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Aquatic Nuisance Species Research Program

Harmful Algal Bloom Interception, Treatment, and Transformation System, "HABITATS"

Pilot Research Study Phase I- Summer 2019

Martin Page, Bruce MacAllister, Angela Urban, Chris Veinotte, Irene MacAllister, Kaytee Pokrzywinski, Jim Riley, Edith Martinez-Guerra, Craig White, Chris Grasso, Al Kennedy, Catherine Thomas, Justin Billing, Andrew Schmidt, Dan Levy, Bill Colona, David Pinelli, and Chandy John

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Final Technical Report (TR)

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Abstract

Nutrient pollution and harmful algal blooms cost the Nation an estimated $1B each year. The U.S. Army Engineer Research and Development Center (ERDC) began research on the Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) project to develop scalable solutions for managing large Harmful Algal Blooms (HABs), with the objective to develop a rapidly deployable system for mitigating large HABs at various design scales. The first year's progress includes: (1) development and deployment of an interception technology that efficiently collects algae at the water surface, (2) validation of high throughput treatment using dissolved air flotation (DAF) technology to clarify algae-laden water, (3) oxidation of the DAF effluent using ozonation for removing microcystin and other potential cyanotoxins, (4) successful permitting with the Florida Department of Environmental Protection for discharging the treated water back to a surface water body at the demonstration site, (5) demonstration of rapid concentration of algae from a natural water source, (6) transformation of concentrated algae from the study site into biocrude oil at bench scale, and (7) development of a scalability analysis model to establish baseline estimates for full scale performance and cost.

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Preface

This study was conducted for the Aquatic Nuisance Species Research Program (ANSRP) via Funding Account Code 96 x 3123; AMSCO Code 008284. The ANSRP is sponsored by Headquarters, U.S. Army Corps of Engineers (HQUSACE) and is assigned to the U.S. Army Engineer Research and Development Center (ERDC) under the purview of the Environmental Laboratory (EL). Dr. Linda Nelson was the ANSRP Program Manager; Dr. Alfred Cofrancesco was Technical Director, Environmental Engineering and Sciences,

The work was performed by the Materials and Structures Branch, of the Facilities Division, U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory (ERDC-CERL). At the time of publication, Ms. Vicki VanBlaricum was Chief of the Materials and Structures Branch; Dr. Christa M. Woodley was Acting Chief of the Facilities Division. The Deputy Director of ERDC-CERL was Dr. Kumar Topudurti and the Director was Dr. Lance D. Hansen.

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

Executive Summary

Nutrient pollution and harmful algal blooms cost the Nation an estimated $1B each year due to their impacts on tourism, health, commerce, and ecosystems. The Water Resources Development Act of 2018 authorized the Engineer Research and Development Center (ERDC) of the U.S. Army Corps of Engineers to perform research to develop scalable solutions for monitoring, preventing, and managing large harmful algal blooms. This report describes the first year's progress of the 3-year HABITATS research project, which is being conducted as part of the Corps' Aquatic Nuisance Species Research Program (ANSRP).

The objective of the HABITATS research project is to develop and demonstrate a scalable capability to remove algae and nutrients from large water bodies while simultaneously stabilizing and recovering resources from the resulting biomass. By the end of the 3-year research project, it is envisioned that a rapidly deployable system for mitigating large harmful algal blooms in an economically viable and sustainable manner will be available for stakeholder adoption and implementation at a variety of design scales.

Harmful Algal Blooms (HABs) can span hundreds of square miles and as such require highly scalable mitigation measures. For mitigating these massive blooms, the ent, and economic feasibility. All three of these challenges are interconnectedkey scalability challenges include process throughput, waste managem. HABITATS addresses the challenges in three complementary steps: interception, treatment, and transformation. In the interception step, algae is collected from the surface of a natural water body using a floating weir skimmer aided by booms that focus the surface algae toward the collection point. In the treatment step, the algae-laden water is clarified by dissolved air flotation (DAF) and then by oxidation, which creates clean water that can be directly returned to the environment, while simultaneously concentrating the algae biomass to minimize the waste stream. In the transformation step, the concentrated algae biomass waste stream is transformed into biocrude fuel and fertilizer via hydrothermal liquefaction to facilitate efficient resource recovery. The innovative coupling of high throughput treatment with a rapid biomass transformation process is a key breakthrough. By simultaneously destroying algal toxins that may be present in the biomass and facilitating resource recovery to reduce waste volumes, energy requirements, and cost, HABITATS provides a potentially scalable approach for mitigating large HAB events.

