.

Reactor 1: Ferrate reaction tank (oxidation process – mixed)

Reactor 2: Ferrate/ferric coagulation tank (particle aggregation process – mixed)

Reactor 3: Clarifier (particle settling)

Electronic Flow control was included. Chemical injection systems for pH and total iron control were included.

Figure 14: Fabrication of Treatment System at FIT

Figure 15: Fabrication of Trailer at FIT

Figure 16: Deployment at Field Site, Retention Pond

Results and Discussion

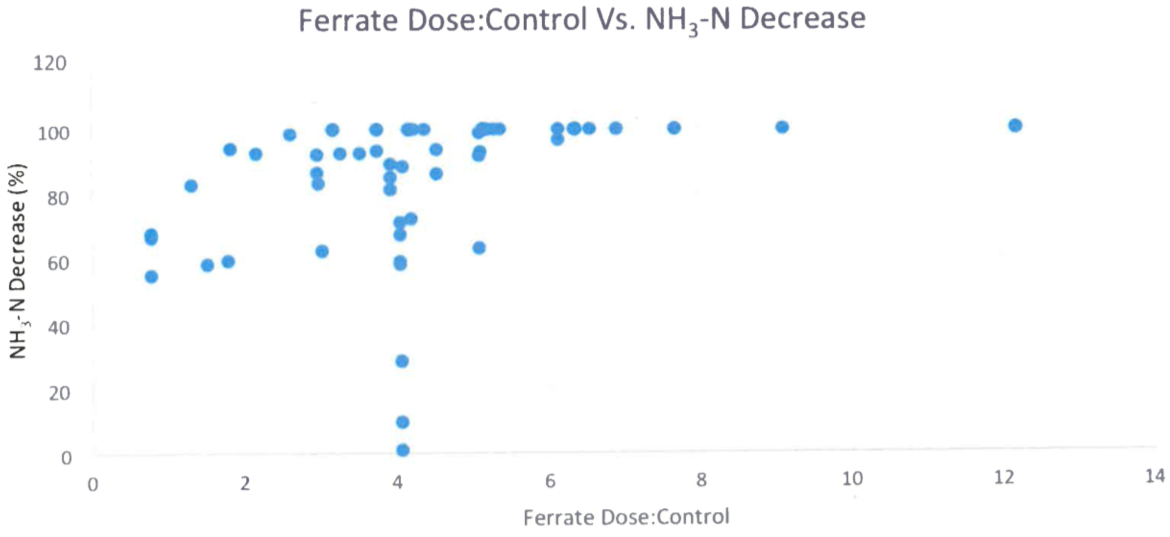
Treatment Results

Initial project work focused on (at laboratory scale) the fundamental chemistry of ferrate-based water treatment systems, determining application issues associated with scale-up of the ferrate synthesis, and handling and storage for the planned pilot treatment experiments.

Specifically:

- Extensive laboratory testing was undertaken to fully define parameters affecting the synthesis of high strength ferrate solutions, including experiments evaluating effects of pH, mixing times and temperatures, volume of reactants, and different anions present on ferrate yield. The results of these fundamental studies have led to a ferrate synthesis "formulation" yielding > 2% ferrate solutions.
- Once the fundamental chemistry of ferrate synthesis was determined, water treatment studies with muck dredge water were undertaken. Overall, >45 bench scale studies, utilizing 10 different muck samples were completed (see Appendix D). Chemical analyses (and equipment) were purchased and developed in order to determine treatment effectiveness. The analytical determinations required modifications in order to deal with the complex ferrate/muck mix of constituents. QA/QC procedures were developed and implemented to assure reliability of the data collected. In addition, one muck sample was split, and analytical data collected by our laboratory were compared to similar analyses run at a separate laboratory, utilizing equipment

with lower levels of detection. Analyses routinely run for each water treatment study included: pH, temperature, PO_4, P_{TOTAL}, NH_4^+, NO_2^-, NO_3^-, N_{TOTAL}, Fe, Turbidity, and TSS.



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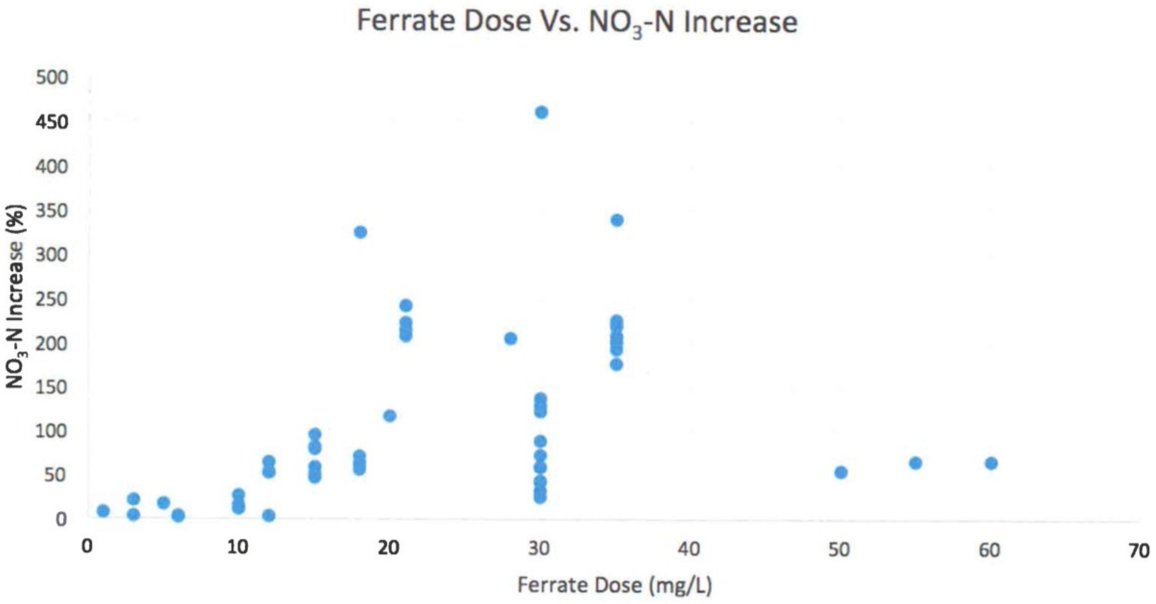

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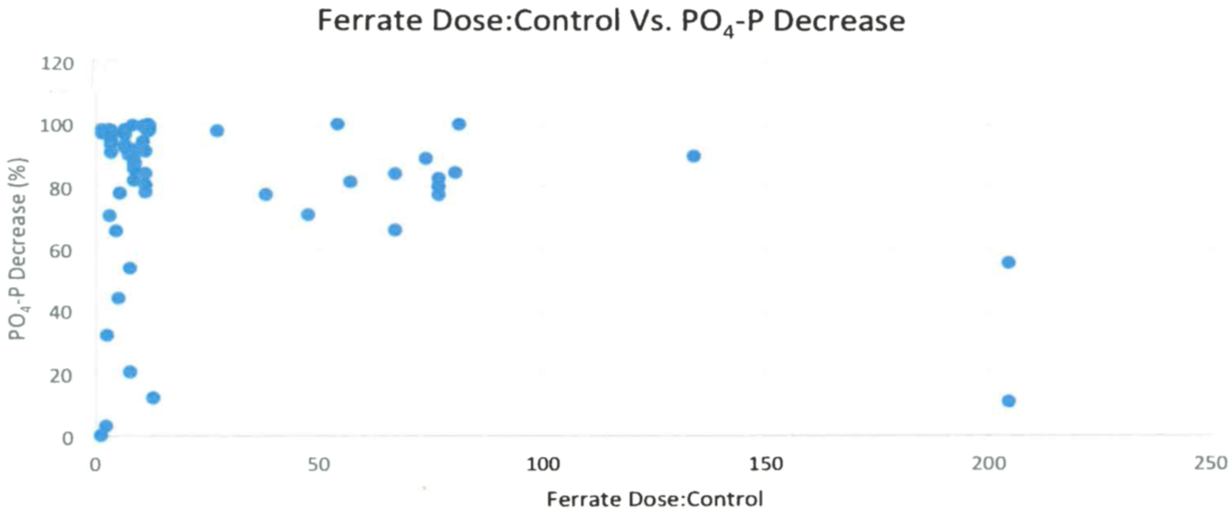
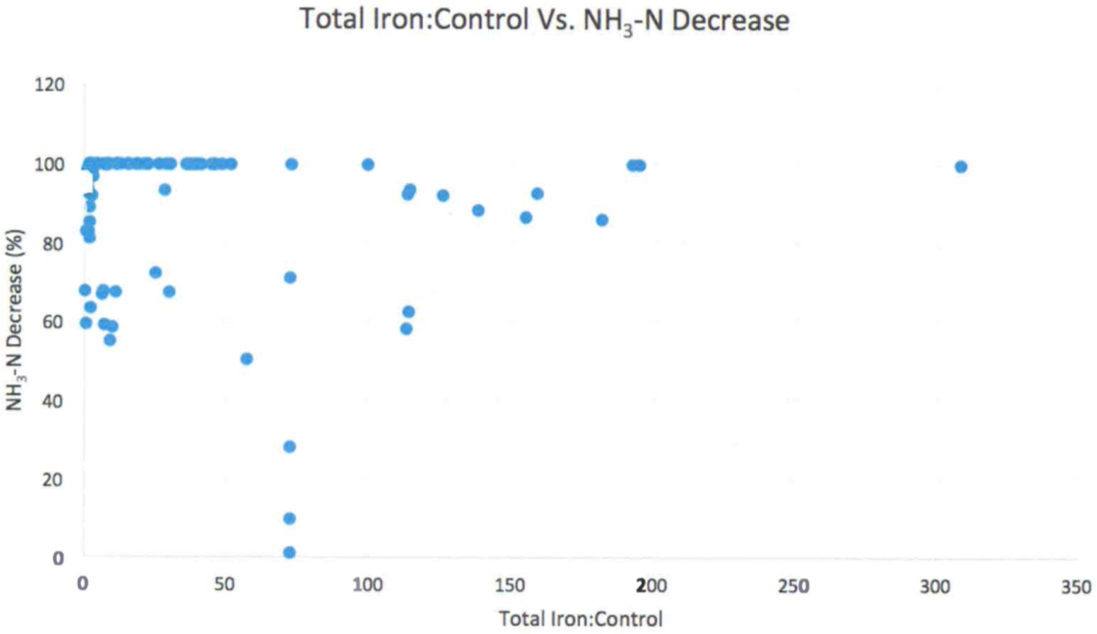
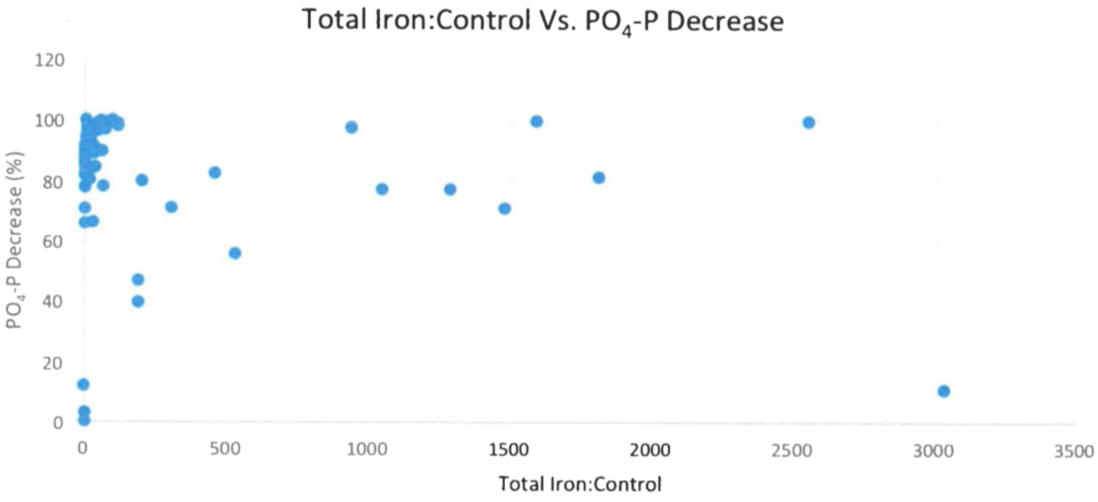

Ferrate Dose:Control Vs. PO_4-P Decrease
PO_4-P Decrease (%)
120
100
80
60
40
20
0
0
50
100
150
200
250
Ferrate Dose:Control

c)


Total Iron:Control Vs. NH_3-N Decrease
NH_3-N Decrease (%)
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
Total Iron:Control

d)

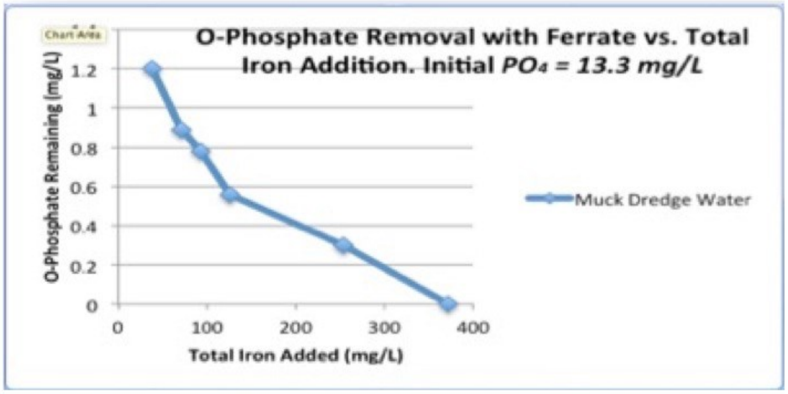


e)

Figure 17: Summation of all bench scale tests of the different muck dredge water samples comparing ferrate dose and total iron concentration to changes in the nutrients due to: ferrate dose- a) NH_3, b) NO_3, c) PO_4, and total iron concentration- d) NH_3, e) PO_4

Muck dredge water samples were collected from the study site periodically throughout the project and brought to the lab for testing. Laboratory testing was performed looking at the effects of both ferrate (Fe^6) and a combination of Fe^{3+} & Fe^{6+} (total iron) on the removal of phosphate- P and different species of nitrogen, Figure 17 a-e. It can be noted (even with scatter in the data) that ferrate "dose" affected the removal of ammonia (oxidation reaction), Figure 17 a, and also affected the removal of phosphorus (precipitation reaction), Figure 17 c. Total iron added (ferrate + ferric) affected the removal of phosphorus, but not ammonia, Figures 17 d and e. It was also seen that ferrate dose affected the formation of nitrate nitrogen, Figure 17 b. The result of these treatment studies was a formulation of ferrate dose + total iron concentration required to remove both N & P from solution (FeO_4^{2-} / NH_4^+ = 3, Fe_{TOTAL} / P_{TOTAL} = 40). Both total N and P were reduced to very low levels, when the correct ferrate/ferric formulation was used.

Treatability results for a "typical" muck dredge water treated with a ferrate were important to analyze, Figure 18. There was >90% destruction of ammonia, >90% destruction of nitrite-nitrogen, and no change in nitrate-nitrogen concentration. Our hypothesis was that all of the nitrogen destroyed was converted to a gaseous form of nitrogen (N_2, N_2O, NO). It was also noted that 65% of the phosphorus was removed and >95% of the suspended solids were removed. Also included in the figure are calculations estimating the chemical cost (ferrate) to simultaneously remove N + P + TSS, $0.30 per pound of each of the target compounds.



Muck Dredge Water	pH	NH_4-N (mg/L)	NO_2-N (mg/L)	NO_3-N (mg/L)	PO_4-P (mg/L)	TSS (mg/L)	Total N+P	Total N+P+TSS
Control	7.5	2.03	0.03	0.36	1.2	185.4		
Treated	7.0	0.16	0.006	0.35	0.4	8.5		
Chemical Cost ($/lb.)	-----	$30.00	-----	-----	$69.0	$0.3	$21.0	$0.3

Figure 18: Treatability Results for a Typical Muck Dredge Water Sample Treated with Ferrate

A significant effort was made to develop protocols and procedures for scaling up the synthesis process and storage capacity of ferrate solutions in anticipation of running a pilot ferrate treatment system. Based on system design parameters, approximately 4 L of ferrate solution was required to operate the pilot plant for 1 hour. Our team purchased a large jacketed beaker, which was connected to the temperature control system. When operational, we were able to synthesize up to a 2-L batch of strong ferrate solution.

Ferrate solutions are unstable, but some storage was required in order to supply the required amount of ferrate for treatment. We explored solution stability enhancement utilizing reduced temperatures. The decay of active ferrate with time at a temperature of -6 C was investigated, Figure 19. This solution maintains good ferrate strength for at least 3 weeks at this temperature.

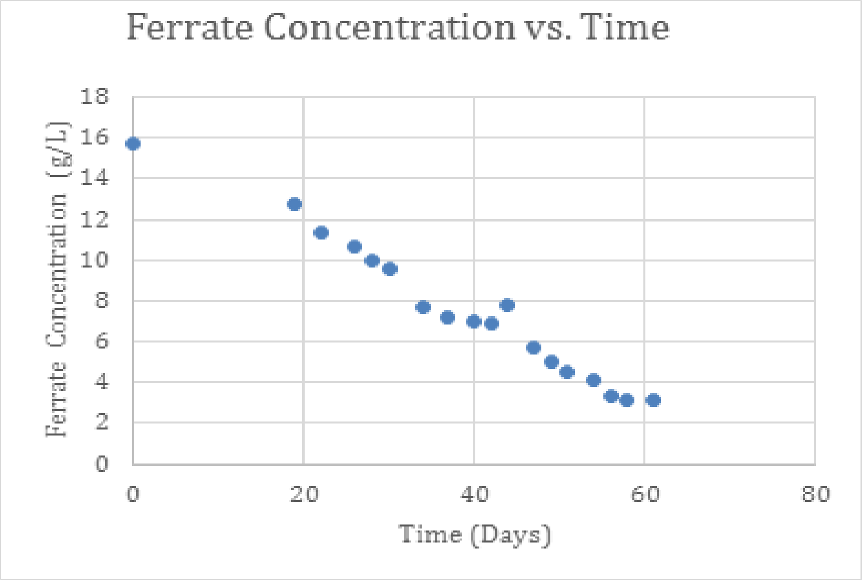


Figure 19: Measured Ferrate Concentration in g/L vs. Time for the Laboratory Testing

During project work on testing (at lab and pilot scale), the fundamental chemistry of ferrate-based water treatment systems was evaluated, as well as safe and efficient handling and storage during the pilot scale treatment experiments. This work included the development of ferrate residual monitoring, which was important during the implementation of the treatment process.

We conducted a series of tests comparing ferrate concentration to pH while measuring Oxidation Reduction Potential (ORP). This was done to see if ORP would be a reliable measure of ferrate in solution using an ORP electrode. However, due to the dependence of ORP on solution pH, the first experiments measured the ORP vs. pH of ferrate in treated water, Figure 20. This was done to determine how much ORP varied with pH.

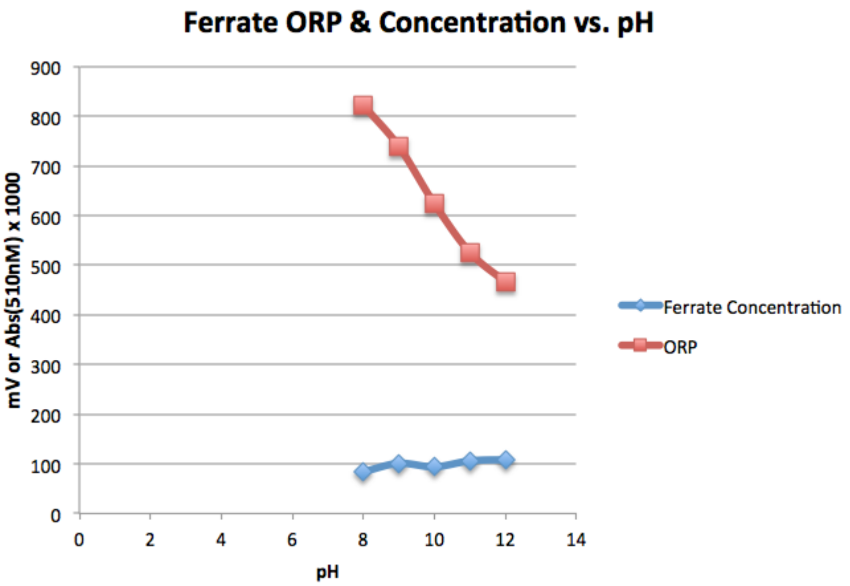


Figure 20: Ferrate ORP & Concentration vs. pH

From these results, we note that ORP was dependent on pH. Therefore, the potential of ferrate in solution must be determined at a fixed pH. ORP can estimate ferrate concentrations at low doses (< 5 mg/L), but was not very sensitive at high doses, Figure 21.

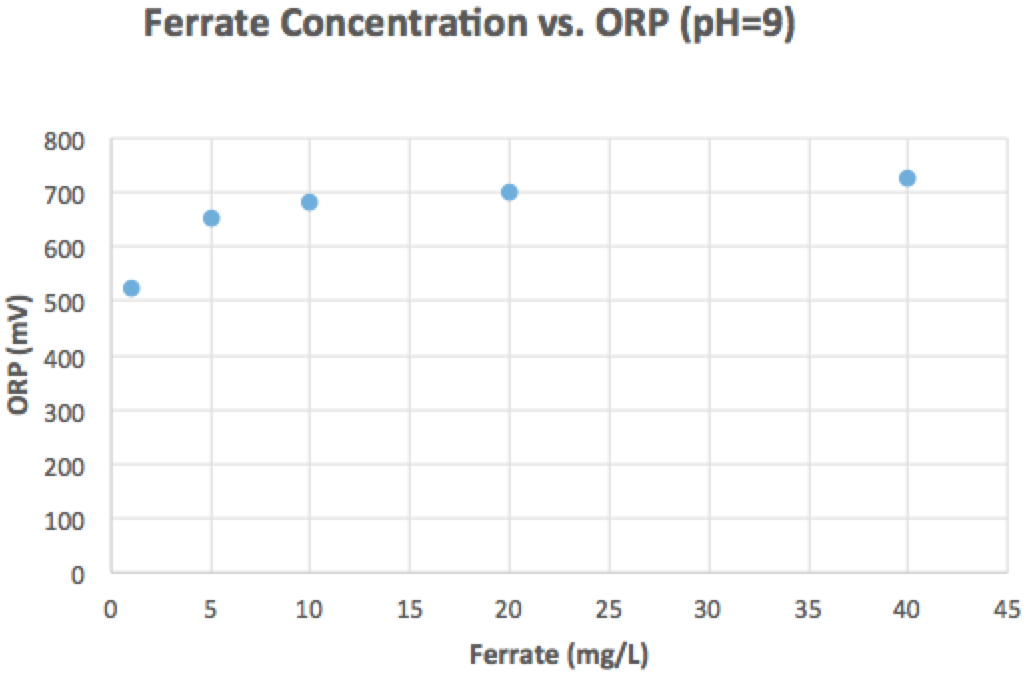


Figure 21: Ferrate Concentration vs ORP

We also investigated total iron (Fe^{6+} and Fe^{3+}) requirements for effective coagulation of precipitate generated from both ferrate and ferric iron addition, Figure 22.