In July of 2019, key components of the HABITATS system were studied at a pilot test site upstream of Moore Haven Lock and Dam on the west side of Lake Okeechobee in Florida. While the test duration was limited by environmental conditions, several key advancements were made. The DAF process was proven highly effective in both clarifying the water and concentrating the algae, greatly reducing the volume of waste to be managed. The clarified and oxidized water had no measurable toxicity and greatly reduced levels of phosphorous and nitrogen, making it much cleaner and suitable for discharge into the environment. The concentrated algal biomass from the demonstration was then transformed into biocrude fuel stock at Pacific Northwest National Laboratory. In addition to the technical advancements, a few deficiencies in the current design were noted that can readily be corrected before the next demonstration. These include the type of coagulant used in the DAF process and the type of press used for downstream dewatering. The improved system will be fully integrated with hydrothermal liquefaction and validated at pilot scale in Year 2, pending funding.

Using the concepts and data from this study, an initial scalability analysis was performed to highlight potential benefits of HABITATS when deployed at scale. As designed, HABITATS is expected to be able to significantly reduce algae levels when deployed upstream of a spillway, with nearly complete removal of algae achievable for conditions when the algae predominantly floating near the water surface, or when spillway discharge flows are below the capacity of the on-shore modular treatment plant. HABITATS is also projected by the scalability model to be net energy positive for influent algae concentrations above 100 mg/L. In addition to confirming benefits, the scalability model helped to identify priority areas for optimization in future research. These include a need for an efficient capability to bring sub-surface algae in a natural water body up toward the surface prior to skimming, which will improve algae removal levels under a broader range of environmental conditions. The scalability analysis also identified focus areas for reducing power consumption, particularly with respect to the oxidation process.

Key successes of the 2019 pilot study

- *Development and rapid deployment of an interception technology designed for efficient collection of algae at the water surface.* The interception system consists of booms that direct surface solids toward a floating weir skimmer. The interception technology can be deployed quickly upstream of spillways, or potentially towed behind vessels on the open water.

- *Validation of high throughput treatment using DAF technology to clarify algae-laden water*. The DAF unit consistently removed in excess of 95% of the algae from the water, which decreased the total phosphorous, nitrogen, and organic carbon concentrations in the water by greater than 95%, 65%, and 50%, respectively.
- *Oxidation of the DAF effluent using ozonation* at doses sufficient for removing microcystin and other potential cyanotoxins.
- *Successful permitting with the Florida Department of Environmental Protection for discharging the treated water back to a surface water body at the demonstration site*. This included a process for on-site effluent water quality monitoring and toxicity testing.
- *Demonstration of rapid concentration of algae from a natural water source*. The DAF unit yielded biomass concentrations on the order of 2%, showing that it could concentrate the algae (and reduce waste volumes) by a factor of greater than 400 for the conditions tested. The waste stream was further concentrated to 12% using a non-optimized belt press system, and additional concentration should be readily feasible in future work.
- *Transformation of concentrated algae from the study site into biocrude oil at bench scale*. The concentrated biomass from the demonstration site was shipped for processing at bench scale in a hydrothermal liquefaction reactor. While algae quantities and yields were limited due to field conditions, conversion to biocrude was observed and was consistent with yield expectations for the conditions tested.
- *Development of a scalability analysis model* to establish baseline estimates for full scale performance, energy consumption, physical footprint, and cost curves.

Key project challenges in FY19

- Limited quantities of algae were present in the water at the permitted demonstration site, which limited the scope of field testing, particularly with regard to the interception and transformation components.
- Limited scalability data for hydrothermal liquefaction, which is a newer technology that was only tested at bench scale in FY19.
- The need for further optimization of DAF and biomass dewatering to increase compatibility with the hydrothermal liquefaction technology and achieve higher biocrude yields.