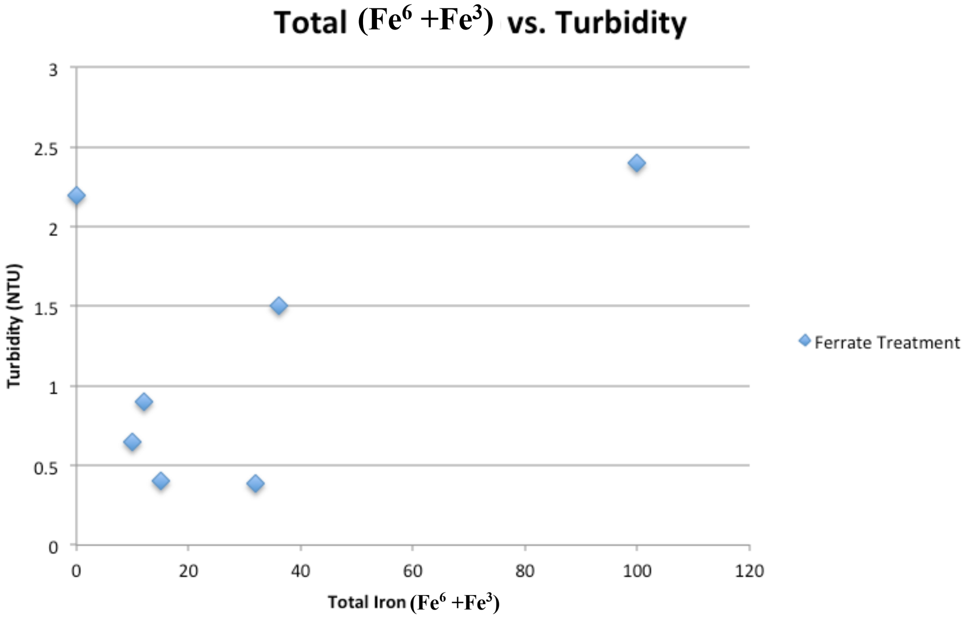


Figure 22: Total (Fe^6 +Fe^3) vs. Turbidity

Bench scale testing showed that coagulation efficiency (measured as turbidity removal) followed the classic charge-neutralization, and charge-reversal model (EPA 2000). Total iron concentrations (approximately 20 mg/L) appeared to be best for optimal coagulation, and we did not observe particle removals due to entrainment or “sweeping” with the hydroxide.

Preliminary work on site included synthesizing 2.8 L of ferrate and transporting it to the trailer on the Tillman Canal location. After extensive field work, we were able to pump muck/water from the canal bottom up to our retention pond, and from there into the trailer, in coordination with the ferrate and ferric dosing pumps. We made two full-scale runs with the system, after implementing changes to correct problems encountered during start up. The pilot system was now fully operational and instrumentation has been calibrated. Tests with the pilot plant have been managed with only one operator (technician), indicating the pilot system was operating according to design.

Background water quality analyses have shown that the nutrients (N & P) were present in the muck dredge water at lower concentrations than typical for muck dredged water in the IRL, but ferrate treatment efficiencies were still very high, Table 3.

Table 3: Muck Dredge Water from the Tillman Canal 3/31/17

	NH_4-N mg/L	**NO_3-N mg/L**	**PO_4-P mg/L**	**$Fe_{(TOTAL)}$ mg/L**	**Turbidity NTU**
Control	0.49	1.25	0.33	>3.0	245
Treated	<0.18 (BDL)	1.43	0.03	0.31	0.41
% Change	(-) >65	(+) 1	(-) 90	(-) >90	(-) 99.8

Because the ammonia and phosphate levels were low in this muck water, the required ferrate dose was reduced for the full-scale pilot testing at the Tillman Canal. It was noted however, that the ferrate treatment system was able to reduce to equipment detection level, constituting > 90% treatment in most cases. Based on these tests, the ferrate dose for the pilot test was adjusted down to 3 mg/L (FeO_4^{2-}).

Preliminary calibration tests at the pilot plant determined the amount of chemical feed (ferrate) that would be required to operate the plant for extended periods of time. In order to minimize the chemical costs, operational flows were reduced to 3 gallons per minute, which allowed us to reduce the quantity of ferrate needed per test down to 1.5 liters.

Tests were also conducted in the laboratory to develop scale-up procedures required to synthesize liter quantities of ferrate solution. Temperature control and mixing intensity were modified, and the laboratory was able to generate ferrate solutions of high quality. A comparison of ferrate solution strength between the small-scale synthesis procedure, and the modified, large-scale system was completed, Table 4. It was noted that the synthesis chemistry proceeds at about the same rate in both systems. This work showed that central large-scale ferrate synthesis systems could provide the treatment chemical to several applications sites treating the muck dredge water.

Table 4: Results of Ferrate Synthesis After Scale-up from Bench Scale to Pilot Plant Scale (40X)

Batch Size	**FeO_4^{2-} Conc. (15 min.) g/L**	**FeO_4^{2-} Conc. (45 min.) g/L**
Bench (50 mL)	12.2	17.2
Pilot Plant (1.5 L)	12.4	15.6

As previously noted, two full-scale test runs were made at the Tillman Canal site. The first runs of the pilot system determined that: 1) the same treatment efficiency (removal/conversion of ammonia) could be achieved as observed at bench scale in the laboratory, and 2) the pilot plant operated as designed, achieving steady state treatment between one and two detention times. The steady state concentrations of nitrate-N, phosphate-P, total iron, and turbidity after ferrate addition were compared, Figure 23. It was noted that chemical parameters are constant after two detention times, and the percent removal of selected nutrients was similar to bench scale tests.

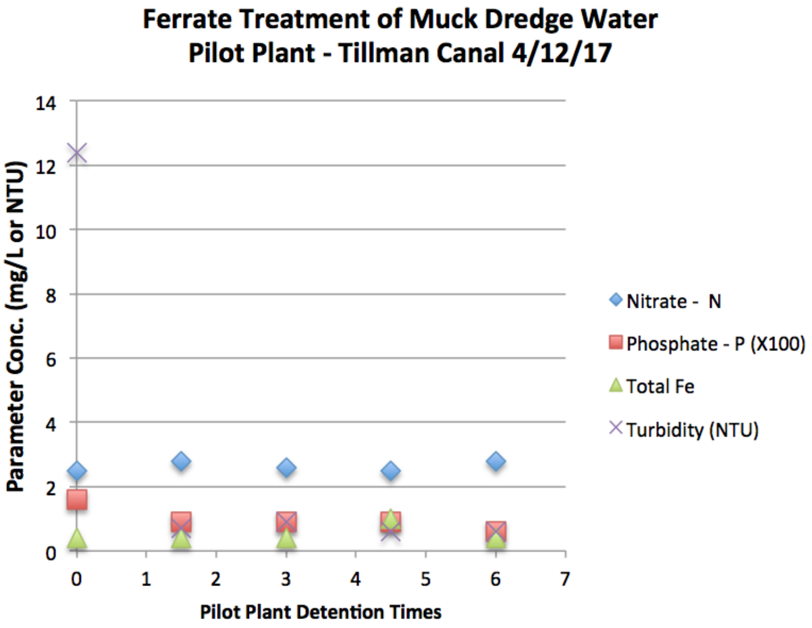


Figure 23: Steady State Concentrations of Nitrate-N, Phosphate-P, Total Iron, and Turbidity After Ferrate Addition

The precipitate from the ferrate treatment was tested as soil conditioner by treating seedling bell pepper plants. A total of 80 seeds were planted, where 40 of them received 4 mL of precipitate every 2 weeks, while the remaining received only water. The plants were bottom irrigated, meaning the red tubs shown in Figure 24 were filled equally with the same amount of water anytime they were watered. Each pot contained holes in the bottom that allowed for the plants to pull water from the red tub when needed. The plants were placed so that each group received equal amounts of sunlight; however, when the test group began to grow large enough to shadow the control group, the placement was rotated. From the two sets of 40, 32 seeds in the control group germinated while 34 seeds in the treatment group germinated. More growth was seen in the

Figure 24: Pepper Plants (Left: Control Right: Treatment)

treatment group as compared to the control. When the first peppers began sprouting, the control group had sprouted four peppers while the treatment group sprouted nine. During the first pepper harvest, one pepper from the control group was harvested, while five peppers from the treatment group were harvested.

Dredging Results

The first tests were completed using only the suction head without a shroud. Sediment analysis was performed and results produced the cumulative distribution curves, Figure 25:

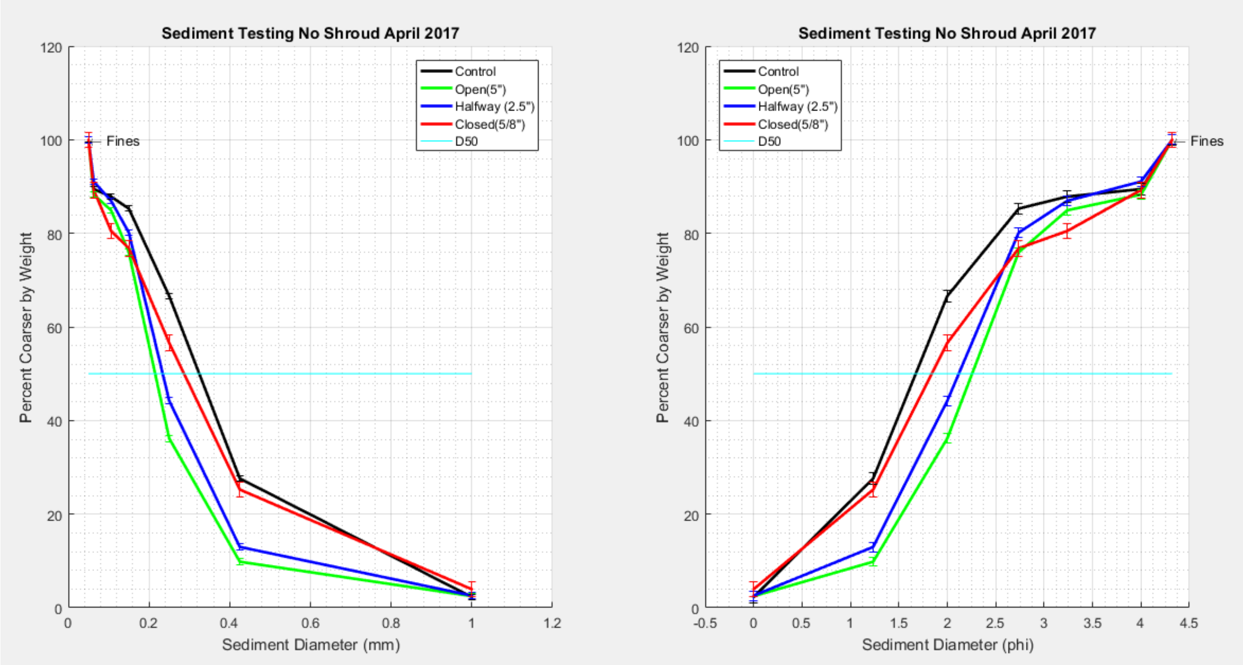


Figure 25: Sediment Distribution, No Shroud

Table 5: Percent Reduction (%) in d50, No Shroud

	Open	Halfway	Closed
mm	33.67	27.91	11.64
Phi	34.77	26.54	9.87

From the cumulative distribution curves, the d50 values were obtained for each sample and percent reductions calculated. From the control to open, there was a 33.67% reduction in d50, Table 5, and approximately 55% preclusion of sediments larger than 0.2 mm at the open setting, Figure 25. The results were promising and confirmed the hypothesis that the sediment size could be managed by controlling the flow area.

Next, a shroud was constructed and attached to the suction head and samples were collected in the lab. The analysis of testing with the rectangular shroud produced the following results, with d50 values indicated by the blue line, Figure 26:

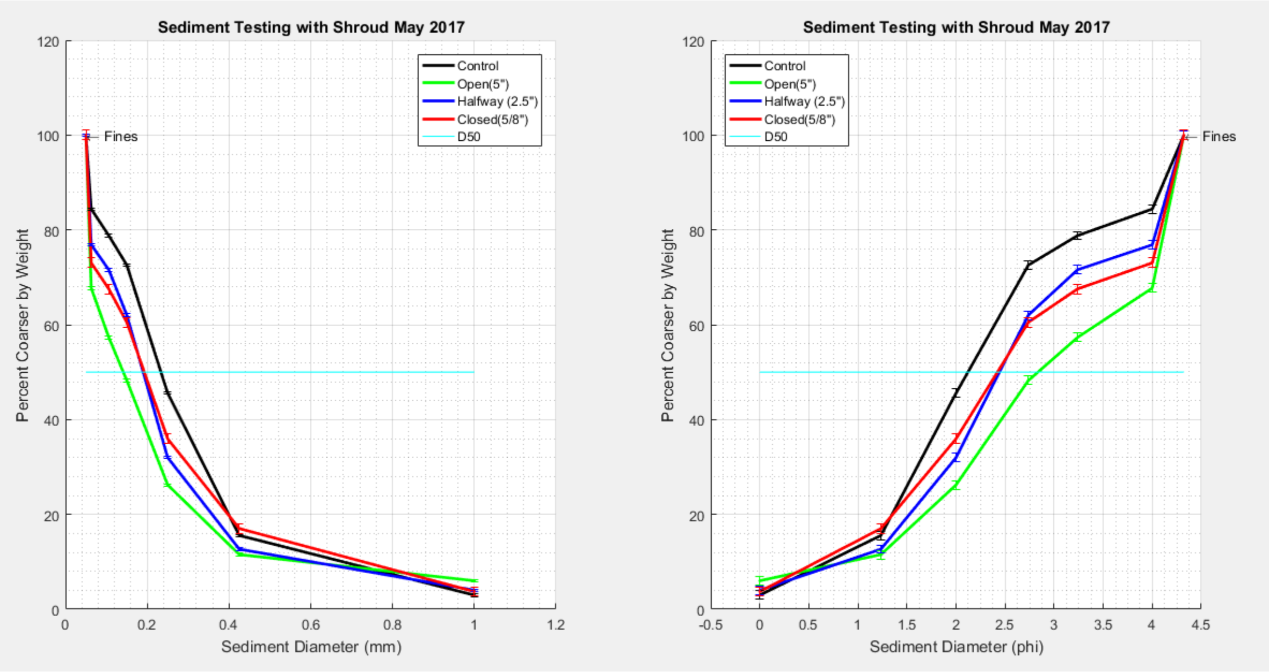


Figure 26: Sediment Distribution, Shroud Only

Table 6: Percent Reduction (%) in d50, Shroud

	Open	Halfway	Closed
Phi	33.63	15.13	14.17
mm	39.45	18.64	17.47

The percent reduction in d50 was greatest at the open setting, followed by halfway and then closed, Table 6. Using only the shroud, sediments were suspended into the water column via the discharge hose and remained well-mixed throughout testing. As expected, the most amount of coarse sediments precluded was with the suction head fully open.

For active jet testing, the first set of tests was performed using a pressure washer as an active jet system. An analysis of the samples collected produced the results in Figure 27.

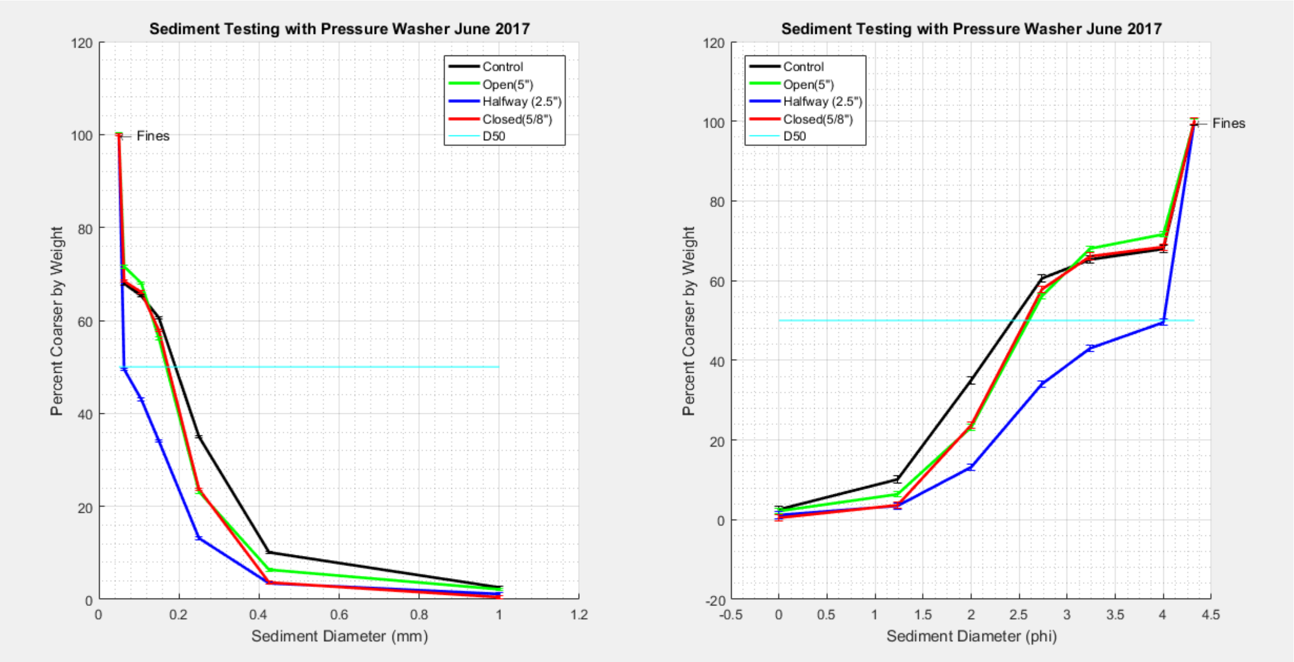
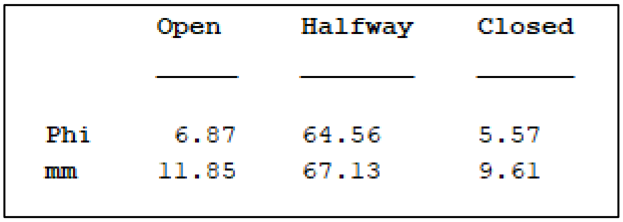


Figure 27: Sediment Distribution, Pressure Washer

Table 7: Percent Reduction (%) in d50, Pressure Washer



	Open	Halfway	Closed
Phi	6.87	64.56	5.57
mm	11.85	67.13	9.61

Using the pressure washer as an active jet produced results that do not follow the desired trend of removing less coarse sediments as the intake area is increased. From Figure 27, we see that there was not much distinction between the open and closed settings. Additionally, the halfway setting yielded better results than the open setting with a 64.56% reduction in d50, Table 7. It was determined that flow from the pressure washer was too fast, suspending sediments unevenly and rapidly. Additionally, quality control was negatively affected with the pressure washer jet system because the pressure washer was not secured to the shroud and was not able to be kept in the same position for each test.

Because of the poor results with the pressure washer jet system, the team developed a more effective setup. A jet ring system was utilized to obtain better control of the suspension and distribution of sediments. An analysis of the jet ring system produced the subsequent results, Figure 28:

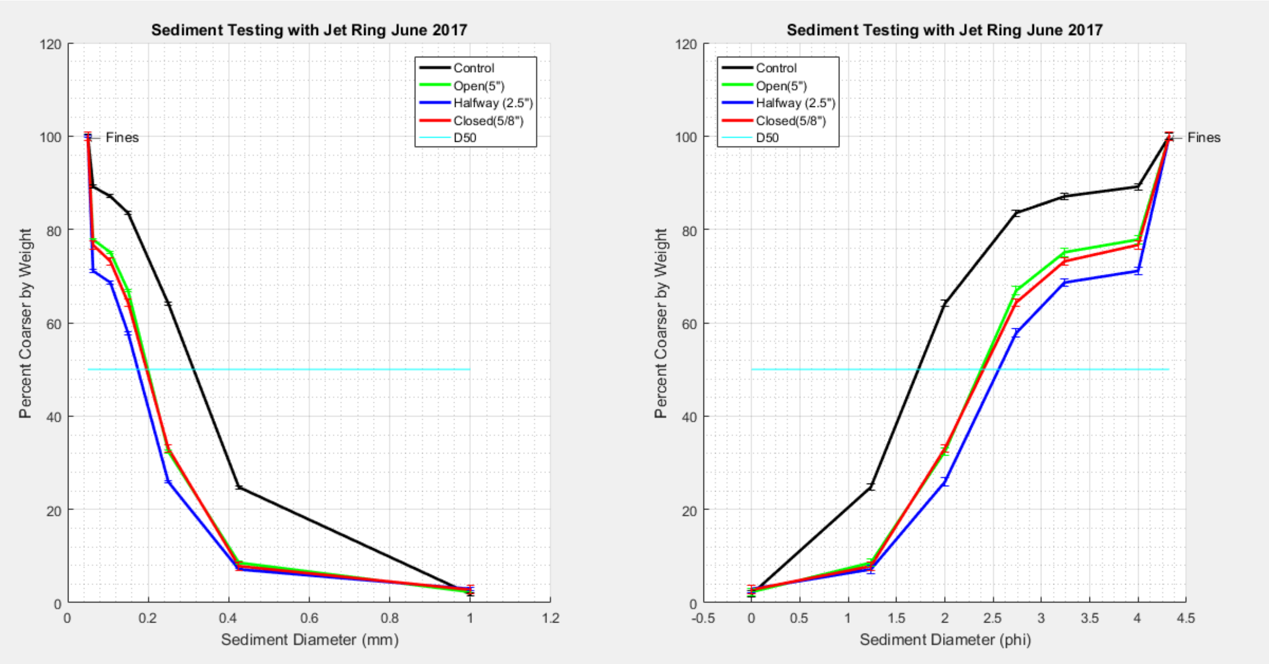


Figure 28: Sediment Distribution, Active Jet Full Flow

Table 8: Percent Reduction (%) in d50, Active Jet Full Flow

	Open	Halfway	Closed
Phi	37.69	48.19	39.04
mm	36.38	44.23	37.38

From a graph of these results, Figure 28, we saw there was not a significant distinction between the suction head set at open, halfway, and closed with percent reductions of approximately 38, 48, and 39% respectively, Table 8. With the jet ring pump running at full flow, it was suspected that the flow was still too fast and was suspending sediment above the suction head intake area instead of gently mobilizing it into the intake flow stream.

To correct this issue, the team connected a ball valve to the discharge side of the pool pump to control the flow through the active jet irrigation hose. Samples were taken with the ball valve half way open thus reducing the flow by half. Sediment analysis was completed and yielded the following, Figure 29:

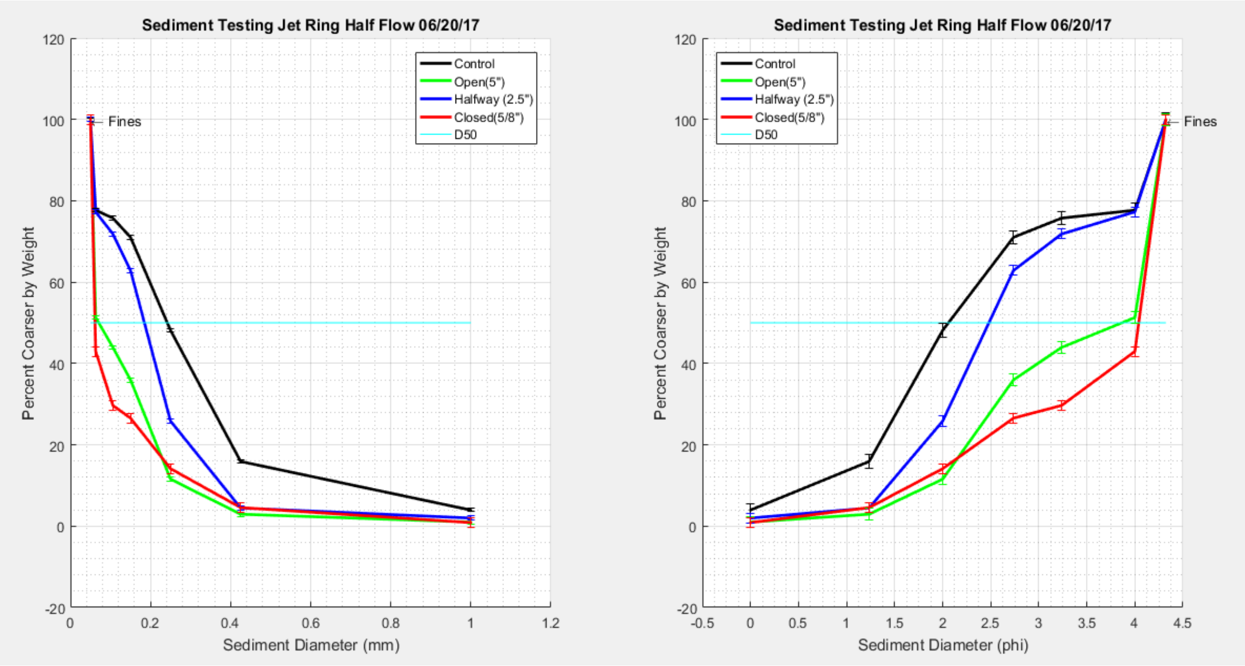


Figure 29: Sediment Distribution, Active Jet Half Flow

Table 9: Percent Reduction (%) in d50, Active Jet Half Flow

	Open	Halfway	Closed
Phi	87.64	20.43	96.10
mm	70.81	23.61	74.61

By controlling the discharge flow rate from the pool pump, there was more distinction between the halfway setting compared to the open and closed settings; however, the largest percent reduction in d50 was with the closed setting, which was not the expected outcome, Table 9. The team suspected that testing with the active jet in the lab does not properly resemble the field environment. In the lab, the slurry mixture was returned to the tank and suspended/mixed sediment sufficiently without the need for another mobilization source. However, in the field this was not the case as the slurry mixture was discharged into retention ponds or sent through the trailer. We expected to see better results with an active jet in the field as there are no other sources of mobilization when testing in the canal.