Year 1 conclusions and recommendations for FY20 research

After the first year of the research project, the data and scalability analyses indicate that the HABITATS approach offers great promise. However, further optimization and extended pilot scale validation studies are required before a truly scalable solution can be recommended for deployment. The following research tasks are recommended:

- Develop an efficient, environmentally-friendly capability to float subsurface algae up to the surface in a natural water body such that it can be efficiently harvested. This will increase the environmental benefits by removing a greater fraction of algae from the water body and increasing the efficiency of the HABITATS process by pre-concentrating the algae.
- Develop a shipboard HABITATS capability to treat HABs out on the open water while they are forming. This will increase deployability for dynamic bloom formation events and potentially limit bloom progression.
- Modify the DAF process to use naturally-derived, organic coagulants instead of inorganic coagulants in order to increase biocrude yields from the downstream hydrothermal liquefaction process.
- Improve the throughput of post-DAF biomass dewatering to enhance scalability by using a screw press instead of a belt press.
- Execute an extended pilot study, to include a pilot scale hydrothermal liquefaction unit at a field site during an HAB event. The baseline testing of the component technologies in FY19 was a good step, and based on these results, longer term pilot studies with an optimized system are recommended.

1 Introduction

1.1 Harmful Algal Bloom impacts on the Nation

Harmful Algal Blooms (HABs) are overgrowths of algae in natural water bodies that negatively impact the environment and the economy. The combination of nutrient pollution and HABs threatens national water supplies and costs $1B per year in tourism and other commercial revenues (USEPA 2019). Awareness of the impacts of HABs has been increasing in recent years, in part due to massive blooms that have formed on multiple occasions in Lake Erie and Lake Okeechobee over the past decade. From 1980 to 2015, the United States reported 620 HAB events to the Harmful Algal Events Dataset, which was the second highest number of reported HAB events reported by country (Sanseverino et al. 2016). Nutrient pollution typically originates from diffuse sources and, given favorable environmental conditions (temperature, nutrient levels, sunlight, stagnation, and other factors), can trigger massive HAB events.

HABs occur naturally all over the world (Kim et al 2008), but with increases in anthropogenic eutrophication, blooms have been occurring more frequently, lasting longer, and expanding geographically (Glibert et al. 2008, Anderson et al. 2012, Mehrubeoglu et al. 2013). Although nutrient changes are believed to contribute to the proliferation of freshwater HAB events like cyanobacteria HABs (cyanoHABs), the precise climatic and water quality conditions that trigger blooms are not well understood. Additionally, the limited ability to predict these events, at both small and large scales, makes them difficult to manage, and can lead to devastating consequences to water quality and detrimental economic impacts.

The reauthorization of Harmful Algal Bloom and Hypoxia Research and Control Act (HABHRCA) in 2014 acknowledged that freshwater HABs and the need for HAB research are a high-priority national issue. Federal policy is that HABs are one of the “most scientifically complex and economically damaging aquatic issues” that poses a “significant challenge to the ability to safeguard the health of the Nation’s coastal and freshwater ecosystems” (NSTC 2016). A summary of the impact of HABs on U.S. Army Corps of Engineers (USACE) operations from indicated a substantial increase in the number of HAB occurrences experienced by districts from 2004-2017, largely dominated by cyanobacteria (Clyde 2019). On average 19% (44 out of 237) of projects managed by the 14 districts that participated in the 2014 survey experienced HABs annually (typically composed of cyanobacteria) with an average of three cyanoHAB events per year.

The most common group of bloom forming algae in freshwater systems are the cyanobacteria (blue-green algae) (Paerl et al. 2001). In the United States, as of 2007, cyanobacteria/toxins have been documented in 43 of the 48 continental states (Erickson 2016, Loftin et al. 2015). Furthermore, the economic impacts of freshwater HABs, like cyanoHABs, have not been well documented but are believed to be substantial (NSTC 2016). Consequently, the mitigation of cyanoHABs has long been a priority among researchers and resource managers. This research has led to the increased knowledge of cyanobacteria growth and bloom dynamics, yet these algae can still cause significant damage to the environment, and pose a risk to human and ecosystem health (NSTC 2016).

Cyanobacteria blooms are of concern in part because they can impede activities such as swimming and fishing, cause odor problems and cause hypoxic/anoxic zones during bloom demise, but the primary concern is linked to their production of highly potent toxins (Graham et al. 2010). Collectively, cyanobacteria produce more than 60 different toxins (cyanotoxins), which include neurotoxins, hepatoxins, cytotoxins, gastrointestinal toxins, and skin irritants (Kutser et al. 2006). According to the U.S. Environmental Protection Agency (USEPA) the most commonly occurring HAB forming genera of cyanobacteria include *Microcystis*, *Anabaena* and *Planktothrix* (*Oscillatoria*). Each of these groups is known to produce toxins; the most commonly observed cyanotoxins in the United States include microcystins, cylindrospermopsin, anatoxins and saxitoxins. Cyanotoxins have been implicated in human and animal illness and death in over 50 countries worldwide, including at least 35 U.S. states (Graham et al. 2010). Toxin production and other effects, including resulting hypoxia, lead to beach and waterway closures that have significant impacts on tourism and local economies.

Cyanobacteria are of concern for USACE, which manages nearly 400 freshwater inland waterways that fulfill a variety of services including flood control, energy production, and navigation as well as recreation, fish and wildlife management and potable water supplies that are covered by the Clean Water Act (Brooks et al. 2015). Additionally, cyanoHABs have been documented as a significant problem in USACE managed waterways where many district managers have reported negative impacts such as fish kills and waterway closures (Herman et al. [in review], Linkov et al. 2008). In addition to USACE Districts, the Great Lakes have become plagued with HABs annually. Most notably are blooms occurring in the Western Lake Erie Basin (WLEB), which can span weeks to months. For example, in 2014 a toxic cyanobacteria, *Microcystis* sp., bloom that occurred near the city of Toledo contaminated drinking water for over 500,000 people, cost over $4M to overcome, and caused an estimated $65M in economic losses (Brooks et al. 2015, GAO 2016). Furthermore, the issue of cyanoHABs is expected to grow as climate change scenarios predict that in the coming years, rivers, lakes and reservoirs will experience heightened conditions that favor cyanobacteria productivity (Paerl 2014).

1.2 Capability development requirement

Currently available technologies for HAB mitigation are not practical at large scales. However, with further research, it may be possible to reduce the impacts of large HAB events with early intervention and high throughput treatment in key locations. If a mitigation approach could be developed that was more practical in terms of costs, manpower, and logistics, it would provide an important tool to communities for HAB control that could complement longer term programs focused on prevention.

To help in addressing this important capability gap, the Water Resources Development Act of 2018 included language authorizing the Aquatic Nuisance Species Research Program (ANSRP) of the U.S. Army Corps of Engineers to perform research to accelerate the development of scalable capabilities for reducing the occurrence and effects of HABs.

> SEC. 140. HARMFUL ALGAL BLOOM TECHNOLOGY DEMONSTRATION.
> (a) IN GENERAL.—The Secretary, acting through the Engineer Research and Development Center of the Chief of Engineers, shall implement a 5-year harmful algal bloom technology development demonstration under the Aquatic Nuisance Research Program. To the extent practicable, the Corps of Engineers shall support research that will identify and develop improved strategies for early detection, prevention, and management techniques and procedures to reduce the occurrence and effects of harmful algal blooms in the Nation's water resources.
> (b) SCALABILITY REQUIREMENT.—The Secretary shall ensure that technologies identified, tested, and deployed under the harmful algal bloom program technology development demonstration have the ability to scale up to meet the needs of harmful-algal-bloom-related events.

1.3 Current HAB prevention and mitigation methods

The development of a scalable HAB mitigation method does not negate the need for ongoing programs to reduce nutrients in the environment or mitigate blooms at small scales. A scalable mitigation approach, however, needs to build beyond these existing capabilities, particularly with respect to removing nutrients from the environment and recovering resources in the process of HAB mitigation.

1.3.1 Nutrient control

Nutrient control at the source or at strategic locations in a watershed could help prevent large HABs from forming since HABs are fueled (and limited) by nutrient levels, among other environmental factors. Limiting total nitrogen and phosphorous, as well as specific forms of these nutrients, could have beneficial effects. This can be achieved by establishing riparian buffers or other storm water controls between nutrient sources and surface water bodies, and by increasing the efficiency of nutrient application to limit fate and transport into the broader environment. Cover crops and other agricultural strategies have an important role to play in many cases. Systems that recover nutrients directly from the water, such as adsorbents, could also play a role. Sediment removal may also have some benefits in lakes with historically high nutrient loads. Infrastructure improvements, such conversion of septic systems to on-site or centralized wastewater treatment systems with nutrient control can also provide benefits in some watersheds. Overall, nutrient control strategies are critical for HAB prevention. However, their implementation at large scales can be a challenge due to a variety of competing interests and economic factors. A more immediate nutrient control strategy might include the use of nutrient inactivants, which are chemicals that can sequester nutrients in open water bodies and reduce their bioavailability.