Passive jets were developed to act as a source of sediment mobilization in the field and eliminate the need for a power source as when using active jets. Testing with passive jets attached to the shroud was completed in the lab on July 26th, July 31st, and August 2nd. Performing sediment analysis yielded the cumulative distribution graph in Figure 30.

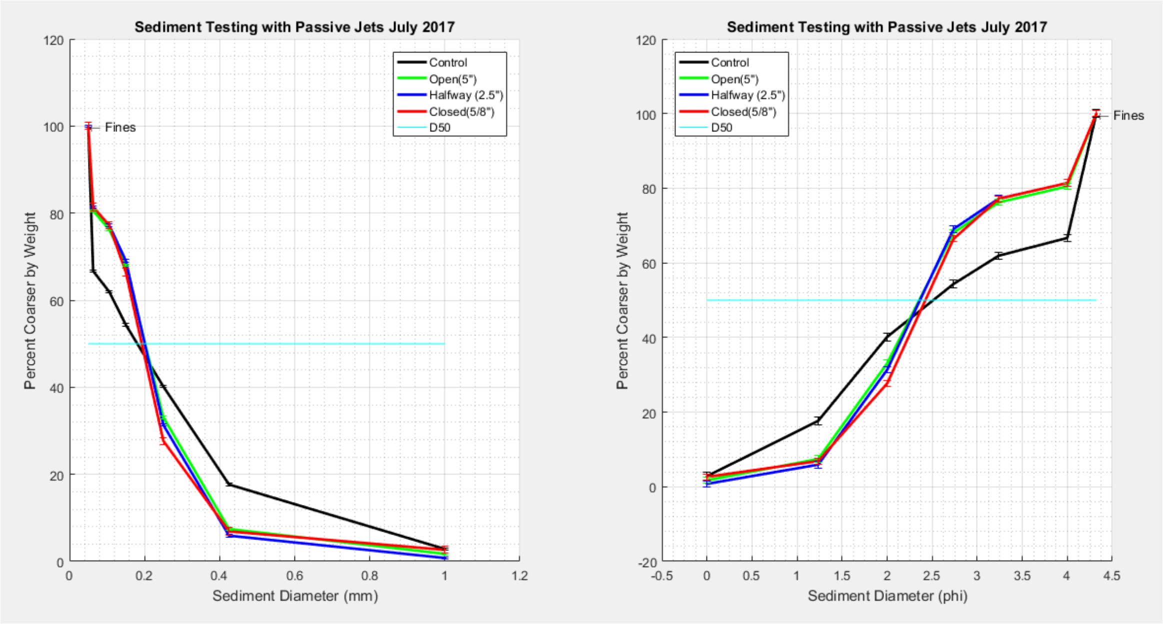


Figure 30: Sediment Distribution, Passive Jets

Table 10: Percent Reduction (%) in d50, Passive Jets

	Open	Halfway	Closed
Phi	6.19	5.85	3.47
mm	-11.68	-11.04	-6.54

The sediment distribution with passive jets revealed very little difference between the three settings of the suction head. At open, halfway, and closed, the variable intake suction head removed relatively the same size of sediment, Figure 30. It was found that the passive jets were bringing in sand from outside of the shroud and jetting sand into the intake area which explained why there was a percent increase in d50 as opposed to a percent reduction, Table 10. The passive jets may either be completely redesigned or simply placed in a more strategic position on the shroud to avoid suctioning sand into the shroud.

For the next set of testing, an extension was attached to the bottom of the shroud, and the suction head itself was removed. Results revealed that there was still a reduction in the overall amount of coarser sediments that are collected, Figure 31. However, the amount of sediment coarser than 0.2mm remained larger in this test as compared to previous tests that included the suction head.

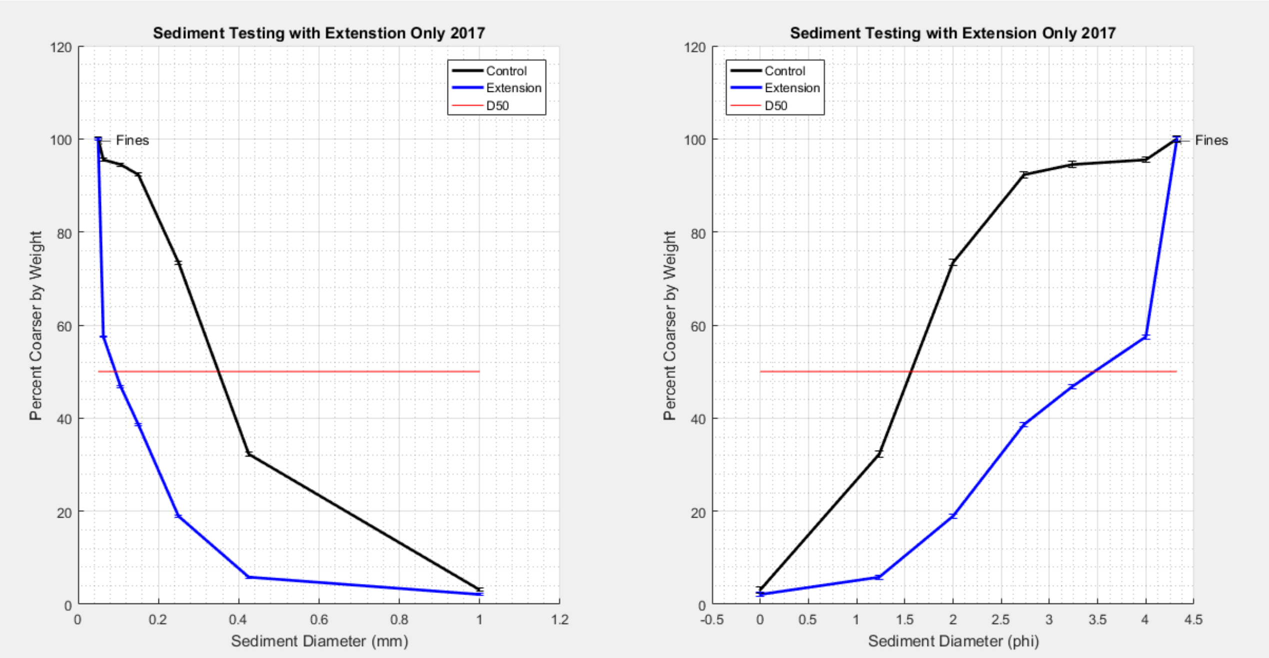
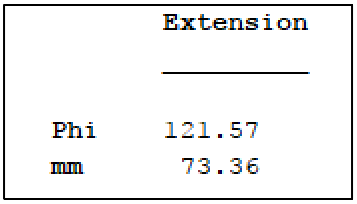


Figure 31: Shroud Extension Results

Table 11: Percent Reduction (%) in d50, Extension



	Extension
Phi	121.57
mm	73.36

Percent reduction in d50 was 73.36%, Table 11, which was one of the largest percent reductions obtained from all the tests. However, although there was a reduction in total amount of coarse sediments removed, there was also a reduction in total amount of fine sediments removed. The total percentage of fine sediments removed when using the shroud extension only was significantly less than the percentage calculated when using the variable intake suction head, particularly the suction head with the shroud. This indicated the need for a variable intake area suction head when attempting to remove just the fine sediment.

Combined system

The combined system of the variable intake area suction head supplying slurry to the trailer underwent testing at the pilot site (Site 3 at C-59 and C-1) with the rectangular shroud on June 29th. The variation in sediment distribution from 3 different sample locations are as follows, Figure 32:

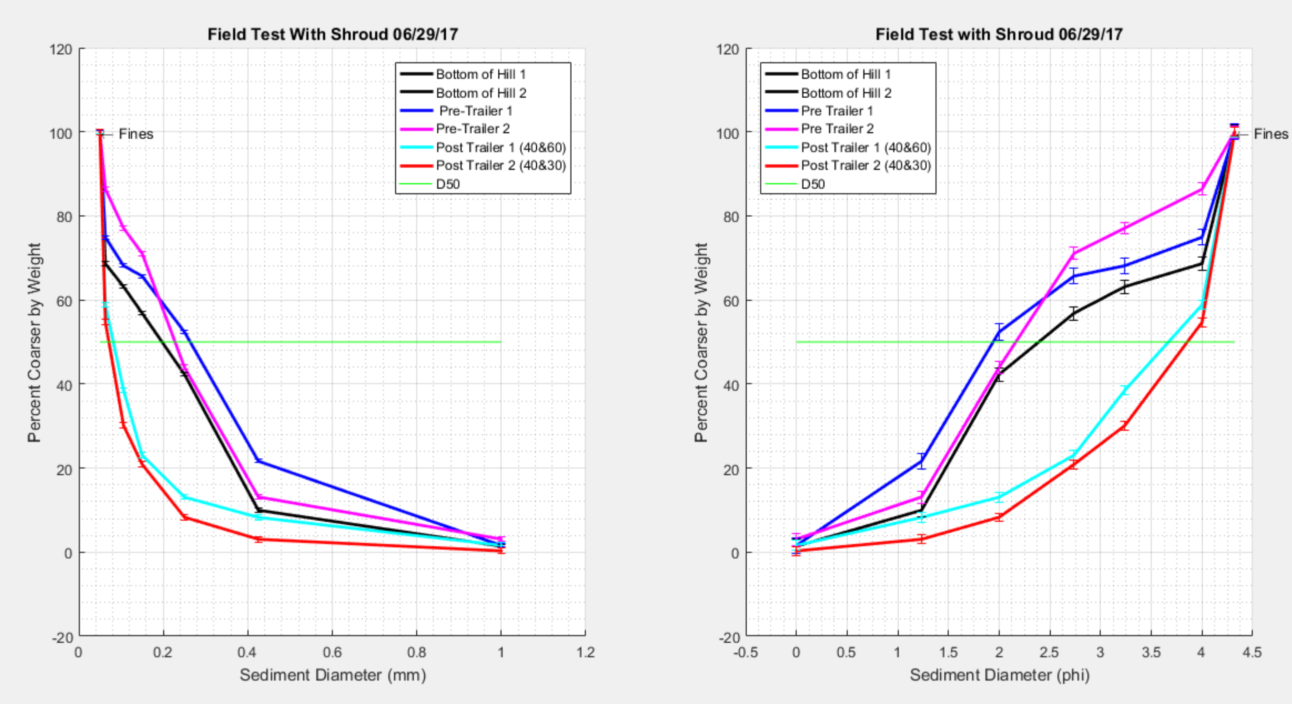
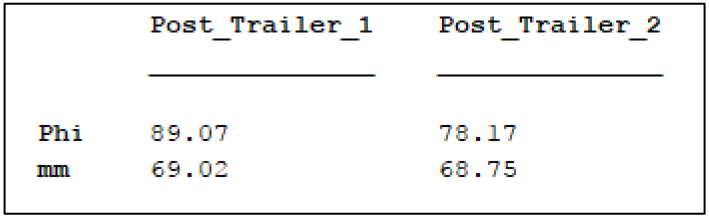


Figure 32: Sediment Distribution, Field Test

Table 12: Percent Reduction (%) in d50, Field Test



```
             Post_Trailer_1          Post_Trailer_2
             ______________          ______________

    Phi      89.07                   78.17
    mm       69.02                   68.75
```

Comparing the distributions related to the combination of hydrocyclones, a number 40 and a 60 mesh (Post Trailer 1), and the combination of a number 40 and a 30 mesh (Post Trailer 2), we saw there was little difference between the two distributions. This can be attributed to the high sediment content in the slurry affecting the hydrocyclones ability to filter (i.e. large amounts of sediment clog the filters). However, when comparing the unfiltered sediment profiles (Pre-Trailer 1 and 2) to that of the filtered ones (Post Trailer 1 and 2), the hydrocyclones did reduce d50 by almost 70% for each arrangement of meshes, Table 12.

Overall results indicated the ability to preclude larger diameter sediments by dynamically changing the intake area of the suction head. Each test was plotted on the same graph for comparison, Figure 33.

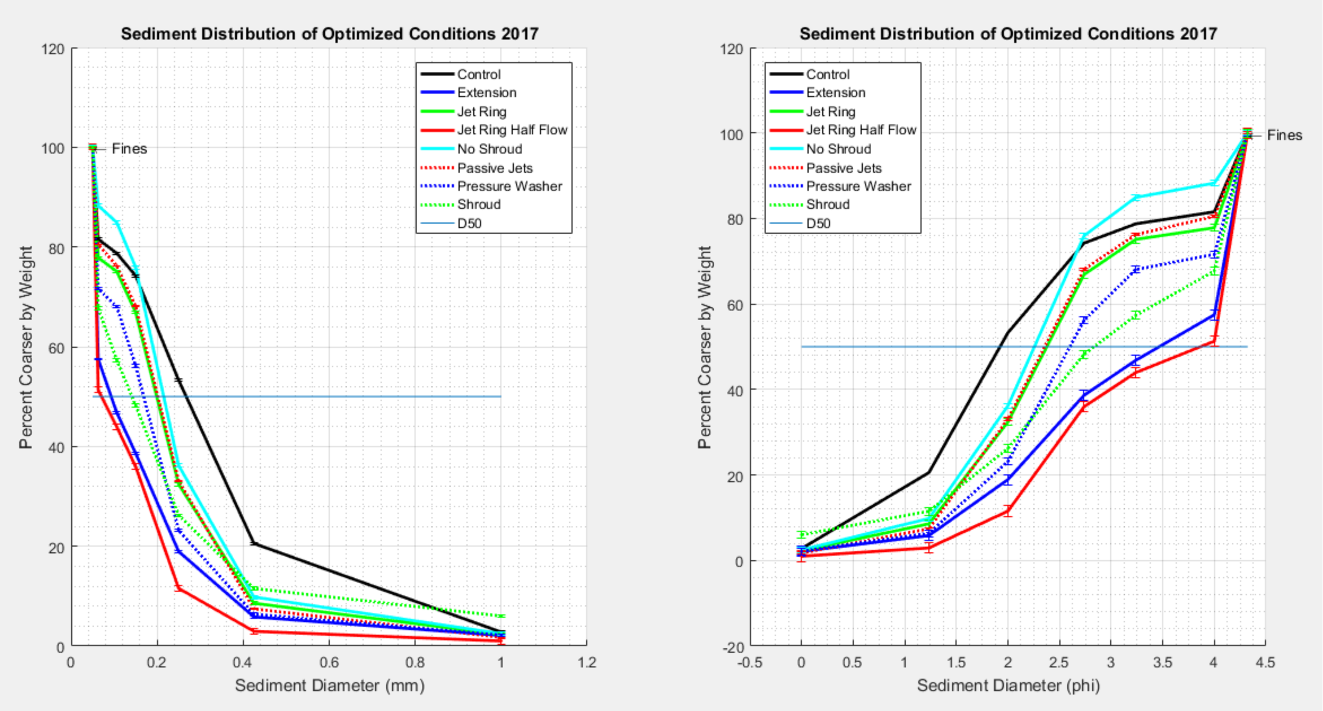
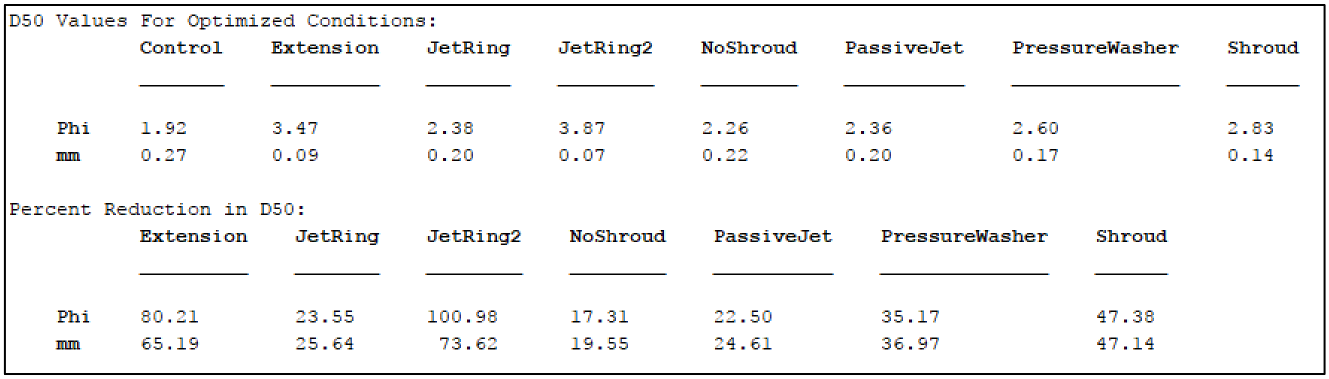


Figure 33: Comparison of Optimized Conditions

Best results were achieved with the active jet at half flow, where we see approximately 75% preclusion of sediments larger than 0.2 mm. The smallest preclusion of sediment was seen with no shroud, where only 45% preclusion was reached.

In addition, a summary of d50 values and percent reduction in d50 were compared, Table 13. At roughly 74% reduction, the jet ring half flow test had the largest percent reduction in d50. Furthermore, the smallest percent reduction was seen with no shroud, around 20%.

Table 13: Summary of d50 Values and Percent Reduction (%) in d50



```
D50 Values For Optimized Conditions:
           Control    Extension    JetRing    JetRing2    NoShroud    PassiveJet    PressureWasher    Shroud
           _______    _________    _______    ________    ________    __________    ______________    ______

    Phi    1.92       3.47         2.38       3.87        2.26        2.36          2.60              2.83
    mm     0.27       0.09         0.20       0.07        0.22        0.20          0.17              0.14

Percent Reduction in D50:
           Extension    JetRing    JetRing2    NoShroud    PassiveJet    PressureWasher    Shroud
           _________    _______    ________    ________    __________    ______________    ______

    Phi    80.21        23.55      100.98      17.31       22.50         35.17             47.38
    mm     65.19        25.64       73.62      19.55       24.61         36.97             47.14
```

The percent weight of sediment compared to total sample weight (i.e. sediment and water) was also determined, Table 14. Excluding the control, the largest amount of sediment was collected with the pressure washer test at the closed setting. That is, 1.6 % of the total sample weight was sediment while 98.4 % of the total sample weight was water. Similarly, the smallest amount of sediment was collected when using the jet ring at half flow and the suction head at an open setting.

Table 14: Percent Sediment of Total Sample Weight

	Control	**Open**	**Halfway**	**Closed**
No Shroud	7.63	1.33	0.86	0.51
Shroud	2.50	0.55	0.93	0.89
Pressure Washer	0.85	0.51	0.30	1.60
Jet Ring Full Flow	1.48	0.38	0.52	0.56
Jet Ring Half Flow	0.18	0.18	0.46	0.21
Passive Jets	0.98	0.57	0.66	0.79
Extension	2.96	0.19		

Note that the extension test has values listed for control and open. The value listed for open is an average of all the samples collected for the extension.

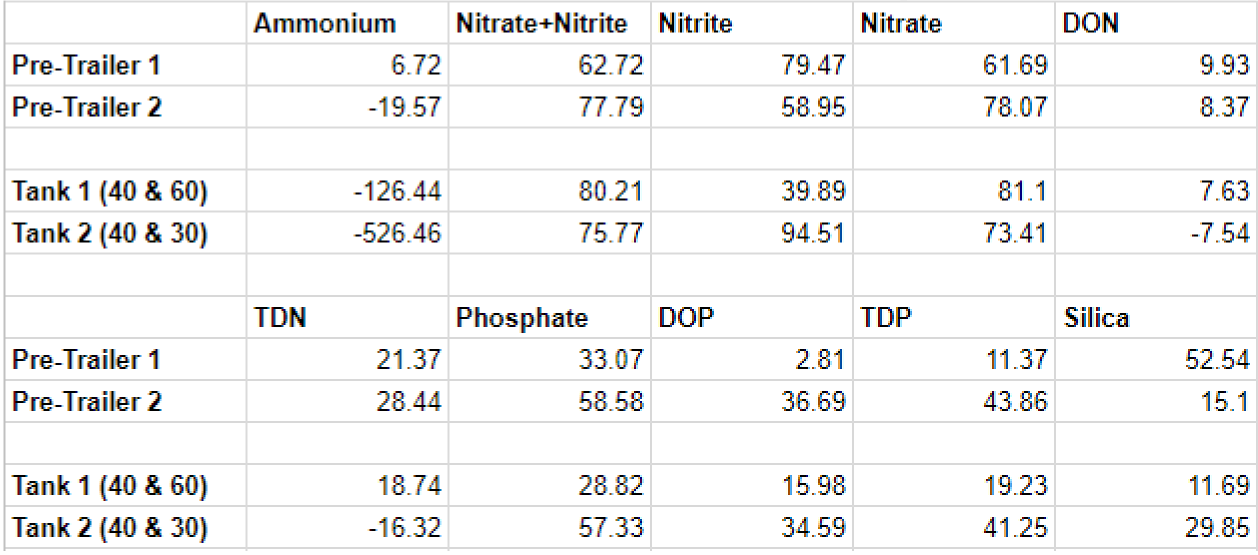
Lastly, the weight of fines compared to total dry sediment weight was determined, Table 15. Excluding the control, the percentage of fines collected was the greatest for the jet ring half flow at the closed setting, 57%. Additionally, at roughly 9%, the percentage of fines was smallest for no shroud at the halfway setting. The highlighted values depict the opening size that collected the largest percent weight of fines for each test. For example, during the no shroud test, the open setting collected the largest percent weight of fines. Although the largest percentage overall was collected with the closed setting during the jet ring half flow test, the largest values for all other tests were seen with the larger opening sizes.

Table 15: Percent Fines of Total Sediment Weight

	Control	**Open**	**Halfway**	**Closed**
No Shroud	20.53	11.80	8.94	10.75
Shroud	15.60	32.27	23.14	26.95
Pressure Washer	32.05	28.39	50.49	21.63
Jet Ring Full Flow	10.67	22.18	28.90	23.32
Jet Ring Half Flow	22.31	48.70	22.73	56.93
Passive Jets	33.33	19.49	18.64	16.10
Extension	4.49	42.51		

As a modification of a full system test, dredge slurry was pumped through the trailer, untreated by ferrate with samples taken before and after hydrocyclone treatment. The samples were then analyzed in the lab to determine the percent reduction in ammonia, nitrate, nitrite, dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), phosphate, dissolved organic phosphorus (DOP), total dissolved phosphorous (TDP), and silica in the dredge slurry following hydrocyclone treatment. This test was preformed twice, so a total of 2 samples were taken at each location. The same samples were then treated with ferrate individually and the same analysis was performed. The system proved efficient in reducing nutrient concentrations using both the hydrocylone and ferrate treatment. There were significant reductions in all categories except ammonium which can be attributed to the fact that ammonium is typically released during dredging. Nitrate+Nitrite, nitrite, and nitrate were all reduced by approximately 70%. DON was reduced by nearly 5%, TDN by 13%, phosphate by 45%, DOP by 23%, TDP by 29%, and silica by 27%, Table 16.

Table 16: Percent Reductions of Treated Canal Samples



	Ammonium	Nitrate+Nitrite	Nitrite	Nitrate	DON
Pre-Trailer 1	6.72	62.72	79.47	61.69	9.93
Pre-Trailer 2	-19.57	77.79	58.95	78.07	8.37
Tank 1 (40 & 60)	-126.44	80.21	39.89	81.1	7.63
Tank 2 (40 & 30)	-526.46	75.77	94.51	73.41	-7.54
	TDN	**Phosphate**	**DOP**	**TDP**	**Silica**
Pre-Trailer 1	21.37	33.07	2.81	11.37	52.54
Pre-Trailer 2	28.44	58.58	36.69	43.86	15.1
Tank 1 (40 & 60)	18.74	28.82	15.98	19.23	11.69
Tank 2 (40 & 30)	-16.32	57.33	34.59	41.25	29.85

Pre-trailer refers to the percent reduction measured in the slurry after coming up from the bottom of the hill, while tank refers to percent reduction measured after pumping the slurry through the hydrocyclones in the trailer.

Conclusion

The team successfully completed the project goals as outlined in the SOW:

- Determine whether a dredge design can efficiently lift the muck from sites in canals, while precluding sand particles (approx. 0.2 mm and larger) from being drawn in by the suction head, under constant flow conditions.
- Determine whether treating dredge spoils (after different separation processes) with ferrate can reduce phosphorus concentrations to very low levels, while also reducing concentrations of ammonia, TOC and suspended solids.

- Determine whether an efficient end use or disposal plan for the solids can be established, including the feasibility of scaling up.

We completed the project goals by confirming that the suction head design was successful at precluding sediments larger than 0.2 mm in diameter while maintaining a constant pump flow. We also showed that greater than 70% reduction in d50 can be achieved, as seen with the jet ring half flow test. Dredge spoils treated with ferrate reduced phosphorus concentrations by 90%, reduced ammonia by 64%, and TOC and suspended solids by more than 95%. Additionally, the treated solids are able to be used as plant fertilizer. The pepper plants treated with the sludge grew faster and produced more fruit than those not supplied with the sludge.

The research and development of the pilot scale Ferrate-based coupled mobile dredge-treatment system indicates that targeted removal of muck in sensitive areas of the lagoon is feasible. The system as designed is small enough to remove muck from shallow sensitive areas including around docks. The ability to limit the solids in the dredge slurry allowed for targeted treatment of the slurry using ferrate and indicated that a flow-through system is feasible for treating the slurry without the need for an upland disposal area (Dredged Material Management Area). A scaled-up system could manage the removal of muck from banks, around structures, and in sensitive habitats. A scaled-up system could also be adjusted to run autonomously and installed as a permanent system in canals to remove muck before it enters the Lagoon.

Based on the information collected throughout the duration of this project and the results discussed previously, the team recommends the following improvements for future testing:

1. Optimize the jet ring system to determine the most efficient jet flow vs. sediment suspension ratio. Implement other suspension systems such as spinning brushes, corkscrews, etc.
2. Expand on the current suction head design to include actuators or levers for controlling intake area size.
3. Perform sediment fall velocity analyses to determine optimal shroud size and associated intake area opening.
4. Perform flow simulation analyses of flow inside the shroud.
5. Determine the sediment profile of material remaining after dredging with suction head and shroud.
6. Employ the use of a larger shroud and begin testing at multiple sites.

Implementing these recommendations will further expand our understanding of the dredge-treatment system and enable the team to improve the efficiency and effectiveness of the system.

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Appendix A: Sediment Analysis Procedure

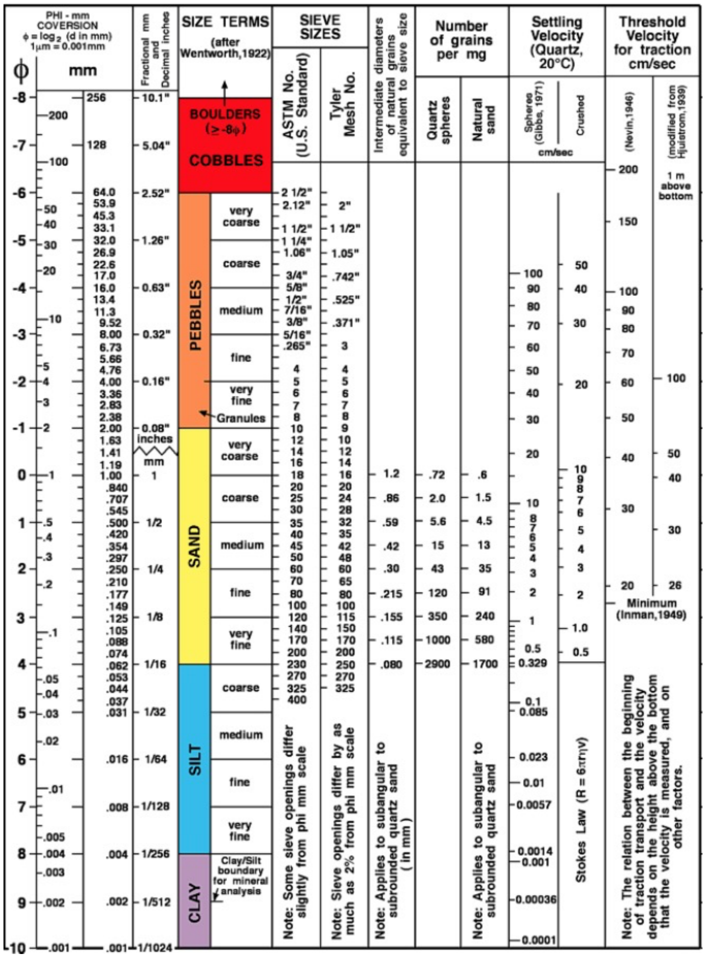
1. Weigh the sample with its container (baggie) 3 times and record the averaged weight.
2. Weigh all the dry and empty sieves 3 times each and record the averaged weight of each.
3. Stack sieves from smallest to largest size (smallest at bottom) ensuring to have a pan at the bottom
4. Hold the baggie such that sediment settles in corner of baggie
5. Cut the corner of the baggie and pour sample over the sieves using the water in the sample to wash it
6. Weigh empty sample container (baggie) and record weight
7. Gently shake/tap sides of sieves one at a time to allow all the water to move through
8. Add a known weight of water as needed to wash additional sediment through sieves and record added water
9. Empty pan contents into additional beakers/pans as needed (pan may get too full to add more water). **Be sure to weigh dry beakers/pans first and record the dry container weight; again, weighing each 3 times and recording the averaged weight of each
10. Weigh the sieves with the sediment/water still on them 3 times each and record the averaged weight of each
11. Weigh the total contents from the pan(s) 3 times and record the averaged weight
12. Use oven to dry all sieves containing sediment/water mix. Allow approximately 15-30 minutes oven drying time for sieves
13. Remove sieves from oven and allow them to cool before weighing
14. Weigh all dried sieves with sediment 3 times each and record average weight of each
15. Use oven to dry pan contents
16. Remove pan(s) from oven and allow them to cool
17. Weigh total dried pan contents 3 times and record averaged weight
18. Clean and dry all sieves/pans after weights have been taken before repeating steps 1-18 for the next sample set

Appendix B: Nomenclature

Variables	**Description**
ρ_s	density of sand
ρ	density of sea water
g	gravitational acceleration
d	diameter of sand particles
C_D	drag coefficient
u	velocity
Ψ	Shields parameter
τ_c	critical shear stress
Q	volume flow rate
V	mean velocity
A	suction head intake area

Appendix C: Wentworth scale

The Wentworth scale is used to specify the diameters of sediments and their related sieve size.



Appendix D: Sediment Velocity Required for Incipient Sediment Motion

Our design was focused on the preclusion of sediment grain sizes 0.2 mm and larger, as stated in the Project Metrics of Subtask 8 in the Statement of Work (SOW). In order to accomplish this, it was imperative to determine the Shields parameter (Ψ), a non-dimensional number used to determine the incipient motion of sediment.

$$\Psi = \frac{\tau_c}{(\rho_s - \rho)gd} \tag{1}$$

Where, τ_c is the dimensionless critical shear stress, or Shields criterion, which indicates force needed to move sediment of a given size. Studies have shown that at a Shield's parameter of 0.03 sediments are likely to move (Dean and Dalrymple 2004). Shear stress can be calculated using the following:

$$\tau = \frac{1}{8}\rho f u^2 \tag{2}$$

Where f is the Darcy-Weisbach friction coefficient. Substituting $f = 4 * C_D$ into Eq. 2:

$$\tau = \frac{1}{2}\rho C_D u^2 \tag{3}$$

Substituting Eq. 3 into Eq. 1 and with specific gravity, $SG = \rho_s/\rho$, we solve for velocity:

$$u = \sqrt{\frac{2\Psi g d SG}{C_D}} \tag{4}$$

Appendix E: Ferrate Treatment System Background Information

Recent projects utilizing a newly commercialized technology, Ferrate(VI), have demonstrated this chemical's ability to both oxidize reduced nitrogen and to precipitate phosphorus. It has been shown that Ferrate(VI) can oxidize all forms of reduced nitrogen, and in many cases, converts the nitrogen directly to N_2 gas. Ferrate(VI) also oxidizes organic-phosphorus complexes, and can precipitate the total phosphorus as a ferric complex (Sharma, et al. 1998)

Iron-VI Ferrate (FeO_4^{2-}) has been studied for many years exploring its potential for use in industry. A significant literature base also exists for environmental applications of ferrate (Yates, 2014). While ferrate has been demonstrated to be an effective environmental treatment chemical, it has not been utilized in the past because of the high cost of production. Recent advances in technology have allowed for the creation of on-site generation equipment that can produce an inexpensive ferrate product.

Ferrates are oxy-anions of iron and have been synthesized in laboratories since the mid-nineteenth century with the iron in oxidation states of between two and eight (FeO_2^{2-} and FeO_5^{2}). While several different ferrates have been studied for commercial exploitation, only Ferrate(VI), i.e. (FeO_4^{2-}) has been utilized for environmental applications. Over 400 published studies have demonstrated the unique treatment capability of Ferrate(VI) for both water and wastewater, as it can simultaneously perform oxidation and disinfection, and because it is unstable, it is quickly reduced to Fe^{3+} which is a coagulant.

Ferrates can be synthesized in several ways, utilizing an oxidation process to convert metallic, ferrous, or ferric iron to a higher valence. The most efficient and cost-effective way to generate ferrate is by aqueous chemical oxidation of ferric iron utilizing chlorine in a caustic medium. This technology is currently used to generate the only commercial ferrate product available in the world. Specifically, a ferric salt, either ferric chloride or ferric sulfate is oxidized to FeO_4^{2-} by hypochlorite (either calcium or sodium) in the presence of sodium hydroxide (equation 5). The feedstocks are inexpensive and readily available at most treatment plants in their commercial forms, i.e. 12% bleach, 40% ferric chloride or sulfate, and 50% caustic.

$$2FeCl_3 + 3NaOCl + 10NaOH \rightarrow 2Na_2FeO_4 + 9NaCl + 5H_2O \tag{5}$$

When added to aqueous systems, Ferrate(VI) is a powerful oxidant which readily decomposes to ferric iron [$Fe(OH)_3$] and oxygen according to:

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + 1.5O_2 + 4OH \tag{6}$$

Appendix F: Treatment System Data

IRL Suspended Particles Settlement test, 6/28/2016

The 5-gallon sample of IRL water (collected on June 24th, 2016) was thoroughly mixed to achieve homogeneity. A sample of 2020mL was immediately retrieve and placed in a 2000mL graduated cylinder. The settling of the suspended particles in the 2020mL sample was measured against the passage of time:

Time (min)	Level of suspended particles (mL)	net settling (mL)
0	2020	0
16	1940	80
30	1900	40
45	1820	80
60	1700	120
75	1625	75
90	1590	35
105	1555	35
120	1530	25
135	1500	30
168	1460	40

The percentage between actual water and settled suspended particle after two hours and 48 minutes was 28 to 72 percent.

Ammonia test, Muck water, 7/12/2016

Samples: Indian River Lagoon water from three different locations.

Method: We dosed the samples with 50 and 100ppm calcium ferrate. Measured pH and lowered it to 9 with 5N sulfuric acid. Following, the samples were mixed at 100rpm in a Phipps & Bird's mixer. Then, they were settled for 10 minutes. Ammonia was measured using the Hach HQ440d multi meter and probe. Control and treated samples were refrigerated and tested for ortho phosphorus using the ascorbic acid colorimetric method and the Hach Dr 6000 spectrometer the following day.

Data:

NH_3 (ppm)

	IR1	**IR2**	**IR3**
Control	23.2	31.3	24.8
50ppm	1.81	15.7	16.9
100ppm	<0.1*	-	-

*Value under detection limits of multi meter

pH

	IR1	**IR2**	**IR3**
Control	7.61	7.94	8.13
50ppm	10.41/9.11	10.01/9.17	10.40/9.09
100ppm	10.62/9.12	-	-

Amounts of 5N Sulfuric acid used (uL) to lower pH above

	IR1	**IR2**	**IR3**
50ppm	21.5	12	19
100ppm	39	-	-

Ortho Phosphorus (ppm)*:

	IR1	**IR2**	**IR3**
Control	2.29	2.69	2.47
50ppm	0.78	0.7	0.82
100ppm	0.24	-	-

*Concentration values were above the calibration curve range (0.01 to 0.2ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove ortho phosphorus from water.

Note: 10 ppm of ferrate was initially dosed to the IR1 and IR3 samples (20 to the second IR1 sample). This was due to a miscue from tech. Samples dosing was corrected after 5 minutes by adding 40ppm to the IR1 and 3 - 50ppm samples and 80 ppm to the 100ppm IR1 sample. There was not enough IR 2 and 3 sample left to dose them at 100ppm.

Ammonia, Phosphorus, Nitrate test, Muck water, 7/18/2016

Samples: Indian River Lagoon water from three different locations. Distilled/De-ionized water was added to “muck”, mixed thoroughly, and let settle for 8 hours.

Method: We dosed the samples with 50, 60 and 70ppm calcium ferrate. Measured pH and lowered it to 9 with 5N sulfuric acid. Following, the samples were mixed at 100rpm in a Phipps & Bird’s mixer for at least 20 minutes. Then, they were settled for 10 minutes. Twenty-five mL were removed from each sample immediately to measure ammonia using the Hach HQ440d multi meter and probe. The goal is to obtain a reduction of ammonia to under 1ppm using the least amount of ferrate. Another 100mL was filtered with a 0.45um filter and refrigerated to measure Ortho-Phosphorus, Nitrate, and Nitrite at a later day. Filtered control and treated samples were tested for ortho-phosphorus the following day of the test using the ascorbic acid colorimetric method with the Systea Easychem Plus nutrient analyzer.

pH

	IR1	**IR2**	**IR3**
Control	7.91	7.89	8.08
50ppm	10.96/9.01	10.9/9.05	11.0/9.15
55ppm	10.9/9.17	10.82/9.1	10.99/9.04
60ppm	10.98/9.16	10.92/9.1	11.18/9.01

Amounts of 5N Sulfuric acid used (uL) to lower pH above

	IR1	**IR2**	**IR3**
50ppm	1900	1900	1700
55ppm	2200	2100	2000
60ppm	2100	2000	2400

Ortho Phosphorus (mg/L)

	IR1	**IR2**	**IR3**
Control	2.94	4.34	1
50ppm	0.47	0.35	0.75
55ppm	0.33	0.29	0.61
60ppm	0.45	0.3	0.42

NH_3 – N (mg/L)

	IR1	**IR2**	**IR3**
Control	9.83	14.1	9.45
50ppm	3.61	2.57	0.15
55ppm	0.81	1.54	<0.1*
60ppm	0.13	0.56	<0.1*

*Value under detection limits of multi meter.

NO_2-N (mg/L)

	IR1	**IR2**	**IR3**
Control	0.013	0.012	0.009
50ppm	0.11	0.23	0.21
55ppm	0.15	0.3	0.08
60ppm	0.06	0.21	0.03

NO_3-N (mg/L)

	IR1	**IR2**	**IR3**
Control	2.98	3.64	3.77
50ppm	7	9.49	6.03

55ppm	6.32	10.05	5.51
60ppm	5.65	8.38	5.4

Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).

Note: There seems to be a correlation between the concentrations of ammonia and amount of thickness of muck. The higher the muck thickness the higher the concentrations and the more ferrate needed to remove it. After analyzing the ammonia for 50 and 60 ppm, we decided to use 55ppm as our third dosage since our goal was to keep the ammonia levels under 1ppm using the least amount of ferrate. Controls R1 and R2 were filtered with a 1um filter and control R3 was filtered with a 1um and then a 0.45um filter (due to the scarcity of water in sediment in R3 control).

Ammonia, pH Manipulation of Sample IR 2, 7/29/2016

Samples: Indian River Lagoon water from location IR 2. Additional distilled/De-ionized water was added to “muck”, mixed thoroughly, and let settle for 48 hours.

Method: We dosed five 250mL samples with 50 ppm calcium ferrate and measured their pH. The pH for the first sample was only measured, but not changed after ferrate dosing. The first sample was placed in the Phipps & Bird’s mixer at 20rpm for at least 20 minutes. Then, then let settle for 10 minutes. The pH of the other 4 samples were lowered to 10, 9, 8 and 7 respectively. The pH of the four remaining samples was lowered using 5N sulfuric acid while fast mixing on a magnetic stirrer. Once desired ph was achieved the samples were placed in the Phipps & Bird’s mixer at 20rpm for at least 20 minutes. Then, then let settle for 10 minutes. All five samples were tested for ammonia using the Hach HQ440d multi meter and probe at this point of the test.

Data:

pH

	IR2
Control	7.77
1st sample	10.68
10pH	10.83/10.03
9pH	10.83/8.93
8pH	10.82/7.95
7pH	10.86/7.07

Amounts of 5N Sulfuric acid used (uL) to lower pH above

	IR2
1st sample	0
10pH	450
9pH	1000
8pH	1150

7pH	1250

NH_3 (ppm)

	IR2
Control	10.2
1st sample	0.40
10pH	0.42
9pH	0.30
8pH	0.43
7pH	1.36

NO_2 – N (mg/L)

	IR2
Control	---
1st sample	0.72
10pH	0.40
9pH	0.19
8pH	0.10
7pH	0.04

NO_3 (ppm)

	IR2
Control	---
1st sample	36.82
10pH	21.39
9pH	17.03
8pH	14.25
7pH	12.90

Note: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.23).

OP vs. Total Phosphorus, 8/2/2016

Samples: Two 250mL Indian River Lagoon water from the IR 2 location. Distilled/De-ionized water was added to “muck”, mixed thoroughly, and let settle for over 48 hours.

Method: We dosed both samples with 75ppm calcium ferrate. Measured pH and lowered it to 9 with 5N sulfuric acid. Both samples were mixed on a magnetic stirrer for 15 minutes. Then, the first sample was transferred to a Phipps & Bird’s to mix for at least 15 minutes and let settle afterwards. Settling time was recorded. For the second sample its pH was further lowered to 7.5

after the 15 minutes of mixing and transferred to a Phipps & Bird's to mix for at least 10 minutes and let settle afterwards. Settling time was also recorded.

Four 50mL extractions were made for each sample and filtered with a 0.45, 1, 8, and 11um filter respectively. Ammonia was measured using the Hach HQ440d multi meter and probe. All samples were tested for ortho-phosphorus ascorbic acid colorimetric method with the Systea Easychem Plus nutrient analyzer. Remainder of all samples was saved to test Total Phosphrus, Nitrate, and Nitrite at a later day.

Data:

	pH	**5N Sulfuric acid used (uL)**
IR2		
Control(untreated)	7.67	
Sample	11.25/9.05	1400
Sample2	11.31/9.09/7.38	1400

Time of Coagulation (minutes)

	IR 2
Sample 1	5
Sample 2	5

Ortho Phosphorus (mg/L)

	Untreated	**pH (9)**	**pH(7.5)**
0.45um	36.743*	6.799	2.841
1um	45.145*	6.778	4.229
8um	36.532*	6.456	3.267
11um	36.908*	6.809	7.698*

*Values outside the calibration curve range.

$NH_3 - N$ (mg/L)

	Untreated	**pH 9**	**pH 7.5**
Control	19.8	6.21	----
0.45um		2.62	1.43
1um		>0.1*	6.8
8um		0.293	0.536
11um		0.0386	0.330

*Values outside the calibration curve range.

$NO_2 - N$ (mg/L)

	Untreated	**pH 9**	**pH 7.5**
0.45um	0.015	0.038	0.011
1um	0.015	0.038	0.015
8um	0.015	0.038	0.011
11um	0.015	0.509	0.013

NO_3 - N (mg/L)

	Untreated	**pH 9***	**pH 7.5***
0.45um	3.524	6.461	19.088
1um	3.072	7.545	8.968
8um	3.162	7.613	8.584
11um	3.117	7.726	8.245

*High Values probably due to not having the enough minimum required volume for the test.

Note: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.23).

Diluted Muck Test 8/15/2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab. Columns of core IR were place in a bucket and thoroughly mixed. A 650mL sample was collected from the bucket and a picture was taken. Then, we added 400mL distilled water and mixed thoroughly letting settle overnight (17 hours).

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle and measured every 5 minutes. When mostly settled, water was able to be collected (250mL) from the top and treated with 50 ppm of calcium ferrate. Its pH was immediately measured after that, lowered to 8 with 5N sulfuric acid, and mixed at 120 rpm in a Phipps & Bird's mixed for 20 minutes. The sample was then let settle for 10 minutes. Ammonia was measured using the Hach HQ440d multi meter and probe, turbidity on a Hach 2100A turbidimeter, and ortho phosphorus using the Systea (Chinchilla Scientific) nutrient analyzer on control and treated samples.

Data:

Sediment Settling

Time (mins)	**Amount(mL)**
0	1,050
5	950
10	900
15	850
20	825
25	810
30	800
35	795
45	785
55	780

pH

Control	8.02
50ppm	10.65/8.1

Amounts of 5N Sulfuric acid used (uL) to lower pH above:

50ppm	1800.0

Ortho Phosphorus (ppm)

Control	13.245*
50ppm	0.0

*Concentration values were above the calibration curve range (0.0 to 5 ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove ortho phosphorus from water.

NH_3 (ppm)

Control	14.2
50ppm	1.09

Phosphorus vs. Concentration of Ferrate, 8/17/2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, 3L of distilled water added, thoroughly mixed, and let settle for two weeks. A 1250mL sample was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle and measured every 5 minutes. When mostly settled, four 250mL samples of water were able to be collected from the top and treated with 5, 10, 20, and 40ppm of calcium ferrate respectively. Its pH was immediately measured after that, lowered to 8 with 5N sulfuric acid, and mixed at 120 rpm in a Phipps & Bird's mixed for 20 minutes. The sample was then let settle for 10 minutes. Ortho phosphorus was measured using the Systea (Chinchilla Scientific) nutrient analyzer on control and treated samples. Smell differentiation test was also conducted.

Data:

	pH	**5N Sulfuric acid used (uL)**
Control	7.75	
5 ppm	9.02/8.04	175
10 ppm	9.69/8.06	200
20 ppm	10.37/8.06	100
40 ppm	10.75/8.1	120

Ortho Phosphorus (ppm)

Control	13.903*
5 ppm	13.892*
10 ppm	13.447*
20 ppm	4.784
40 ppm	1.755

*Concentration values were above the calibration curve range (0.0 to 5ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove ortho phosphorus from water.

Note: A strong putrid odor (most likely from sulfur in water) was coming out from our control sample. There was a correlation between increased treatment with ferrate and odor elimination. Specially, after 20ppm.

Phosphorus, Ammonia (Sulfuric acid vs $FeCl_3$) Test 8/19/2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 2L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, seven 250mL water samples were collected from the top and treated with 15, 15, 15, 15, 25, 35 and 50ppm of calcium ferrate. Its pH was immediately measured after that. The pH of the 15, 25, 35, 50ppm was lowered to 8 with 5N sulfuric acid, and mixed at 120 rpm in a Phipps & Bird's mixed for 20 minutes. The sample was then let settle for 10 minutes. The pH of the other 15, 15, and 15ppm treated samples was lowered using ferric chloride to 8, 7.5, and 7 respectively. Ortho phosphorus was measured using the Systea (Chinchilla Scientific) nutrient analyzer on control and treated samples. Also, a sulfide test was conducted using the Hach HS-WR hydrogen sulfide portable colorimetric kit. A smell differentiation test was also conducted. Ammonia test was done with the Hach HQ 440d tabletop multi meter and probe.

Data:

	pH	**5N Sulfuric acid used (uL)**	**40% Ferric Chloride used (uL)**
Control		8.16	
15 ppm		10.17/8.08	345
25 ppm		10.61/8.06	460
35 ppm		10.87/8.08	720
50 ppm		10.99/8.06	1003
15 ppm	8 pH	10.00/7.91	200
15 ppm	7.5 pH	10.24/7.58	220
15 ppm	7 pH	10.47/6.98	300

	pH	**Ortho Phosphorus (ppm)**	**NH_3 (ppm)**
Control		14.616*	9.2
15 ppm		4.29	6.24
25 ppm		3.26	3.31
35 ppm		1.45	1.17
50 ppm		0.856	0.305
15 ppm	8	0.488	6.4
15 ppm	7.5	0.269	6.25
15 ppm	7	0.285	8.65

*Concentration value was above the calibration curve range (0.0 to 5 ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove ortho phosphorus from water.

Note: Measurements of sulfide in samples was zero. This could have been due that the samples were prepared (removed from the "muck" and decanted) the day before. Even though samples were covered the sulfide reacted with remaining air forming a "dome" on the parafilm cover. Samples for sulfide study must be prepared just prior to test. No discernible odor was noticed.

Sulfide/Smell (Sulfuric acid vs $FeCl_3$) Test 8/22/2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 2L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, seven 250mL water samples were collected from the top and treated with 15, 15, 15, 15, 25, 35 and 50ppm of calcium ferrate. Its pH was immediately measured after that. The pH of the 15, 25, 35, 50ppm was lowered to 8 with 5N sulfuric acid, and mixed at 120 rpm in a Phipps & Bird's mixed for 20 minutes. The sample was then let settle for 10 minutes. The pH of the other 15, 15, and 15ppm treated samples was lowered using ferric chloride to 8, 7.5, and 7 respectively. A sulfide test was conducted using the Hach HS-WR hydrogen sulfide portable colorimetric kit analyzer on control and treated samples. A smell differentiation test was also conducted.

Note: No sulfide was registered when testing control. Testing could not be continued without a control reference. It is probable that smell from the "muck" is not a result of sulfide. However, when consulting with outside labs they were able to measure sulfide on location due to its volatility. Future sulfide tests/measurements will be done on location.

Time for Flock Formation (1, 5, 10 20 min) 8/30/2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, a 1.2L (200mL was used as control) water sample was collected from the top with a syringe and treated with 15ppm calcium ferrate. Its pH was immediately measured after that. The pH of the sample was lowered to 7.5 respectively with 5N sulfuric acid and mixed at 140 rpm in a Phipps & Bird's mixer for 20 minutes. At the 1, 5, 10, and 20 minutes after the pH reached 7.5, a 125ml was removed from the sample. Immediately, 25mL was used for ammonia test, 50 ml was filtered with a 1um filter for total phosphorus and treated with 1 drop phenolphthalein and 0.5g of potassium persulfate, 50ml was +treated with 1 drop phenolphthalein and 0.5g of potassium persulfate for total phosphorus test as well. Total phosphorus was measured using the persulfate digestion method and the Systea (Chinchilla Scientific) nutrient analyzer. The remainder of the 1.2L sample was then let settle for 10 minutes after the 20 minutes mixing. Then ammonia and total phosphorus was also measured using the process described above.

Data:

	pH	**5N Sulfuric acid used (uL)**
Control	7.84	N/A
15ppm	10.81/7.76	1400

		Unfiltered	***Filtered***
	NH_3 (ppm)	**Total P (ppm)**	**Total P (ppm)**
Control	6.7	19.255	17.874
1 min	3.72	18.759	16.419
5 min	3.26	18.276	16.379
10min	3.26	18.451	11.504
20min	4.09	18.383	16.969
Settled	4.4	8.494	4.106

*Concentration value was above the calibration curve range (0.0 to 10 ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove phosphorus from water.

Diluted Ferric Chloride Test, September 1st, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1L sample of the mix was collected from the bucket. The stock ferric chloride 40% was further diluted to by 50, 25, and 10% with 10N HCl.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, four 250mL of water sample were collected from the top with a syringe and treated with 60ppm calcium ferrate and mix at 140 rpm in a Phipps & Bird's mixer for 5 minutes.
Its pH was immediately measured after that. The pH of all 4 samples was lowered to 7.5 with 40% ferric chloride, 50% diluted ferric chloride, 25% diluted ferric chloride, and 10% diluted ferric chloride respectively, mixed for 20 minutes in the Phipps & Bird's mixer at 30rpm, and then let settle. Ammonia was measured on all the samples with the Hach HQ440D multimeter and probe. Ortho phosphorus was measured with the Systea (Chinchilla Scientific) nutrient analyzer after filtration with a 1um filter.

Data:

	pH	**Ferric Chloride used (uL)**
Stock ferric	11.77/7.97	600.0
50% Stock	11.63/8.0	600.0
25% Stock	11.73/7.92	600.0
10% Stock	1.80/7.88	640.0

	NH_3 (ppm)	**Ortho P (ppm)**
Control	4.93	16.675
Stock ferric	>0.1	3.671
50% Stock	>0.1	1.483
25% Stock	>0.1	3.247
10% Stock	>0.1	2.670

*Concentration value was above the calibration curve range (0.0 to 10 ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove phosphorus from water.

Diluted Ferric Chloride Test, September 2nd, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1L sample of the mix was collected from the bucket. The stock ferric chloride 40% was further diluted to by 50, 35, 25, and 10% with 10N HCl.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, five 200mL of water sample were collected from the top with a syringe and treated with 60ppm calcium ferrate and mix at 140 rpm in a Phipps & Bird's mixer for 5 minutes.

Its pH was immediately measured after that. The pH of all 4 samples was lowered to 7.5 with 40% ferric chloride, 50% diluted ferric chloride, 35% diluted ferric chloride, 25% diluted ferric chloride, and 10% diluted ferric chloride respectively, mixed for 20 minutes in the Phipps & Bird's mixer at 30rpm, and then let settle. Ammonia was measured on all the samples with the Hach HQ440D multimeter and probe. Ortho phosphorus was measured with the Systea (Chinchilla Scientific) nutrient analyzer after filtration with a 0.45um filter. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	**Ferric Chloride used (uL)**
Control	7.67	N/A
Stock ferric	11.69/7.92	500.0
50% Stock	11.63/8.08	500.0
35% Stock	11.63/7.30	500.0
25% Stock	11.83/7.72	460.0
10% Stock	11.78/7.32	500.0

	NH_3 (ppm)	**Ortho P (ppm)**	**Turbidity (NTU)**	**Total Iron Used (mg/L)**
Control	9.44	11.779	162.00	0.0
Stock ferric	<0.1	<0.1	2.82	372.15
50% Stock	<0.1	0.105	2.02	200.04
35% Stock	<0.1	0.286	2.27	148.40

25% Stock	<0.1	0.245	2.69	107.09
10% Stock	<0.1	0.774	2.25	62.35

*Concentration value was above the calibration curve range (0.0 to 10 ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove phosphorus from water.

Notes:

Total Iron Used:
Ferrate – 60mg/L for all treated samples:
Weight of Iron 55.845g
Weight of ferrate 120g

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 60 = 27.9225mg/L of Fe added.
To Lower pH with 40% w/v Ferric chloride we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845g
Weight of ferric chloride 162.204g
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

Iron in Stock Ferric Chloride 40% – 34.4288 x 0.4 = 13.76912g/100mL
We used 0.5mL to lower pH then:
13.76912g/100mL = 0.1376912g/mL x 0.5mL = 0.0688456g of Fe in 200mL or 344.228mg/L

Iron in 40% Stock 50% diluted – 13.76912% x 0.5 = 6.88456g/100mL
We used 0.5mL to lower pH then:
6.88456g/100mL = 0.0688456g/mL x 0.5mL = 0.0344228g of Fe in 200mL or 172.114mg/L

Iron in 40% Stock 35% diluted – 13.76912% x 0.35 = 4.819192g/100mL
We used 0.5mL to lower pH then:
4.819192g/100mL = 0.04819192g/mL x 0.5mL = 0.02409596g of Fe in 200mL or 120.4798mg/L

Iron in 40% Stock 25% diluted – 13.76912% x 0.25 = 3.44228g/100mL
We used 0.46mL to lower pH then:
3.44228g/100mL = 0.0344228g/mL x 0.46mL = 0.015834488g of Fe in 200mL or 79.17244mg/L

Iron in 40% Stock 10% diluted – 13.76912% x 0.1 = 1.376912g/100mL
We used 0.5mL to lower pH then:
1.376912g/100mL = 0.01376912g/mL x 0.5mL = 0.0688456g of Fe in 200mL or 34.4228mg/L

Diluted Ferric Chloride Test, September 8th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1L sample of the mix was collected from the bucket. The stock ferric chloride 40% was further diluted to by 50, 35, 25, and 10% with 10N HCl.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, eight 250mL of water sample were collected from the top with a syringe. Three of the samples were treated at 15, 25 and 25ppm calcium ferrate and mix in a magnetic mixer during the lowering the pH to 7.5 with 6N HCl. Mixing continued for five minutes and then let settle. Ammonia was measured on all 3 samples with the Hach HQ440D multimeter and probe to determine the optimal strength of ferrate for ammonia removal. Once the optimal strength of ferrate was determined the other five samples were treated with 35ppm calcium ferrate and placed in magnetic mixer. Its pH was immediately measured after that. The pH of all 5 samples was lowered to 7.5 with 40% ferric chloride, 50% diluted ferric chloride, 35% diluted ferric chloride, 25% diluted ferric chloride, and 10% diluted ferric chloride respectively while mixed on a magnetic stirrer. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm, and then let settle for ten minutes. Ammonia was measured on all the samples with the Hach HQ440D multimeter and probe. Ortho phosphorus was measured with the Systea (Chinchilla Scientific) nutrient analyzer after filtration with a 0.45um filter. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	**Ferric Chloride used (uL)**	**6N HCl used (uL)**
Control	7.93	N/A	N/A
Ammonia 15	10.2/7.56	N/A	300
Ammonia 25	10.73/7.77	N/A	450
Ammonia 35	11.01/7.69	N/A	650
Stock ferric	10.98/7.90	430	N/A
50% Stock	10.97/7.98	400	N/A
35% Stock	10.96/7.57	400	N/A
25% Stock	10.96/7.57	400	N/A
10% Stock	10.92/7.66	400	N/A

	NH_3 (ppm)	**Ortho P (ppm)**	**Turbidity (NTU)**	**Total Iron Used (mg/L)**
Control	8.41	13.354*	221	0.0
Ammonia 15	3.43	N/A	N/A	N/A
Ammonia 25	1.44	N/A	N/A	N/A
Ammonia 35	<0.1	N/A	N/A	N/A
Stock ferric	<0.1	0.305	1.26	253.11698
50% Stock	<0.1	0.5605	2.42	126.44108
35% Stock	<0.1	0.778	2.54	93.395197
25% Stock	<0.1	0.89	3.25	71.364605
10% Stock	<0.1	1.2055	1.35	38.318717

*Concentration value was above the calibration curve range (0.0 to 10 ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove phosphorus from water.

Notes:
Total Iron Used:
<u>Ferrate – 35mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 35 = 16.288125mg/L of Fe added.
To Lower pH with 40% w/v Ferric chloride we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845g
Weight of ferric chloride 162.204g
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

Iron in Stock Ferric Chloride 40% – 34.4288 x 0.4 = 13.76912g/100mL
We used 0.5mL to lower pH then:
13.76912g/100mL = 0.1376912g/mL x 0.43mL = 0.059207216g of Fe in 250mL or 236.828864mg/L

Iron in 40% Stock 50% diluted – 13.76912% x 0.5 = 6.88456g/100mL
We used 0.5mL to lower pH then:
6.88456g/100mL = 0.0688456g/mL x 0.4mL = 0.02753824g of Fe in 250mL or 110.15296mg/L

Iron in 40% Stock 35% diluted – 13.76912% x 0.35 = 4.819192g/100mL
We used 0.5mL to lower pH then:
4.819192g/100mL = 0.04819192g/mL x 0.4mL = 0.019276768g of Fe in 250mL or 77.107072mg/L

Iron in 40% Stock 25% diluted – 13.76912% x 0.25 = 3.44228g/100mL
We used 0.46mL to lower pH then:
3.44228g/100mL = 0.0344228g/mL x 0.4mL = 0.01376912g of Fe in 250mL or 55.07648mg/L

Iron in 40% Stock 10% diluted – 13.76912% x 0.1 = 1.376912g/100mL
We used 0.5mL to lower pH then:
1.376912g/100mL = 0.01376912g/mL x 0.4mL = 0.005507648g of Fe in 250mL or 22.030592mg/L

Total Iron Test, September 12th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 2L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, eight 250mL of water sample were collected from the top with a syringe. Three of the samples were treated at 35, 45 and 50ppm calcium ferrate and mix in a magnetic mixer during the lowering the pH with stock 40% Ferric Chloride. The pH range was between 8 and 7, while keeping the range of total iron between 250 and 370ppm of Fe. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm, and then let settle for ten minutes. Ammonia was measured on all the samples with the Hach HQ440D multimeter and probe. Ortho phosphorus was measured with the Systea (Chinchilla Scientific) nutrient analyzer after filtration with a 0.45um filter. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	**Ferric Chloride used (uL)**
Control	8.08	N/A
35ppm	0.87/7.07	420
45ppm	11.10/7.89	450
45ppm	11.11/6.67	500
50ppm	11.16/6.99	570
50ppm	11.18/8.06	530

	NH_3 (ppm)	**Ortho P (ppm)**	**Turbidity (NTU)**	**Total Iron Added (mg/L)**
Control	6.53	12.99*	37.00	N/A
35ppm	<0.1	0.08	1.38	247.61
45ppm	<0.1	0.08	1.15	268.79
45ppm	<0.1	0.16	1.36	296.32
50ppm	<0.1	0.24	0.99	337.20
50ppm	<0.1	0.09	0.94	315.17

*Concentration value was above the calibration curve range (0.0 to 10 ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove phosphorus from water.

Notes:
Total Iron Used:
<u>Ferrate – 35mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 35 = 16.288125mg/L of Fe added.
- 55.845/120 = 46.5375% x 45 = 20.941875mg/L of Fe added.
- 55.845/120 = 46.5375% x 50 = 23.26875mg/L of Fe added.

To Lower pH with 40% w/v Ferric chloride we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845g
Weight of ferric chloride 162.204g
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912g/100mL
We used 0.5mL to lower pH then:
13.76912g/100mL = 0.1376912g/mL x 0.420mL = 0.057830304g of Fe in 250mL or 231.321216mg/L
= 0.1376912g/mL x 0.450mL = 0.06196104g of Fe in 250mL or 247.84416mg/L
= 0.1376912g/mL x 0.500mL = 0.0688456g of Fe in 250mL or 275.3824mg/L
= 0.1376912g/mL x 0.570mL = 0.078483984g of Fe in 250mL or 313.935936mg/L
= 0.1376912g/mL x 0.530mL = 0.072976336g of Fe in 250mL or 291.905344mg/L

pH Lowered with HCl, September 14th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1.5L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, six 250mL of water sample were collected from the top with a syringe. All samples were treated with 35ppm calcium ferrate and mixed in a magnetic mixer for 5 minutes. This was followed by lowering the pH to 9.0, 8.5, 8.0, 7.5, 7.0, and 6.5 respectively with 6N HCl. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm, and then let settle for ten minutes. Ammonia was measured on all the samples with the Hach HQ440D multimeter and probe. Ortho phosphorus was measured with the Systea (Chinchilla Scientific) nutrient analyzer after filtration with a 0.45um filter. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH:	**HCl used (uL)**
Control	8.88	N/A
9.0	10.97/9.09	520
8.5	10.92/8.58	540
8.0	10.95/8.09	580
7.5	10.96/7.58	590
7.0	10.95/7.05	590
6.5	10.96/6.49	700

	NH_3 (ppm)	**Ortho P (ppm)**	**Turbidity (NTU)**
Control	6.81	12.758*	188
9.0	<0.1	2.328	2.12
8.5	<0.1	1.823	3.96
8.0	<0.1	1.656	2.15
7.5	<0.1	1.552	1.31
7.0	<0.1	1.264	0.51
6.5	<0.1	1.047	1.00

*Concentration value was above the calibration curve range (0.0 to 10 ppm). Data is shown only as prove of concept that ferrate is capable to significantly remove phosphorus from water.

Notes:

Total Iron Used:

Ferrate – 35mg/L for all treated samples:

Weight of Iron 55.845g

Weight of ferrate 120g

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 35 = 16.288125mg/L of Fe added.

pH Lowering and Turbidity Test, September 16th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1.25L sample of the mix was collected from the bucket.

	pH	**Ferric (uL)**	**6N HCL (uL)**	**Turbidity (NTU)**	**Total Iron used (ppm)**
Control	7.84	N/A	N/A		163
HCl	11.15/6.92	N/A	730		16.29
Not filtered				1.07	
8u				0.33	
1u				0.32	
Stock Ferric	11.16/7.00	460	N/A		269.64
Not filtered				0.73	
8u				0.54	
1u				0.21	
50% diluted	11.15/6.86	480	N/A		148.47
not filtered				0.53	
8u				0.23	
1u				0.11	
25% diluted	11.13/6.88	400	N/A		71.36
not filtered				0.41	
8u				0.23	
1u				0.11	
10% diluted	11.10/6.74	500	N/A		43.83
not filtered				0.27	
8u				0.28	
1u				0.14	

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, five 250mL of water sample were collected from the top with a syringe. All samples were treated with 35ppm calcium ferrate and mix in a magnetic mixer during the lowering of the pH to 7.0 with 6N HCL, stock 40% Ferric Chloride, 50% diluted stock Ferric Chloride, 25% diluted stock Ferric Chloride, and 10% diluted stock Ferric Chloride respectively. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm, and then let settle for 30 minutes. Turbidity was measured with a Hach 2100Q portable turbidimeter after no filtration, with a 1u filter, and with an 8u filter respectively for all the samples. Total Iron left in sample (IS) was measured using the Hach D 6000 spectrometer and the Ferro-Ver method.

Total Iron Used:
<u>Ferrate – 35mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 35 = 16.288125mg/L of Fe added.
To Lower pH with 40% w/v Ferric chloride we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845g
Weight of ferric chloride 162.204g
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912g/100mL
We used 0.5mL to lower pH then:
13.76912g/100mL = 0.1376912g/mL x 0.460mL = 0.063337952g of Fe in 250mL or 253.351808mg/L

<u>Iron in 40% Stock 50% diluted</u> – 13.76912% x 0.5 = 6.88456g/100mL
We used 0.5mL to lower pH then:
6.88456g/100mL = 0.0688456g/mL x 0.48mL = 0.033045888g of Fe in 250mL or 132.183552mg/L

<u>Iron in 40% Stock 25% diluted</u> – 13.76912% x 0.25 = 3.44228g/100mL
We used 0.46mL to lower pH then:
3.44228g/100mL = 0.0344228g/mL x 0.4mL = 0.01376912g of Fe in 250mL or 55.07648mg/L

<u>Iron in 40% Stock 10% diluted</u> – 13.76912% x 0.1 = 1.376912g/100mL
We used mL to lower pH then:
1.376912g/100mL = 0.01376912g/mL x 0.5mL = 0.00688456g of Fe in 250mL or 27.53824mg/L

pH Lowering and Turbidity Test, September 16th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1.25L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, five 250mL of water sample were collected from the top with a syringe. All samples were treated with 35ppm calcium ferrate and mix in a magnetic mixer during the lowering of the pH to 7.0 with 6N HCL, stock 40% Ferric Chloride, 50% diluted stock Ferric Chloride, 25% diluted stock Ferric Chloride, and 10% diluted stock Ferric Chloride respectively. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm, and then let settle for 30 minutes. Turbidity was measured with a Hach 2100Q portable turbidimeter after no filtration, with a 1u filter, and with an 8u filter respectively for all the samples. Total Iron left in sample (IS) was measured using the Hach D 6000 spectrometer and the Ferro-Ver method.

Data:

	pH	**Ferric (uL)**	**6N HCL (uL)**	**Turbidity (NTU)**	**Total Iron used (ppm)**
Control	8.01	N/A	N/A	163	N/A
HCl	11.15/7.15	N/A	670		16.29
Not filtered				1.07	
8u				0.33	
1u				0.32	
Stock Ferric	11.17/7.12	430	N/A		253.12
Not filtered				0.73	
8u				0.54	
1u				0.21	
50% diluted	11.15/6.86	480	N/A		134.7
not filtered				0.53	
8u				0.23	
1u				0.11	
25% diluted	11.13/6.88	400	N/A		74.12
not filtered				0.41	
8u				0.23	
1u				0.11	
10% diluted	11.10/6.74	500	N/A		35.87
not filtered				0.27	
8u				0.28	
1u				0.14	

Notes:
Total Iron Used:
<u>Ferrate – 35mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 119.843g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 35 = 16.288125mg/L of Fe added.
To Lower pH with 40% w/v Ferric chloride we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845g
Weight of ferric chloride 162.204g
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912g/100mL
We used 0.5mL to lower pH then:
13.76912g/100mL = 0.1376912g/mL x 0.430mL = 0.059207216g of Fe in 250mL or 236.828864mg/L

<u>Iron in 40% Stock 50% diluted</u> – 13.76912% x 0.5 = 6.88456g/100mL
We used 0.5mL to lower pH then:
6.88456g/100mL = 0.0688456g/mL x 0.430mL = 0.029603608g of Fe in 250mL or 118.414432mg/L

<u>Iron in 40% Stock 25% diluted</u> – 13.76912% x 0.25 = 3.44228g/100mL
We used 0.46mL to lower pH then:
3.44228g/100mL = 0.0344228g/mL x 0.420mL = 0.014457576g of Fe in 250mL or 57.830304mg/L
<u>Iron in 40% Stock 10% diluted</u> – 13.76912% x 0.1 = 1.376912g/100mL
We used mL to lower pH then:

1.376912g/100mL = 0.01376912g/mL x 0.41mL = 0.0056453392g of Fe in 250mL or 22.5813568mg/L

pH Lowering and Turbidity Test, September 21st, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1.25L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, five 250mL of water sample were collected from the top with a syringe. All samples were treated with 35ppm calcium ferrate and mix in a magnetic mixer during the lowering of the pH to 7.0 with 6N HCL, stock 40% Ferric Chloride, 50% diluted stock Ferric Chloride, 25% diluted stock Ferric Chloride, and 10% diluted stock Ferric Chloride respectively. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm, and then let settle for 30 minutes. Turbidity was measured with a Hach 2100Q portable turbidimeter after no filtration, with a 1u filter, and with an 8u filter respectively for all the samples. Nitrite was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe.

Data:

	pH	**Ferric (uL)**	**6N HCL (uL)**	**Turbidity (NTU)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**
Control	7.89	N/A	N/A	219	N/A	9.34	0.04	1.46
HCl	11.23/7.15	N/A	670		16.29	N/A	0.11	4.27
Not filtered				1.28				

8u				0.64				
1u				0.23				
Stock Ferric	11.27/7.13	450	N/A		264.13	0.64	0.03	4.04
Not filtered				0.52				
8u				0.19				
1u				0.25				
50% diluted	11.27/7.13	470	N/A		145.72	<0.1	0.08	4.5
not filtered				1.6				
8u				0.74				
1u				0.11				
25% diluted	11.22/7.17	440	N/A		76.87	<0.1	0.07	4.68
not filtered				0.17				
8u				0.26				
1u				0.1				
10% diluted	11.27/7.12	440	N/A		40.51	<0.1	0.11	4.63
not filtered				0.43				
8u				0.49				
1u				0.11				

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).

Total Iron Used:
<u>Ferrate – 35mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 35mg/L = 16.288125mg/L of Fe added.
To Lower pH with 40% w/v Ferric chloride we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845g
Weight of ferric chloride 162.204g
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912g/100mL
We used 0.5mL to lower pH then:

13.76912g/100mL = 0.1376912g/mL x 0.450mL = 0.06196104g of Fe in 250mL or 247.84416mg/L

<u>Iron in 40% Stock 50% diluted</u> – 13.76912% x 0.5 = 6.88456g/100mL
We used 0.5mL to lower pH then:
6.88456g/100mL = 0.0688456g/mL x 0.470mL = 0.032357432g of Fe in 250mL or 129.429728mg/L

<u>Iron in 40% Stock 25% diluted</u> – 13.76912% x 0.25 = 3.44228g/100mL
We used 0.46mL to lower pH then:
3.44228g/100mL = 0.0344228g/mL x 0.440mL = 0.015146032g of Fe in 250mL or 60.584128mg/L

<u>Iron in 40% Stock 10% diluted</u> – 13.76912% x 0.1 = 1.376912g/100mL
We used mL to lower pH then:
1.376912g/100mL = 0.01376912g/mL x 0.44mL = 0.00605584128g of Fe in 250mL or 24.2233648mg/L

Acid and Ferric Sulfate to Lower pH Test, October 3rd, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1.0L sample of the mix was collected from the bucket.
Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, four 250mL of water sample were collected from the top with a syringe. All samples were treated with 30ppm sulfate ferrate and mix in a magnetic mixer during the lowering of the pH to 10, 9, and 8.0 respectively with 5N H_2SO_4. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 30 minutes at 30rpm. At this point the pH of all samples was lowered to 7.5 with Ferric Sulfate, mixed for 15 minutes, and let settle for 10 minutes. The pH of the fourth sample was directly lowered to 7.5 with ferric sulfate, and mixed for 30 minutes in the Phipps & Bird's mixer at 30rpm, then let to settle for 10 minutes. Nitrite was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe.

Data:

	pH	**5N H_2SO_4 (uL)**	**Ferric (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**
Control	8	N/A	N/A	N/A	7.4	0.02	1.49	14.07
7.5	11.05/7.56	N/A	350	16.29	534.76	2.15	1.87	0.27
10/7 pH	11.18/10.08/7.59	340	140	222.28	2.42	0.02	2.12	0.5
9/7 pH	11.17/9.08/7.55	500	40	73.48	3.09	0.09	2.58	0.96
8/7 pH	11.14/8.04/7.54	540	25	51.16	3.04	0.07	2.82	1.08

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).

Total Iron Used:
<u>Ferrate – 30mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 30mg/L = 13.96125mg/L of Fe added.

<u>Iron in Stock Ferric Sulfate 60% (12% Fe)</u> – 12g/100g of Fe in solution.
Density of Ferric sulfate = 3.1g/mL, then 100g/3.1g/mL = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.

We used 0.xxxmL to lower pH then:

0.372g/mL x 0.350mL = 0.1302g of Fe in 250mL x 4 x 1,000.00= 520.8mg/L

0.372g/mL x 0.140mL = 0.05208g of Fe in 250mL x 4 x 1,000.00 = 208.32mg/L

0.372g/mL x 0.040mL = 0.01488g of Fe in 250mL x 4 x 1,000.00 = 59.52mg/L

0.372g/mL x 0.025mL = 0.0093g of Fe in 250mL x 4 x 1,000.00 = 37.2mg/L

Ferric Sulfate to Lower pH vs. Time Test, October 4th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1.0L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, four 250mL of water sample were collected from the top with a syringe. All samples were treated with 30ppm sulfate ferrate and mix in a magnetic mixer during the lowering of the pH to 7.5 with 60% Ferric Sulfate at 30 seconds, 2, 5, and ten minutes after ferrate dosing. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm. Nitrite was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe.

Data:

	pH	**Ferric (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**
Control	8.00	N/A	N/A	7.40	0.02	1.49	14.07
30 sec	11.17/7.56	350	534.76	5.31	0.06	1.96	0.23

2 min	11.16/7.36	350	534.76	6.68	0.03	3.41	0.15
5 min	11.22/7.53	350	534.76	6.59	0.03	3.32	0.158
10 min	11.17/7.49	350	534.76	7.49	0.03	3.55	0.264

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).

Total Iron Used:

<u>Ferrate – 30mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 30mg/L = 13.96125mg/L of Fe added.

<u>Iron in Stock Ferric Sulfate 60% (12% Fe, W/W)</u> – 12g/100g of Fe in solution.
Density of Ferric sulfate = 3.1g/mL, then 100g/3.1g/mL = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.350mL to lower pH then:
0.372g/mL x 0.350mL = 0.1302g of Fe in 250mL x 4 x 1,000= 520.8mg/L

Ferric Chloride vs. Ferric Sulfate in Ferrate Synthesis, October 12th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 0.5L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, two 250mL of water sample were collected from the top with a syringe. The first sample was treated with 35ppm sulfate ferrate and mix in a magnetic mixer during the lowering of the pH to 7.5 with Ferric Sulfate. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm and let to settle for 10 minutes. The second sample was given the same treatment except it was treated with ferrate chloride and the pH was lowered with ferric chloride. Nitrite and ortho phosphorus was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe.

Data:

	pH	**Ferric (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**
Control	7.9	N/A	N/A	6.75	0.56	1.33
SO_4	11.31/7.59	440	671.01	<0.1	0.02	4.02
Cl_3	11.23/7.55	410	242.1	<0.1	0.04	4.34

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).

Total Iron Used:

<u>Ferrate – 35mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 35mg/L = 16.288125mg/L of Fe added.

<u>Iron in Stock Ferric Sulfate 60% (12% Fe)</u> – 12g/100g of Fe in solution.
Density of Ferric sulfate = 3.1g/mL, then 100g/3.1g/mL = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.140mL to lower pH then:
0.372g/mL x 0.440mL = 0.16368g of Fe in 250mL x 4 x 1,000.00 = 654.72mg/L
To Lower pH with <u>40% w/v Ferric chloride</u> we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845g
Weight of ferric chloride 162.204g
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912g/100mL
We used 0.5mL to lower pH then:
13.76912g/100mL = 0.1376912g/mL x 0.410mL = 0.06196104g of Fe in 250mL or 225.813568mg/L

Ammonia vs. Ferrate Strength Ratios October 17th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 1.75L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, seven 250mL of water sample were collected from the top with a syringe. The first four samples were treated according to the contents of ammonia in the control sample at ratios of 3:1, 4:1, 5:1, and 6:1 respectively with ferrate chloride and mix in a magnetic mixer during the lowering of the pH to 7.5 with Ferric Chloride. Then, the samples were immediately transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm and let to settle for 10 minutes. Nitrite was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe.

Once the best ammonia and nitrate reductions were shown, we treated three more samples with the 3:1 (7 x 3 = 21ppm ferrate) ratio strength of ferrate chloride. The pH of the samples was lowered to 9, 8.5 and 8 respectively with ferric chloride. Then mixed in the Phipps & Bird's mixer to be mixed for 20 minutes at 130rpm and let to settle for 10 minutes. Nitrite was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe.

Data:

	pH	**Ferric (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**
Control	8.14	N/A	N/A	6.63	0.44	1.28
21 ppm	11.1/7.38	300	175	<0.1	0.02	4.13
28 ppm	11.34/7.51	320	189.28	<0.1	0.01	3.91
35 ppm	11.49/7.47	410	242.1	<0.1	0.01	5.62
42 ppm	11.88/7.24	500	294.93	<0.1	0.01	198.34
9 pH	11.03/8.93	200	119.93	<0.1	0.15	3.96
8.5 pH	11.02/8.43	210	125.43	<0.1	0.08	2.76
8 pH	11.01/8.04	250	147.4	<0.1	0.08	4.38

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).
Total Iron Used:

<u>Ferrate – 35mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 21mg/L = 9.772875mg/L of Fe added.
55.845/120 = 46.5375% x 28mg/L = 13.0305mg/L of Fe added.
55.845/120 = 46.5375% x 35mg/L = 16.288125mg/L of Fe added.
55.845/120 = 46.5375% x 42mg/L = 19.54575mg/L of Fe added.

To Lower pH with <u>40% w/v Ferric chloride</u> we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845g
Weight of ferric chloride 162.204g
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912g/100mL
We used 0.5mL to lower pH then:
13.76912g/100mL = 0.1376912g/mL x 0.300mL = 0.04130736g of Fe in 250mL or 165.22944mg/L
13.76912g/100mL = 0.1376912g/mL x 0.320mL = 0.044061184g of Fe in 250mL or 176.244736mg/L
13.76912g/100mL = 0.1376912g/mL x 0.410mL = 0.056453392g of Fe in 250mL or 225.813568mg/L
13.76912g/100mL = 0.1376912g/mL x 0.500mL = 0.0688456g of Fe in 250mL or 275.3824mg/L
13.76912g/100mL = 0.1376912g/mL x 0.200mL = 0.02753824g of Fe in 250mL or 110.15296mg/L

13.76912g/100mL = 0.1376912g/mL x 0.210mL = 0.028915152g of Fe in 250mL or 115.660608mg/L
13.76912g/100mL = 0.1376912g/mL x 0.250mL = 0.0344228g of Fe in 250mL or 137.6912mg/L

Ammonia vs. Ferrate Strength Ratios: Part II, October 19th, 2016

Samples: Indian River (IR) Lagoon Muck from Dr. Trefry's lab (8/2/2016). Columns of core IR were place in a bucket, distilled water added to it and thoroughly mixed. A 0.75L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, seven 250mL of water sample were collected from the top with a syringe. Once again, the ratio of ferrate with the best ammonia and nitrate reductions shown, 3:1 (7 x 3 = 21ppm ferrate) was used to treat three more samples. The pH of the samples was lowered to 9, 8.5 and 8 respectively with 6N HCl. Fifty micro liters of Sodium thiosulfate (0.25M) was added to the samples to completely eliminate the ferrate in the samples (read in the Hach DR 6000 spectrometer at 510nm). Then mixed in the Phipps & Bird's mixer to be mixed for 20 minutes at 130rpm and let to settle for 10 minutes. Nitrite was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe.

Data:

	pH	**6N HCL used (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**
Control	8.08	N/A	N/A	5.37	0.58	1.26
9 pH	11.02/9.12	300	9.77	0.59	0.3	16.03
8.5 pH	10.99/8.4	350	9.77	0.81	0.22	10.1
8 pH	11/7.97	430	9.77	1.02	0.22	19.74

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).

Total Iron Used:
<u>Ferrate – 35mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 21mg/L = 9.772875mg/L of Fe added.

New Muck Treated with Ferric Sulfate in Ferrate Synthesis, October 26th, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 0.5L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, one 250mL of water sample was collected from the top with a syringe. The sample was treated with a 5 to 1 ferrate to ammonia ratio, or 5ppm, sulfate ferrate and mix in a magnetic mixer for 10minutes. Then, the pH of the sample was lowered of the pH to 7.5 with 5N sulfuric acid. Then, the sample was transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm (coagulate) and let to settle for 10 minutes. Nitrite and ortho phosphorus was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	**6N HCL used (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Turbidity (NTU)**
Control	7.29	N/A	N/A	0.82	0.01	0.31	0.39	472
9 pH	10.17/ 7.61	170	2.33	0.03	0.02	0.37	0.34	46.9

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
<u>Ferrate – 5mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 5mg/L = 2.326875mg/L of Fe added.

New Muck Treated with Ferric Sulfate in Ferrate Synthesis, October 26th, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 0.5L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, one 250mL of water sample was collected from the top with a syringe. The sample was treated with a 5 to 1 ferrate to ammonia ratio, or 5ppm, sulfate ferrate and mix in a magnetic mixer for 10minutes. Then, the pH of the sample was lowered of the pH to 7.5 with 5N sulfuric acid. Then, the sample was transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm (coagulate) and let to settle for 10 minutes. Nitrite and ortho phosphorus was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	**Fe_2SO_4 (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Turbidity (NTU)**
Control	7.29	N/A	N/A	0.82	0.01	0.31	0.39	472
9 pH	10.17/7.61	170	2.33	0.03	0.02	0.37	0.34	46.9

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
<u>Ferrate – 5mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 5mg/L = 2.326875mg/L of Fe added.

New Muck Treated with Ferric Sulfate and Bleach in Ferrate Synthesis, November 4th, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 0.5L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, one 250mL of water sample was collected from the top with a syringe. The sample was treated with a 3:1 (3ppm) sulfate ferrate to ammonia ratio and mixed in a magnetic mixer for 10 minutes. Then, the pH of the sample was lowered of the pH to 7.5 with 60% (W/W) ferric sulfate. Then, the sample was transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm (coagulate) and let to settle for 10 minutes. Nitrite and ortho phosphorus was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	**Fe_2SO_4 (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Total P (mg/L)**	**Turbidity (NTU)**
Control	7.29	N/A	N/A	0.66	0.01	0.24	0.39	1.06	472
3 pH	10.01 /7.25	80	120.44	0.09	0.003	0.28	0.11	4.6	

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
<u>Ferrate – 3mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g
<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 3mg/L = 1.396125mg/L of Fe added.

<u>Iron in Stock Ferric Sulfate 60% (12% Fe)</u> – 12g/100g of Fe in solution.
Density of Ferric sulfate = 3.1g/mL, then 100g/3.1g/mL = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.05mL to lower pH then:
0.372g/mL x 0.080mL = 0.02976g of Fe in 250mL x 4 x 1,000.00 = 119.04mg/L

New Muck Treated with Ferric Sulfate and Bleach in Ferrate Synthesis, November 6th, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 0.5L sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, two 250mL of water sample were collected from the top with a syringe. The samples were treated with a 3:1 (6ppm) sulfate ferrate to ammonia ratio and mixed in a magnetic mixer for 10 minutes. Then, the pH of the samples was lowered of the pH to 7 and 6.5 with 60% (W/W) ferric sulfate respectively. Then, the samples were transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30rpm (coagulate) and let to settle for 10 minutes. Nitrite and ortho phosphorus was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	Fe_2SO_4 (uL)	Total Fe used (mg/L)	NH_3-N (mg/L)	NO_2-N (mg/L)	NO_3-N (mg/L)	Ortho-P (mg/L)	Total Fe (mg/L)	Turbidity (NTU)
Control	7.53	N/A	N/A	2.03	0.01	0.36	4.33	2.31	54.3
7 pH	10.79 /6.9	170	255.75	0.16	0.002	0.35	0.08	1.08	2.48
6.5 pH	11.05 /6.45	210	315.27	0.27	0.002	0.35	0.14	1.29	3.33

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrite was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
<u>Ferrate – 6mg/L for all treated samples:</u>
Weight of Iron 55.845g
Weight of ferrate 120g

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 6mg/L = 2.79225mg/L of Fe added.

<u>Iron in Stock Ferric Sulfate 60% (12% Fe)</u> – 12g/100g of Fe in solution.
Density of Ferric sulfate = 3.1g/mL, then 100g/3.1g/mL = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.17mL and 0.21mL to lower pH then:
0.372g/mL x 0.17mL = 0.02976g of Fe in 250mL x 4 x 1,000.00 = 252.96mg/L
0.372g/mL x 0.21mL = 0.02976g of Fe in 250mL x 4 x 1,000.00 = 312.48mg/L

New Muck Treated with Ferric Sulfate and Bleach in Ferrate Synthesis, November 14th, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 1.5*L* sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, three 250*mL* of water sample were collected from the top with a syringe. The samples were treated with a 10, 20, and 30*ppm* sulfate ferrate respectively and mixed in a magnetic mixer for 10 minutes. Then, the pH of the samples was lowered of the pH to 7.5 with 60% (W/W) ferric sulfate respectively. Then, the samples were transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30*rpm* (coagulate) and let to settle for 10 minutes. Nitrite and ortho phosphorus was measured using the Systea (Chinchilla) nutrient analyzer. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	**Fe_2SO_4 (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Total Fe (mg/L)**	**Turbidity (NTU)**
Control	7.75	N/A	N/A	3.06	0.004	0.35	0.37	1.32	19.2
10	11.13/7.57	230	347	0.24	0.01	0.4	0.01	0.39	0.99
20	11.88/7.57	390	589	<0.1	0.002	0.77	<0.001	0.51	1.06
30	12.17/7.56	625	943.96	<0.1	0.002	1.99	<0.001	0.19	0.52

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrite was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
Ferrate – 10, 20, and 30*mg/L* for each respective sample:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 10*mg/L* = 4.65375*mg/L* of Fe added.
46.5375% x 20*mg/L* = 9.3075*mg/L* of Fe added.
46.5375% x 30*mg/L* = 13.96125*mg/L* of Fe added.

Iron in Stock Ferric Sulfate 60% (12% Fe) – 12*g*/100*g of Fe in solution.*
Density of Ferric sulfate = 3.1*g/mL*, then 100*g*/3.1*g/mL* = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.23*mL,* 0.39*mL* and 0.625*mL* to lower pH then:
0.372g/mL x 0.23mL = 0.08556g of Fe in 250mL x 4 x 1,000.00 = 342.24mg/L
0.372g/mL x 0.39mL = 0.14508g of Fe in 250mL x 4 x 1,000.00 = 580.32mg/L
0.372g/mL x 0.625mL = 0.2325g of Fe in 250mL x 4 x 1,000.00 = 930.00mg/L

New Muck Treated with Ferric Sulfate and Bleach in Ferrate Synthesis, November 17th, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 1.5*L* sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, three 250*mL* of water samples were collected from the top with a syringe. The samples were treated with a 4:1, 5:1 and 6:1 (12, 15, and 18*ppm*) sulfate ferrate to ammonia ratio respectively and mixed in a magnetic mixer for 10 minutes. Then, the pH of the samples was lowered of the pH to 7 with 60% (W/W) ferric sulfate. Then, the samples were transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30*rpm* (coagulate) and let to settle for 10 minutes. Ortho phosphorus and total iron were measured (after filtration with a 1*um* filter) using the Hach DR 6000 spectrometer and PhosphoVer/Ferricver powder pillows method respectively. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured (after filtration with a 1*um* filter) with a Hach 2100Q portable turbidimeter.

Data:

	pH	**Fe_2SO_4 (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Total Fe (mg/L)**	**Turbidity (NTU)**
Control	8.01	N/A	N/A	2.94	0.01	0.37	0.32	0.76	10.5
4:1	11.04 /7.45	270	407.3	0.34	0.001	0.38	0.07	2.47	5.78
5:1	11.69 /7.61	310	468.3	0.22	0.001	0.54	0.09	1.9	3.43
6:1	11.83 /7.49	380	573.8	<0.1	0.002	0.63	0.06	2.12	3.26

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrite was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
Ferrate – 12, 15 and 18*mg/L* for all treated samples:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 12*mg/L* = 5.5845*mg/L* of Fe added.
55.845/120 = 46.5375% x 15*mg/L* = 6.980625*mg/L* of Fe added.
55.845/120 = 46.5375% x 18*mg/L* = 8.37675*mg/L* of Fe added.

Iron in Stock Ferric Sulfate 60% (12% Fe) – 12*g*/100*g of Fe in solution.*

Density of Ferric sulfate = 3.1*g/mL*, then 100*g*/3.1*g/mL* = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.27*mL*, .31*mL*, and 0.38*mL* to lower pH then:
0.372g/mL x 0.27mL = 0.02976g of Fe in 250mL x 4 x 1,000.00 = 401.76mg/L
0.372g/mL x 0.31mL = 0.02976g of Fe in 250mL x 4 x 1,000.00 = 461.28mg/L
0.372g/mL x 0.38mL = 0.02976g of Fe in 250mL x 4 x 1,000.00 = 565.44mg/L

Ferric Chloride Dilutions to Lower pH, November 20th, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 1.5*L* sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, three 250*mL* of water samples were collected from the top with a syringe. Two samples were treated with a 4:1 ferrate (10ppm, made with Ferric chloride) to ammonia ratio each and mixed in a magnetic mixer for 10 minutes. Then, the pH of the samples was lowered to 7.5; one sample with 50% stock dilution with 6N HCl and the second with 50% stock dilution with distilled/deionized water. Then, the samples were transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30*rpm* (coagulate) and let to settle for 10 minutes. The third sample was also treated as above described, but its pH was lowered to 8.0 with 50% stock dilution with 6N HCl. Ortho phosphorus and total iron were measured (after filtration with a 1*um* filter) using the Hach DR 6000 spectrometer and PhosphoVer/Ferricver powder pillows method respectively. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured with a Hach 2100Q portable turbidimeter.
The third sample was also treated with ferrate as above described, but its pH was lowered to 8.0 with 50% stock dilution with 6N HCl.

Data:

	pH	**Fe_2SO_4 (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Total Fe (mg/L)**	**Turbidity (NTU)**
Control	7.72	N/A	N/A	2.39	0.002	0.45	0.13	1.32	197
50%/ HCl	10.15/ 7.49	200	59.73	0.67	0.001	0.57	0.02	0.33	1.54
50%/ H_2O	9.88/7.59	480	136.84	1.19	0.002	0.52	0.03	0.53	1.55
50%/ 8 pH	9.87/8.05	80	26.7	0.78	0.02	0.42	0.03	0.22	0.84

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrite was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
Ferrate – 10*mg/L* for all treated samples:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 10*mg/L* = 4.65375*mg/L* of Fe added.

Iron in 40% Stock 50% diluted – 13.76912% x 0.5 = 6.88456g/100mL
We used 0.20, 0.48, and 0.080*mL* to lower pH then:
6.88456g/100mL = 0.0688456g/mL x 0.2mL = 0.01376912g of Fe in 250mL or 55.07648mg/L
6.88456g/100mL = 0.0688456g/mL x 0.48mL = 0.033045888g of Fe in 250mL or 132.14mg/L
6.88456g/100mL = 0.0688456g/mL x 0.08mL = 0.005507648g of Fe in 250mL or 22.030592mg/L

CO_2 to Lower pH, November 29th, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 1.5*L* sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, two 250*mL* of water samples were collected from the top with a syringe. Two samples were treated with a 3:1 ferrate (18ppm, made with Ferric chloride) to ammonia ratio each and mixed in a magnetic mixer for 10 minutes. Then, the pH of both samples was lowered to 7.5 and 8.0 with CO_2 respectively. Then, the pH of the second (8.0 pH) sample was further lowered to 7.5 with stock 40% ferric chloride. Then, both samples were transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30*rpm* (coagulate) and let to settle for 10 minutes. Ortho phosphorus and total iron were measured (after filtration with a 1*um* filter) using the Hach DR 6000 spectrometer and PhosphoVer/Ferricver powder pillows method respectively. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured with a Hach 2100Q portable turbidimeter.
The third 250*mL* sample was also treated as above, but its pH was lowered to 7.5 with 40*%* stock Ferric Chloride.

Data:

	pH	**Fe_2Cl_3 (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Total Fe (mg/L)**	**Turbidity (NTU)**
Control	8.01	N/A	N/A	5.84	<0.001	0.44	0.09	0.65	12.8
7.5 pH	11.44/7.58	N/A	8.4	0.05	0.02	0.72	0.17	0.51	11.3

8.0 pH	11.5/7.9 5/7.56	70	46.93	0.04	0.02	0.69	0.04	0.11	0.77
7.5Ferric	12/7.55	470	267.2	<0.01	0.002	1.87	0.08	6.14	5.71

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrite was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
<u>Ferrate – 18*mg/L* for all treated samples:</u>
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 18*mg/L* = 8.37675*mg/L* of Fe added.
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912*g*/100*mL*
We used 0.07*mL* and 0.470*mL* to lower pH then:
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.07*mL* = 0.009638384g of Fe in 250*mL* or 38.553536*mg/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.47*mL* = 0.064714864g of Fe in 250*mL* or 258.859456*mg/L*

CO_2 to Lower pH plus 70, 50, and 25 uL Ferric Chloride, December 2nd, 2016

Samples: Muck samples from the Palm Bay location site (10/26/2016). Muck was collected in a bucket, distilled water added to it and thoroughly mixed. A 1.5*L* sample of the mix was collected from the bucket.

Method: The above described sample was once again mixed thoroughly in the morning of the test, let to settle. When settled, three 250*mL* of water samples were collected from the top with a syringe. Two samples were treated with a 3:1 ferrate (12*ppm*, made with Ferric chloride) to ammonia ratio each and mixed in a magnetic mixer for 10 minutes. Then, the pH of all three samples was lowered to 8.0 with CO_2. Then, 70, 50, and 25*uL* of stock 40% ferric chloride were added to the first, second, and third sample respectively. Then, the samples were transferred to the Phipps & Bird's mixer to be mixed for 20 minutes at 30*rpm* (coagulate) and let to settle for 10 minutes. Ortho phosphorus and total iron were measured (after filtration with a 1*um* filter) using the Hach DR 6000 spectrometer and PhosphoVer/Ferricver powder pillows method respectively. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Turbidity was measured with a Hach 2100Q portable turbidimeter.

Data:

	pH	**Fe_2Cl_3 (uL)**	**Total Fe used (mg/L)**	**NH_3-N (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Total Fe (mg/L)**	**Turbidity (NTU)**
Control	7.74	N/A	N/A	4.02	0.007	0.36	1.03	6.85	206
70 uL	11.01/8.06/7.8	70	44.2	0.4	0.01	0.56	0.02	0.21	1.98
50 uL	11.10/8.04/7.82	50	33.12	0.25	0.013	0.55	0.023	0.37	1.86
25 uL	11.11/8.04/7.93	25	19.35	0.37	0.02	0.59	0.01	0.33	0.9

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrite was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
<u>Ferrate – 12*mg/L* for all treated samples:</u>
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 12*mg/L* = 5.5845*mg/L* of Fe added.
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912*g*/100*mL*
We used 0.07*mL*, 0.05*mL*, and 0.025*mL* to lower pH then:
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.07*mL* = 0.009638384g of Fe in 250*mL* or 38.553536*mg/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.05*mL* = 0.00688456g of Fe in 250*mL* or 27.53824*mg/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.025*mL* = 0.00344228g of Fe in 250*mL* or 13.76912*mg/L*

Freezing ferrate, December 15th, 2016

Procedure: We made calcium ferrate and right after the 60 minutes reaction we connected the jacketed beaked containing the ferrate to a water cooling unit (FTS Systems). The jacketed beaker was also placed on a magnetic stirrer and was being stirred continuously. We pumped cold water through the jacketed beaker containing the ferrate starting at 14°C. Then, we started lowering the gradually temperature to 10, 5 and 0°C. After that we continued to lower the temperature one degree at a time.

Results: The magnetic stir bar in the ferrate never slowed down as the water reached -27°C. By then, most of the water in the cooling system reservoir tank had solidified; the water pump in the reservoir and the hose returning water had also frozen and stopped pumping water. The water trapped in the hoses and jacketed beaker seemed to go up in temperature slightly.

Conclusion: Using the jacketed beaked to pump freezing water does not seem to be an accurate procedure to look at ferrate's freezing point. All we could observe was that at -10°C water was still pumping through the hoses and the ferrate was still nice and liquid.

Nutrient's Behavior in Muck with Passage of Time, January 12th, 2017

Samples: A 12L muck sample was collected from the Florida Institute of Technology's Anchorage dock location.

Muck was collected in a bucket and 4L of distilled water added to it and thoroughly mixed. A 1.5*L* sample of the mix was collected for analysis.

Method: The above-described sample was once again mixed thoroughly prior to the test, let to settle. When settled, a total of 200*mL* of sample was collected from the top with a syringe and used for analysis. Ortho phosphorus and total iron were measured using the Hach DR 6000 spectrometer and PhosphoVer/Ferricver powder pillows method respectively. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Total Suspended Solids (TSS) were measured by filtering (*1um*) 100*mL* of sample and then drying the filter in oven. The filter was weighted to calculate TSS (Standard Methods 2540 D).

Measurements described above were conducted 1, 2, and 5 days after sample collection.

Data:

Day	**pH**	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**Total Fe (mg/L)**	**TSS (mg/L)**
1	7.99	1.51	4.269	0.845*	2.65	0.07
2	7.89	4.64	5.873	1.344*	3.03*	0.16
5	8.04	3.55	3.795	0.519	3.72*	0.12

*Values above Total Iron (3mg/L) and Original PO_4 (2.5mg/L) values.

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrite was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Nutrient's Behavior in Muck with Passage of Time, January 18th, 2017

Samples: A 12L muck sample was collected from the Florida Institute of Technology's Anchorage dock location.

Muck and 4L lagoon water were collected in separate buckets. The 4L of Lagoon water was added to the muck and thoroughly mixed and let to settle for 24 hours. Sample was stirred once again and 1L of it was collected by decanting.

Method: The 1L sample was let to settle and then two hundred *mL* of sample was collected from the top with a syringe and used for analysis. Ortho phosphorus and total iron were measured using the Hach DR 6000 spectrometer and PhosphoVer/Ferricver powder pillows method respectively. Ammonia and nitrate were measured with the Hach HQ 440D multimeter and probe. Total Suspended Solids (TSS) were measured by filtering (1um and 11um) 100mL of sample and then drying the filter in oven. The filter was weighted to calculate TSS (Standard Methods 2540 D).

The filtered water was used to measure again Ortho phosphorus and Total Iron. We wanted to see if there was interference in our unfiltered measurement on these two colorimetric analyses. Measurements described above were conducted 1, 2, and 5 days after sample collection.

Data:

Day	**pH**	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**Ortho-P (mg/L)**	**1 *um***	**11*um***	**Total Fe (mg/L)**	**1 *um***	**11 *um***	**TSS (1 *um*)**	**11 *um***
1	7.85	0.288	11.46	0.28	0.23	0.22	0.89	0.33	0.62	0.08	0.02
2	8.08	0.519	13.26	0.196	0.17	0.163	0.35	0.24	0.20	0.04	0.06
5	7.45	1.85	4.608	0.127	0.111	0.124	0.08	0.06	0.07	0.03	0.01

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Nitrite was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrite (0.30434782). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.32631579).

Samples: A 12L muck sample was collected from the Florida Institute of Technology's Anchorage dock location.
Muck and 4L lagoon water were collected in separate buckets. The 4L of Lagoon water was added to the muck and thoroughly mixed and let to settle for 24 hours. Sample was stirred once again and 1.5L of it was collected by decanting.

Method: The 1.5L sample was let to settle and five 250 *mL* (sixth 250sample was the control) samples were collected from the top with a syringe and used for analysis. Ammonia of the control sample was first measured. Then, we dosed the other five samples with calcium ferrate at 1:1, 1.5:1, 2:1, 3:1, and 4:1 ferrate to ammonia ratio and mixed for 15 minutes on a magnetic stirrer at high speed. Lowering the pH of the samples to 7.5 with CO_2 followed. All five samples were transferred to a Phipps & Bird mixer to mix at 30 rpm for 20 minutes. Finally, we filtered the samples with a 1*um* filter and then measured ammonia and nitrate with the Hach HQ440 multimeter and respective probes.

Data:

	pH	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**
Control	7.59	3.29	5.21
1:1	9.31/7.64	0.298	5.69
1.5:1	9.81/7.5	<0.018	5.399
2:1	10.26/7.59	<0.018	5.65
3:1	10.43/7.45	<0.018	5.69
4:1	10.36/7.53	<0.018	5.65

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).

3:1 Ratio with Varying pH Test, January 26th, 2017

Samples: A 12L muck sample was collected from the Florida Institute of Technology's Anchorage dock location.
Muck and 4L lagoon water were collected in separate buckets. The 4L of Lagoon water was added to the muck and thoroughly mixed and let to settle for 24 hours. Sample was stirred once again and 1.5L of it was collected by decanting.

Method: The 2L sample was let to settle and seven 250 *mL* (seventh 250 sample was the control) samples were collected from the top with a syringe and used for analysis. Ammonia of the control sample was first measured. Then, we dosed the other five samples with calcium ferrate at a 3:1 ferrate to ammonia ratio and mixed for 15 minutes on a magnetic stirrer at high speed. Lowering the pH of the samples to 10, 9, 8.5, 8, 7.5, and 7 respectively with CO_2 followed. All six samples were transferred to a Phipps & Bird mixer to mix at 30 rpm for 20 minutes. Finally, we filtered the samples with a 1*um* filter and then measured ammonia and nitrate with the Hach HQ440 multimeter and respective probes. We also measured total iron using the persulfate digestion method and the Hach DR 6000 "phosphover" method.

Data:

	pH	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**Total PO_4-P (mg/L)**
Control	7.73	3.33	5.128	0.196
10	10.46/10.03	0.0679	16.106	0.049
9	10.47/9.02	0.552	28.463	0.052
8.5	10.40/8.48	0.172	25.752	0.059
8	10.33/8.05	0.274	30.948	0.078
7.5	10.33/7.55	<0.018	25.98	0.085
7	10.31/7.05	<0.018	28.915	0.046

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897). Phosphorus was calculated by measuring phosphate and then multiplying the nitrate results by the fraction of Phosphorus in Phosphate (0.326).

One and a half microliters of 1.0*M* Sodium thiosulfate were added to all six samples after final mix in the Phipps & Bird mixer to accelerate ferrate coagulation.

3:1 Ratio with Varying pH/Sodium Thiosulfate Interference Test, January 30th, 2017

Samples: A 12L muck sample was collected from the Florida Institute of Technology's Anchorage dock location.

Muck and 4L lagoon water were collected in separate buckets. The 4L of Lagoon water was added to the muck and thoroughly mixed and let to settle for 24 hours. Sample was stirred once again and 1.5L of it was collected by decanting.

Method: The 2.5L sample was let to settle and three 35o *mL* (fourth 250 sample was the control) samples were collected from the top with a syringe and used for analysis. Ammonia of the control sample was first measured. Then, we dosed the other five samples with sodium ferrate at a 3:1 ferrate to ammonia ratio (12 ppm). We mixed the samples and lowered the pH to 9, 8, and 7 respectively with 5N sulfuric acid. A 60 milliliters sample was collected to measure ammonia, nitrate, and ferrate strength at the 1, 5, 10, 20, and 30 minutes of mixing. Finally, we filtered the samples with a 1*um* filter and then measured ammonia and nitrate with the Hach HQ440 multimeter and respective probes. Ferrate strength was measured with the Hach DR 6000 at 510nm.

Data:

	pH	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**Ferrate Strength (510nm absorbance)**
Control	7.39	3.90	2.44	N/A
pH 9				
1 minute	10.73/9.1	2.91	78.612	0.025
5 minutes	9.05	2.84	83.13	0.098
10 minutes	9.06	3.21	82.00	0.036
20 minutes	8.95	2.94	80.419	0.026
30 minutes	8.80	2.62	80.193	0.048
pH 8				
1 minute	8.20	2.88	93.069	0.132
5 minutes	8.22	2.74	96.46	0.01
10 minutes	8.25	2.47	94.65	0.10
20 minutes	8.30	2.22	93.52	0.08
30 minutes	8.30	2.16	99.4	0.12
pH 7				
1 minute	10.77/6.77			
5 minutes	7.07	2.70	90.810	0.037
10 minutes	7.36	3.06	94.199	0.015
20 minutes	7.50	2.44	91.714	0.011

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).
One microliter of 1.0*M* Sodium thiosulfate were added to all six samples after final mix in the Phipps & Bird mixer to accelerate ferrate coagulation.
Sample's pH for 7 and 9 was lowered after 1 minute after dosing and time counted right after dosing.
Sample pH 8 was lowered after 1minute dosing and then time started counting.
At pH 7, 1 minute and 30 minute samples were lost due to error.

3:1 Ratio with Varying pH/Sodium Thiosulfate Interference Test, February 2nd, 2017

Samples: A 12L muck sample was collected from the Florida Institute of Technology's Anchorage dock location.

Muck and 4L lagoon water were collected in separate buckets. The 4L of Lagoon water was added to the muck and thoroughly mixed and let to settle for 24 hours. Sample was stirred once again and 600L of it was collected by decanting.

Method: The 600L sample was let to settle and two 250*mL* (remainder 100*mL* sample was the control) samples were collected from the top with a syringe and used for analysis. Ammonia of the control sample was first measured. Then, we dosed the first sample with sodium ferrate at a 3:1 ferrate to ammonia ratio (12*ppm*) while mixing on a magnetic mixer at high speeds. We lowered the pH to 7 with 5*N* sulfuric acid after 5 minutes of mixing. Then the sample was transferred to a Phipps & Bird mixer to slowly mix (30*rpm*) for 15 minutes. At this point, we filtered the samples with a 1*um* filter followed by measurements of ammonia and absorbance (at 510*nm*). We are looking for a reduction in ammonia from the control sample. If a reduction occurs then:

The second 250*mL* sample was dosed with sodium ferrate at a 3:1 ferrate to ammonia ratio (12*ppm*) while mixing on a magnetic mixer at high speeds. This is followed right after with a lowering of the sample's pH to 9 with 5*N* sulfuric acid and started the stop watch as the sample mixed. We removed 55*mL* of sample at the 2 and 10 minutes point; lowering their pH to 6.5 with 5*N* sulfuric acid to stop the ferrate reaction. Right after, we filtered the samples with a 1*um* filter followed by measurements of ammonia, nitrate, and absorbance (at 510 *nm*).

Ammonia and nitrate with the Hach HQ440 multimeter and respective probes. Ferrate strength was measured with the Hach DR 6000 at 510*nm*.

Data:

	pH	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**Ferrate Strength (510nm absorbance)**
Control	7.78	3.51	6.144	0.067
1st sample	10.57/7.01	<0.018	7.77	0.004
2nd sample*	10.35/8.81			
2 minutes	8.73/5.96	<0.018	7.16	0.006
10 minutes	8.63/6.61	<0.018	6.957	0.005

*Reaction stopped

Notes: Nitrogen was calculated by measuring nitrate and then multiplying the nitrate results by the fraction of nitrogen in nitrate (0.225897).

Nitrate in Distilled Water, February 15th, 2017

Samples: Prepared 3, 5, and 8mg/L NO_3-N standards. These are 250mL prepared with potassium nitrate.

Method: All three samples were treated with 3:1 ferrate to N ratio (9, 15, and 27mg/L) and their pH was lowered to 10 with 6N HCl. We mixed the samples with a Phipps & Bird mixer at 90rpm for 60 minutes. Then, their pH was lowered to 8.0 with Ferric Chloride and then mixed for 15 minutes with a Phipps & Bird mixer. Nitrate was measured with the Hach HQ 440D multimeter and probe. Nitrite was measured using the Systea (Chinchilla) nutrient analyzer. A fourth 250mL of distilled/deionized water was treated as the other 3 samples above.

Data:

	pH	**HCl (uL)**	**Ferric (u/L)**	**Total Fe used (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**
3	12.05/9.46*/7.00	470	10	9.696	0.0035	5.93
5	12.40/10.19/7.15	320	15	15.2421	0.0125	9.93
9	12.65/10.05/7.99	640	15	15.2997	0.078	17.5
DW	12.24/10.12/7.82	400	10	12.4883	0.017	2.16

*The pH of the sample at 3ppm went much lower than the target of ten (3.6). NaOH 50% was used to bring the pH back up. On the 9ppm sample 50% diluted stock Ferric chloride was used instead of the stock ferric chloride. All untreated standards measured < 0.001ppm NO_2-N. Measured NO_3-N for original/untreated samples was 3.35, 5.38, and 9.07mg/L respectively.

Total Iron Used:
<u>Ferrate – 9, 15, and 24*mg/L* for all treated samples:</u>
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 9 = 4.188375*mg/L* of Fe added.
55.845/120 = 46.5375% x 15 = 6.980625*mg/L* of Fe added.
55.845/120 = 46.5375% x 24 = 11.169*mg/L* of Fe added.

To Lower pH with 40% w/v Ferric chloride we used 10 and 15uL (0.01 and 0.015mL) on the samples:
Weight of Iron 55.845*g*
Weight of ferric chloride 162.204*g*
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912*g*/100*mL*
We used 0.5*mL* to lower pH then:
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.01*mL* = 0.001376912g of Fe in 250*mL* or 5.507648*mg/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.015*mL* = 0.002065368g of Fe in 250*mL* or 8.261472*mg/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.015*mL* = 0.002065368g of Fe in 250*mL* or 8.261472*mg/L*
(divided by 2 since we used 50% diluted ferric chloride, 4.130736)

<u>Iron in Stock Ferric Sulfate 60% (12% Fe)</u> – 12*g*/100*g of Fe in solution.*
Density of Ferric sulfate = 3.1*g/mL*, then 100*g*/3.1*g/mL* = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.

We used 0.140*mL* to lower pH then:
0.372g/mL x 0.440mL = 0.16368g of Fe in 250mL x 4 x 1,000.00 = 654.72mg/L

To Lower pH with <u>40% w/v Ferric chloride</u> we used 500uL (0.5mL) on the samples:
Weight of Iron 55.845*g*
Weight of ferric chloride 162.204*g*
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

<u>Iron in Stock Ferric Chloride 40%</u> – 34.4288 x 0.4 = 13.76912*g*/100*mL*
We used 0.5*mL* to lower pH then:
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.410*mL* = 0.06196104g of Fe in 250*mL* or 225.813568*mg/L*

Nitrate in Distilled Water, February 17th, 2017

Samples: Prepared 3, 5, and 8mg/L NO_3-N standards. These are 250mL prepared with potassium nitrate.

Method: All three samples were treated with 3:1 ferrate Sulfate to N ratio (12, 21, and 33mg/L). We mixed the samples with a Phipps & Bird mixer at 90rpm for 60 minutes. Then, their pH was lowered to 8.0 with 5N Sulfuric Acid and then mixed for 15 minutes with a Phipps & Bird mixer. Nitrate was measured with the Hach HQ 440D multimeter and probe. Nitrite was measured using the Systea (Chinchilla) nutrient analyzer. A 250mL of distilled/deionized water was treated as the other 3 samples above respectively.

Data:

	pH	**H_2SO_4 (uL)**	**Total Fe used (mg/L)**	**NO_2-N (mg/L)**	**NO_3-N (mg/L)**
4.12	12.47/7.73	420	5.58	0.006	5.84
DW 3	12.49/7.99	450	5.58	0.007	0.98
6.77	12.79/8.07	765	9.77	0.030	11.0
DW 5	12.82/7.63	800	9.77	0.023	1.80
11.03	13.02/8.16	1210	15.36	0.086	18.3
DW 8	12.98/8.13	1160	15.36	0.081	2.84
DW 5.1	12.54/8.10	780	9.77	1.93	<0.018

Notes: All untreated standards measured < 0.001ppm NO_2-N. Measured NO_3-N for original/untreated samples was 4.12, 6.77, and 11.03mg/L respectively. The DW 5.1 water sample was treated like the DW 5, but ammonia was read as well.

Total Iron Used:
<u>Ferrate – 12, 21, and 33*mg/L* for all treated samples:</u>
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 12 = 5.5845*mg/L* of Fe added.
55.845/120 = 46.5375% x 21 = 9.7729*mg/L* of Fe added.
55.845/120 = 46.5375% x 33 = 15.3574m*g/L* of Fe added.

Lowering pH to 9.5 with Acid and CO_2; February 24th, 2017

Samples: Sample was surface water collected from the deployment site at the Tillman canal site in Palm Bay, Florida. A 1.25L sample was used for this test.

Method: We dosed two 250mL samples with 15mg/L of Sulfate ferrate and another two 250mL at a 3:1 ferrate to ammonia ratio (3) while fast mixing on a magnetic stirrer. The remainder of the sample was our control. The pH of the samples was lowered to 9.5 right after dosing. We used CO_2 to lower the pH on one of each (15mg/L and 3:1), while 5N H_2SO_4 was used to lower the pH of the remaining two samples. Total iron of the sample was measured in the Hach DR 6000 spectrometer (Ferrover procedure) at 1, 5, 10, and 20 minutes after reaching the target pH. We measured ammonia and pH with the Hach HQ440 benchtop multi-meter and respective intelical probes.

Data:

	pH	H_2SO_4 (uL)	Fe added (uL)	Total Fe (mg/L)	NH_3-N (mg/L)
Control	7.68	N/A	N/A	<0.18	
15mg/L	11.79/9.56	335	6.98		
*H2SO4					
1					>3.0
5					>3.0
10					>3.0
20					>3.0
CO_2					
1	11.94/9.54	N/A	6.98		
5					>3.0
10					>3.0
20					>3.0
3:1 Ratio					>3.0
H_2SO_4	10.96/9.5	25	1.396		
1				2.72	
5				2.04	
10				1.24	
20				2.64	
CO_2	9.76/9.4	N/A	1.396		
1				1.41	
5				1.27	
10				2.25	

Total Iron Used:

<u>Ferrate – 9, 15, and 24*mg/L* for all treated samples:</u>
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 3 = 1.396*mg/L* of Fe added.
55.845/120 = 46.5375% x 15 = 6.980625*mg/L* of Fe added.

Lowering pH to 9.5 with Acid and CO_2; February 28th, 2017

Samples: Sample was surface water collected from the deployment site at the Tillman canal site in Palm Bay, Florida. A 1.25L sample was used for this test.

Method: We dosed two 250mL samples with 15mg/L of Sulfate ferrate and another two 250mL at a 3:1 ferrate to ammonia ratio (3ppm) while fast mixing on a magnetic stirrer. The remainder of the sample was our control. The pH of the samples was lowered to 9.5 right after dosing. We used CO_2 to lower the pH on one of each (15mg/L and 3:1), while 5N H_2SO_4 was used to lower the pH of the remaining two samples. We extracted a 10mL volume from the samples at 1, 5, 10, and 20 minutes after reaching the target pH, filtered them with a 0.45*um* filter and measured ferrate strength in the Hach DR 6000 spectrometer at 510nm. We measured ammonia, ORP-Redox, and pH with the Hach HQ440 benchtop multi-meter and respective intelical probes.

Data:

	pH	H_2SO_4 (uL)	Fe added (uL)	Ferrate (510nm)	ORP(mV)	NH_3-N (mg/L)
Control	7.98	N/A	N/A	N/A	220.1	<0.18
15mg/L	11.95/9.55	420	6.98	0.138		
*H2SO4						
1				0.256	546	
5				0.081	573	
10				0.079	605	
20				0.288	643	
*Sample was filtered through a 1um filter						
CO_2	11.72/9.52	N/A	6.98	0.138		
1				0.085	560	
5				0.083	638	
10				0.083	649	
20				0.084	658	
3:1 Ratio	10.21/9.53	50	1.396	0.028		
H_2SO_4						
1				0.029	483	
5				0.023	585	
10				0.022	618	
20				0	644	
CO_2	10.03/9.52	N/A	1.396	0.028		
1				0.016	568	
5				0.02	629	
10				0.008	654	
20				0.012	682	

Total Iron Used:
Ferrate – 9, 15, and 24*mg/L* for all treated samples:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 3 = 1.396*mg/L* of Fe added.
55.845/120 = 46.5375% x 15 = 6.980625*mg/L* of Fe added.

Three to one Ferrate ammonia/40 to 1 Iron to phosphorus; March 3rd, 2017

Samples: Sample was water and muck from the deployment site at the Tillman canal site in Palm Bay, Florida. It was pumped from the boat in the canal to the trailer. A 250*mL* sample was used for this test.

Method: We dosed a 250mL sample at a 3:1 ferrate to ammonia ratio (3ppm or 1.396mg/L as iron) while fast mixing on a magnetic stirrer. We let it mix for 10 minutes. Then, the pH of the samples was lowered to eight with 35*uL* of diluted (1 in 20 with 5N H_2SO_4) ferric sulfate (2.604 mg/L as iron) and additional 5N H_2SO_4. The sampled was then transferred to be mixed at 30rpm on the

Phipps & Bird mixer for 25 minutes. Finally, we let the sample settle for 30 minutes. We measured ammonia, nitrate, and pH with the Hach HQ440 benchtop multi-meter and respective intelical probes. We filtered 60mL of the sample with a 1*um* filter and measured phosphorus and iron with the Hach DR 6000.

Data:

	pH	**H_2SO_4 (uL)**	**Fe added (uL)**	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**PO_4-P***	**Total Fe (mg/L)**
Control	7.60	N/A	N/A	<0.18	1.61	0.0816	0.21
3ppm	9.95/8.00	10	35	<0.18	2.07	0.0065	0.56

*Phosphorus was calculated by measuring nitrate and then multiplying the phosphate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
<u>Ferrate – 9, 15, and 24*mg/L* for all treated samples:</u>
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 3 = 1.396*mg/L* of Fe added.

<u>Iron in Stock Ferric Sulfate 60% (12% Fe) 1 in 20 dilution</u> – 12*g*/100*g of Fe in solution.*
Density of Ferric sulfate = 3.1*g/mL*, then 100*g*/3.1*g/mL* = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.005*mL* to lower pH then:
0.372g/mL x 0.05 (1 in 20 dilution) x 0.0350mL = 0.000651g of Fe in 250mL x 4 x 1,000.00 = 2.604mg/L

Samples: Distilled/De-ionized water.

Method: Five 250mL samples of Distilled/de-ionized water were dosed with 1, 5, 10, 20, and 40 *mg/L* of sulfate ferrate respectively and mixed on a magnetic mixer. We measured pH, ORP and took 10mL of sample to measure absorbance at 510 *nm* right after dosing.
Data:

	pH	**ORP (mv)**	**Absorbance (510 nm)**	**Total iron used (mg/L)**
1	10.71	458.8	0.027	0.465375
5	11.45	490.5	0.063	2.326875
10	11.90	506.9	0.143	4.65375
20	12.19	513.5	0.254	9.3075
40	12.51	515.5	0.542	18.615

Total Iron Used:
<u>Ferrate – 9, 15, and 24*mg/L* for all treated samples:</u>
Weight of Iron 55.845*g*

Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 1 = 0.465375*mg/L* of Fe added.
55.845/120 = 46.5375% x 5 = 2.326875*mg/L* of Fe added.
55.845/120 = 46.5375% x 10 = 4.65375m*g/L* of Fe added.
55.845/120 = 46.5375% x 20 = 9.3075m*g/L* of Fe added.
55.845/120 = 46.5375% x 40 = 18.615m*g/L* of Fe added.

ORP Calibration: Ferrate Concentration Vs. pH, March 8th, 2017

Samples: Distilled/De-ionized water.

Method: Five 250mL samples of Distilled/de-ionized water were dosed with 10 *mg/L* of sulfate ferrate and mixed on a magnetic mixer. Right after, we lowered the pH of each sample respectively to 12, 11, 10, 9, and 8 with CO_2. We measured ORP and took 10*mL* of sample to measure absorbance at 510 *nm* right after reaching target pH (after filtering with 1*um* filter).

Data:

	pH	**ORP (mv)**	**Absorbance (510 nm)**	**Total iron used (mg/L)**
12	11.74	466.2	0.109	4.65375
11	11.81/11.07	526.2	0.106	4.65375
10	11.64/10.07	623.6	0.094	4.65375
9	11.57/9.05	738.7	0.101	4.65375
8	11.68/7.35	822.0	0.084	4.65375

Total Iron Used:
Ferrate – 9, 15, and 24*mg/L* for all treated samples:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 10 = 4.65375m*g/L* of Fe added.

ORP Calibration: Ferrate Concentration Vs. ORP: pH Controlled, March 14th, 2017

Samples: Distilled/De-ionized water.

Method: Five 250mL samples of Distilled/de-ionized water were dosed with 1, 5, 10, 20, and 40 *mg/L* of sulfate ferrate respectively and mixed on a magnetic mixer. The pH of all the samples were lowered to nine with CO_2. We measured ORP and took 10*mL* of sample to measure absorbance at 510*nm* right after dosing.

Data:

	pH	**ORP (mv)**	**Absorbance (510 nm)**	**Total iron used (mg/L)**
1	10.30/8.99	521.7	0.01	0.47
5	11.34/9.07	652.3	0.06	2.33
10	11.83/8.94	683.5	0.15	4.65
20	12.21/9.09	698.7	0.31	9.30
40	12.47/9.03	725.5	0.70	18.61

Total Iron Used:
Ferrate – 9, 15, and 24*mg/L* for all treated samples:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 1 = 0.465375*mg/L* of Fe added.
55.845/120 = 46.5375% x 5 = 2.326875*mg/L* of Fe added.
55.845/120 = 46.5375% x 10 = 4.65375m*g/L* of Fe added.
55.845/120 = 46.5375% x 20 = 9.3075m*g/L* of Fe added.
55.845/120 = 46.5375% x 40 = 18.615m*g/L* of Fe added.

Three to one Ferrate ammonia/40 to 1 Iron to phosphorus; March 16th, 2017

Samples: Sample was water and muck from the deployment site at the Tillman canal site in Palm Bay, Florida. It was pumped from the boat in the canal to the trailer. A 250*mL* sample was used for this test.

Method: We dosed a 250mL sample at a 3:1 ferrate to ammonia ratio (3ppm or 1.396mg/L as iron) while fast mixing on a magnetic stirrer. We let it mix for 10 minutes. Then, the pH of the samples was lowered to eight with 35*uL* of diluted (1 in 20 with *5N* H_2SO_4) ferric sulfate (2.604 mg/L as iron) and additional 5*N* H_2SO_4. The sampled was then transferred to be mixed at 30rpm on the Phipps & Bird mixer for 25 minutes. Finally, we let the sample settle for 30 minutes. We measured ammonia, nitrate, and pH with the Hach HQ440 benchtop multi-meter and respective intelical probes. We filtered 60mL of the sample with a 1*um* filter and measured phosphorus and iron with the Hach DR 6000.

Data:

	pH	**H_2SO_4 (uL)**	**Fe added (uL)**	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**PO_4-P* (mg/L)**	**Total Fe (mg/L)**
Control	7.96	N/A	N/A	<0.18	1.46	0.04568	1.71
3ppm	9.77/8.01	N/A	35	<0.18	1.88	0.01305	0.99

*Phosphorus was calculated by measuring nitrate and then multiplying the phosphate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:

Ferrate – 9, 15, and 24*mg/L* for all treated samples:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 3 = 1.396*mg/L* of Fe added.

Iron in Stock Ferric Sulfate 60% (12% Fe) 1 in 20 dilution – 12*g*/100*g of Fe in solution.*
Density of Ferric sulfate = 3.1*g/mL*, then 100*g*/3.1*g/mL* = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.005*mL* to lower pH then:
0.372g/mL x 0.05 (1 in 20 dilution) x 0.0350mL = 0.000651g of Fe in 250mL x 4 x 1,000.00 = 2.604mg/L

Three to one Ferrate ammonia/40 to 1 Iron to phosphorus, pH 7.5; March 17th, 2017

Samples: Sample was water and muck from the deployment site at the Tillman canal site in Palm Bay, Florida. It was pumped from the boat in the canal to the trailer. A 250*mL* sample was used for this test.

Method: We dosed a 250mL sample at a 3:1 ferrate to ammonia ratio (3ppm or 1.396mg/L as iron) while fast mixing on a magnetic stirrer. We let it mix for 10 minutes. Then, the pH of the samples was lowered to 7.5 with 35*uL* of diluted (1 in 20 with *5N* H_2SO_4) ferric sulfate (2.604 mg/L as iron) and additional 5*N* H_2SO_4. The sampled was then transferred to be mixed at 30rpm on the Phipps & Bird mixer for 25 minutes. Finally, we let the sample settle for 30 minutes. We measured ammonia, nitrate, and pH with the Hach HQ440 benchtop multi-meter and respective intelical probes. We filtered 60mL of the sample with a 1*um* filter and measured phosphorus and iron with the Hach DR 6000.

Data:

	pH	**H_2SO_4 (uL)**	**Fe added (uL)**	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**PO_4-P***	**Total Fe (mg/L)**
Control	7.96	N/A	N/A	<0.18	1.46	0.046	1.71
3ppm	9.79/7.53	55	35	<0.18	2.20	0.01305	0.99

*Phosphorus was calculated by measuring nitrate and then multiplying the phosphate results by the fraction of Phosphorus in Phosphate (0.32631579).

Total Iron Used:
Ferrate – 9, 15, and 24*mg/L* for all treated samples:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 3 = 1.396*mg/L* of Fe added.

Iron in Stock Ferric Sulfate 60% (12% Fe) 1 in 20 dilution – 12*g*/100*g of Fe in solution.*

Density of Ferric sulfate = 3.1*g/mL*, then 100*g*/3.1*g/mL* = 32.258064mL is the volume of 100g of solution
Then, 12 g / 32.258064mL = 0.372g/mL of iron per mL of solution.
We used 0.005*mL* to lower pH then:
0.372g/mL x 0.05 (1 in 20 dilution) x 0.0350mL = 0.000651g of Fe in 250mL x 4 x 1,000.00 = 2.604mg/L

Settling Time for pH Samples Lowered with 40% Stock Ferric and 50% Diluted Ferric; March 23rd, 2017

Samples: Sample was water and muck from the deployment site at the Tillman canal site in Palm Bay, Florida. It was pumped from the boat in the canal to the small retention pond. Six 250*mL* samples were used for this test.

Method: We dosed all six 250mL samples at a 3:1 ferrate to ammonia ratio (3ppm or 1.396mg/L as iron) while fast mixing on a magnetic stirrer. We let it mix for 10 minutes. Then, the pH of two of the samples was lowered to 7.5, 8.0, and 8.5 respectively. One set of 7.5, 8.0, and 8.5 pH was lowered with 40% stock ferric chloride and the second set with 50% diluted stock Ferric chloride: 6N HCl. The sampled was then transferred to be mixed at 30rpm on the Phipps & Bird mixer for 20 minutes. Finally, we let the sample settle for 30 minutes. Time for settling was monitored. We also measured for turbidity and total Iron. We measured turbidity with the Hach 2100Q portable turbidimeter. We filtered 60mL of the sample with a 1*um* filter and measured iron with the Hach DR 6000.

Data:

	pH	**Fe_2Cl_3 (uL)**	**Fe added (mg/L)**	**Turbidity (NTU)**	**Total Fe (mg/L)**
Control	7.72	N/A	N/A	2.17	0.12
Stock 40% Fe_2Cl_3					
7.5	10.43/7.56	180	100.5337	2.37	1.58
8.0	9.94/8.06	55	31.6881	0.39	0.15
8.5	10.15/8.58	20	12.4113	0.87	0.17
50% Diluted Stock Fe_2Cl_3					
7.5	10.42/7.56	125	35.8188	1.46	0.41
8.0	10.43/8.06	50	15.1651	0.38	0.28
8.5	10.26/8.49	30	9.65747	0.65	0.69

Notes: It took about 15 minutes for the iron precipitate to settle at the bottom.
Total Iron Used:
Ferrate – 3*mg/L* for all treated samples:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 3 = 1.396*mg/L* of Fe added.

To Lower pH with 40% w/v Ferric chloride we used 10 and 15uL (0.01 and 0.015mL) on the samples:
Weight of Iron 55.845*g*
Weight of ferric chloride 162.204*g*
Percentage of Iron in Ferric 55.845/162.204 = 34.4288%

Iron in Stock Ferric Chloride 40% – 34.4288 x 0.4 = 13.76912*g*/100*mL*
We used 0.125*mL* to lower pH then:
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.125*mL* = 0.0172114g of Fe in 250*mL* or 34.4228*g/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.05*mL* = 0.00688456g of Fe in 250*mL* or 13.76912*mg/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.03*mL* = 0.004130736g of Fe in 250*mL* or 8.261472*mg/L*
(divided by 2 since we used 50% diluted ferric chloride, 4.130736)
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.18*mL* = 0.024784416g of Fe in 250*mL* or 99.137664*g/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.055*mL* = 0.007573016g of Fe in 250*mL* or 30.292064*g/L*
13.76912*g*/100*mL* = 0.1376912*g/mL* x 0.02*mL* = 0.002753824g of Fe in 250*mL* or 11.015296*g/L*

Large Scale Treated Samples; March 28, 2017

Sample: Tillman canal water in a retention pond flowing through the trailer at 3gallons/min.

Procedure: We treated the flow with 3ppm of calcium ferrate and mix water in a 40 gallons tank for about 10 minutes. Then, the water escapes the first tank from the top into a line where the pH was lowered to 8 with 50% diluted stock (40%) ferric chloride and 6N HCl before it went to a second tank. Treated water was slowly mixed in the second tank for about 15 minutes and escaped to a third settling tank. We collected a 250mL water sample (Settled) from the top of the third tank (clarifier). Water drained from the top of the third tank down to a bucket. We collected three 250ml samples from the overflow water coming out of the bucket at half hour intervals (1, 2, 3).

Test: We tested the samples in the lab for pH, ammonia, and nitrate (Hach HQ440 multimeter). Also, we measured phosphorus and total iron (Hach DR 6000 spectrometer). Finally, turbidity was measured with the Hach 2100Q turbidimeter.

	pH	**Fe added (mg/L)**	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**PO_4-P (mg/L)**	**Total Fe (mg/L)**	**Turbidity (NTU)**
Control	7.72	N/A	<0.18	1.95	0.009	0.12	2.17
1	8.22	38.8	<0.18	2.68	0.009	0.35	0.81
2	8.04	38.8	<0.18	2.22	0.012	0.60	1.32
3	7.85	38.8	<0.18	2.20	0.009	0.68	1.62
Set.	7.65	38.8	<0.18	2.19	0.009	1.62	2.47

Three to one Ferrate ammonia/40 to 1 Iron to phosphorus, pH 8.0; March 31st, 2017

Samples: Sample was a mix of 80% water and 20% muck from the deployment site at the Tillman canal site in Palm Bay, Florida. This mix should be representative to the conditions on the canal. A 250*mL* sample was used for this test.

Method: We dosed a 250*mL* sample at a 3:1 ferrate to ammonia ratio (3*ppm* or 1.396*mg/*L as iron) while fast mixing on a magnetic stirrer. We let it mix for 10 minutes. Then, the pH of the sample was lowered to 8 with 40*uL* of ferric chloride (22.031*mg/L* as iron). The sample was then transferred to be mixed at 30*rpm* on the Phipps & Bird mixer for 20 minutes. Finally, we let the sample settle for 30 minutes. We measured ammonia, nitrate, and pH with the Hach HQ440 benchtop multi-meter and respective intelical probes. We filtered 60*mL* of the sample with a 1*um* filter and measured phosphorus and iron with the Hach DR 6000. We read the turbidity with the Hach 2100Q turbidimeter.

Data:

	pH	**Fe_2Cl_3 (uL)**	**Fe added (mg/L)**	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**PO_4-P* (mg/L)**	**Total Fe (mg/L)**	**Turbidity (NTU)**
Control	7.65	N/A	N/A	0.494	1.25	0.3328	>3.05	245
3ppm	9.42/7.98	40**	23.427	<0.18	1.43	0.0326	0.31	0.41

*Phosphorus was calculated by measuring nitrate and then multiplying the phosphate results by the fraction of Phosphorus in Phosphate (0.32631579).

**We used 35*uL* of 40*%* stock ferric chloride and 10*uL* of 50*%* diluted stock ferric.

Total Iron Used:
Ferrate – 3 *mg/L*:
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

Percentage of Iron in Ferrate - 55.845/120 = 46.5375% x 3 = 1.396*mg/L* of Fe added.

Iron in 40*%* Stock 50*%* diluted – 13.76912*%* x 0.5 = 6.88456*g*/100*mL*
We used 0.035 of stock 40*%* Ferric and 0.01 of 50*%* diluted stock ferric to lower pH then:
6.88456*g*/100*mL* = 0.0688456g/mL x 0.01*mL* = 0.000688546*g* of Fe in 250*mL* (x 4 x 1000) or 2.754*mg/L*
13.76912*g*/100*mL* = 0.1376912g/mL x 0.035*mL* = 0.004819192*g* of Fe in 250*mL* (x 4 x 1000) or 19.277*mg/L*

Three to one Ferrate ammonia/40 to 1 Iron to phosphorus, pH 8.0; April 4th, 2017

Samples: Sample was a mix of 80*%* water and 20*%* muck from the deployment site at the Tillman canal site in Palm Bay, Florida. This mix should be representative to the conditions on the canal. A 250*mL* sample was used for this test.

Method: We dosed a 250*mL* sample at a 3:1 ferrate to ammonia ratio (3*ppm* or 1.396*mg/*L as iron) while fast mixing on a magnetic stirrer. We let it mix for 10 minutes. Then, the pH of the sample was lowered to 8 with 40*uL* of ferric chloride (22.031*mg/L* as iron). The sample was then transferred to be mixed at 30*rpm* on the Phipps & Bird mixer for 20 minutes. Finally, we let the sample settle for 30 minutes. We read the turbidity with the Hach 2100Q turbidimeter with samples filtered with a 0.45, 1, 8, and 11um filters respectively and one last one not filtered at all.

Data:

	pH	**Fe_2Cl_3** (uL)**	**Fe added (mg/L)**	**Turbidity (NTU)**
Control	7.65	N/A	N/A	245
None	9.42/8.15	40	23.427	2.06
0.45um	9.42/8.15	40	23.427	0.19
1 um	9.42/8.15	40	23.427	0.58
8 um	9.42/8.15	40	23.427	1.12
11um	9.42/8.15	40	23.427	0.72

**We used 35*uL* of 40% stock ferric chloride and 10*uL* of 50% diluted stock ferric.

Total Iron Used:
<u>Ferrate – 3 *mg/L*:</u>
Weight of Iron 55.845*g*
Weight of ferrate 120*g*

<u>Percentage of Iron in Ferrate</u> - 55.845/120 = 46.5375% x 3 = 1.396*mg/L* of Fe added.

<u>Iron in 40% Stock 50% diluted</u> – 13.76912% x 0.5 = 6.88456*g*/100*mL*
We used 0.035 of stock 40% Ferric and 0.01 of 50% diluted stock ferric to lower pH then:
6.88456*g*/100*mL* = 0.0688456g/mL x 0.01*mL* = 0.000688546*g* of Fe in 250*mL* (x 4 x 1000) or 2.754*mg/L*
13.76912*g*/100*mL* = 0.1376912g/mL x 0.035*mL* = 0.004819192*g* of Fe in 250*mL* (x 4 x 1000) or 19.277*mg/L*

Large Scale Treated Samples; April 12th, 2017

Sample: Tillman canal water in a retention pond flowing through the trailer at 3gallons/min. The pond was filled with canal water on Wednesday of the week, but not treated until the next morning. As a result, the muck in the water had settled at the bottom by then.

Procedure: We treated the flow with a 3:1 (3ppm, we kept the pH of the sample treating tank between 10.5 and 10.6 since the ferrate was two days old and had lost some strength) of calcium ferrate to ammonia and mixed water in a 40 gallons tank for about 15 minutes. Then, the water escapes the first tank from the top into a line where the pH was lowered to 8 (we kept the pH of the tank between 8.1 and 8.2) with 50% diluted stock (40%) ferric chloride and 6N HCl before it went to a second tank. Treated water was slowly mixed in the second tank for about 15 minutes and escaped to a third settling tank. Once all the ferrate and ferric concentration were stable, we ran the system for 30 to 45 minutes. Then, we collected three 250ml samples from the overflow water coming out of the bucket at 15 minutes intervals (1, 2, 3 and 4).

Test: We tested the samples in the lab for pH, ammonia, and nitrate (Hach HQ440 multimeter). In addition, we measured phosphorus and total iron (Hach DR 6000 spectrometer). Finally, turbidity was measured with the Hach 2100Q turbidimeter.

	pH	**Fe added (mg/L)**	**NH_3-N (mg/L)**	**NO_3-N (mg/L)**	**PO_4-P (mg/L)**	**Total Fe (mg/L)**	**Turbidity (NTU)**
Control	7.93	N/A	<0.18	2.47	0.016	0.41	12.4
1	8.05	38.8	<0.18	2.82	0.009	0.41	0.67
2	8.25	38.8	<0.18	2.56	0.009	0.41	0.87
3	8.23	38.8	<0.18	2.50	0.009	1.00	0.60
4	8.19	38.8	<0.18	2.82	0.006	0.44	0.58

Notes: The pH of the treated samples with 3mg/L of ferrate is about 7.65 to 7.8 when the water sample is mixed with the "muck" and about 10.4 to 10.55 when the "muck" is settled at the bottom according to lab tests. The pH of the 1st tank (treatment tank) at the site is used as an additional monitoring factor of ferrate concentration in addition to our calculations.

Measuring Ammonia in "Muck" With Passing Time; April 19th, 2017

Samples: Sample was a 3.5L mix of 65% water and 35% muck from the deployment site at the Tillman canal site in Palm Bay, Florida. The sample was thoroughly mix with our drill/pain mixer pallet device.

Method: A 25mL sample was taken from the sample right after mixing and the ammonia concentration was measured. We let the sample settle and took samples for ammonia concentration readings with passing time. We measured ammonia with the Hach HQ440 benchtop multi-meter and respective Intellical probe.

Data:

Time (min)	**NH_3-N (mg/L)**
0	1.21/1.14
15	0.962/0.942
30	1.47/1.34
45	1.66/1.66
60	1.81
90	0.627
120	0.975
180	0.561
24H	0.423

Ferrate Nutrients Summary: Samples Received July 7, 2017

Please note that concentrations are in micrograms N or P/L with 2 or 3 significant figures, except for silica in mg Si/L

DON = dissolved organic nitrogen, TDN = total dissolved nitrogen, DOP = dissolved organic phosphorus, TDP = total dissolved phosphorus

Sample ID	Ammonium (µM)	Ammonium (µg N/L)	Nitrate-Nitrite (µM)	Nitrate + Nitrite (µg N/L)	Nitrite (µM)	Nitrite (µg N/L)	Nitrate (µM)	Nitrate (µg N/L)	DON (µM)	DON (ug N/L)
Pre-trailer 1 Untreated	5.3	75	14.5	202	0.84	11.7	13.6	191	45	635
Pre-trailer 2 Untreated	4.5	63	24.8	347	0.36	5.1	24.4	342	50	702
Tank 1 Untreated	3.8	53	17	238	0.37	5.2	16.7	233	45	624
Tank 2 Untreated	3.5	49	15.6	219	1.75	24.5	13.9	194	39	550
Pre-trailer 1 Treated	5	70	5.4	75	0.17	2.4	5.2	73	41	572
Pre-trailer 2 Treated	5.4	75	5.5	77	0.15	2.1	5.4	75	46	643
Tank 1 Treated	8.6	120	3.4	47	0.22	3.1	3.1	44	41	576
Tank 2 Treated	21.9	307	3.8	53	0.1	1.3	3.7	52	42	592
Mean										612
SD										49
RSD	Residual SD = (SD/mean)*100%					8				
Typical Values										
Turkey Creek		35		130		6		124		450
IRL (mouth TC)		40		10		-	-			650

Sample ID	TDN (µM)	TDN (µg N/L)	Phosphate (µM)	Phosphate (µg P/L)	DOP (µM)	DOP (µg P/L)	TDP (µM)	TDP (µg P/L)	Silica (µM)	Silica (mg Si/L)
Pre-trailer 1 Untreated	65	912	0.84	25.9	2.12	66	3	92	405	11.4
Pre-trailer 2 Untreated	79	1111	1.48	45.9	3.04	94	4.5	140	240	6.7
Tank 1 Untreated	65	915	0.89	27.6	2.64	82	3.5	109	219	6.2
Tank 2 Untreated	58	818	1.45	44.9	3.5	108	4.9	153	286	8.1
Pre-trailer 1 Treated	51	717	0.56	17.4	2.06	64	2.6	81	192	5.4
Pre-trailer 2 Treated	57	795	0.61	19	1.92	60	2.5	79	204	5.7
Tank 1 Treated	53	744	0.64	19.7	2.21	69	2.8	88	193	5.4

Tank 2 Treated	68	952	0.62	19.1	2.29	71	2.9	90	201	5.7
Mean						77				
SD						17				
RSD		22								
Typical Values										
Turkey Creek		615		54		10		64		4.6
IRL (mouth TC)		700		20		20		40		3