1.3.2 Chemical methods for HAB mitigation

Chemical control strategies are the most studied of all mitigation strategies. For large bloom events, chemical management strategies are traditionally ineffective due to the cost associated with using chemical techniques, potential environmental impacts, and the temporary nature of the mitigation effort. Chemical control of cyanobacteria can provide short-term temporary relief from the devastating impacts of cyanoHAB events. There are several algaecide products registered by the U.S. Environmental

Protection Agency (USEPA) for use in aquatic environments, including copper-based products, peroxide-based products, and endothall. Of the registered algaecides, copper-based products are the most widely used, but peroxide-based products are becoming increasingly more common, as peroxide products are known to have a rapid decay and are not believed to build-up in the sediments or accumulate in higher trophic level organisms. Limitations of chemical methods include their temporary impact, potential environmental collateral damage, and inability to remove the nutrients that cause the problem.

1.3.3 Physical methods

Before the HABITATS project, physical methods promoted for removal of algae from the environment included suction surface skimmers, dissolved air flotation (DAF) systems, pump and treat adsorption systems, and even air bubble curtains for partial containment. Sediment inactivation or removal, water column aeration/oxygenation, or water circulation in lakes may also have some benefits. While potentially helpful at small scales, such as marinas or small lakes, none of these methods incorporates a solution for dealing with the resultant potentially toxic, concentrated algal biomass once removed. Mass transfer and cost effectiveness at large scales is also a barrier. However, the potential benefits of nutrient and algal toxin removal make physical methods a relatively attractive approach.

1.3.4 Biological methods

The use of biological competitors, inhibitors, or predators to control HABs is being studied. Some companies are marketing microbe-based bioaugmentation formulations to outcompete the algae for nutrients. Other creative ideas, such as the use of specific strains of bacteriophage or gene silencing molecules that can selectively suppress cyanobacteria, are being studied. In general, biological approaches may present risks in terms of potential secondary environmental impacts, and at large scales, mass transfer limitations can present a significant challenge.

1.4 HABITATS project overview

1.4.1 Research objective and vision

The HABITATS research objective is to develop and demonstrate a scalable capability to remove algae and nutrients from large water bodies while simultaneously stabilizing and recovering resources from the resulting biomass. By the end of the 3-year research project, it is envisioned that a rapidly deployable system for mitigating large HABs in an economically viable and sustainable manner will be available to stakeholders for adoption and implementation at a variety of design scales.

1.4.2 Technical approach

The key challenges for large scale HAB mitigation include process throughput, waste management, and economic feasibility. All three of these challenges are interconnected. HABITATS integrates several high throughput technologies that have been used for other applications before this study, but their integration for large scale HAB mitigation is novel and requires optimization research. The greatest advancement of the HABITATS approach is the coupling of treatment with a rapid transformation process to efficiently manage the waste stream of concentrated algae, simultaneously destroying algal toxins that may be present and allowing resource recovery to reduce waste volumes, energy requirements, and cost.

The HABITATS project has three key steps (Figure 1-1). In the Interception step, it uses skimming technology to selectively focus and remove algae near the water surface. In the Treatment step, it uses physical clarification processes that separate the algae from the water, resulting in a concentrated algae stream and a clean water stream. The clean water stream receives additional oxidative treatment to ensure removal of toxins before returning the water back into the environment.

Figure 1-1. Overview of the three key steps in the HABITATS approach for intercepting, treating, and transforming algae-laden waters.

In the Transformation step, the concentrated algae is destroyed and converted to useful byproducts using a process called hydrothermal liquefaction (HTL). HTL is an emerging technology that uses high temperature and pressure to break down the algae, toxins, and other organic compounds and convert them into benign products such as hydrocarbons and nutrients that can be used for fuel and fertilizer, respectively. Appendix A includes a summary of the field demonstration.

1.4.2.1 Interception

A boom skimmer system based on previous work in cleaning up oil spills was modified for concentrating and removing algae from large natural water bodies. In planning the first phase of the HABITATS demonstration study, two options were considered for the interception step. The first was an 'active' shipboard approach, in which a barge-mounted harvesting system would be towed out on the lake to collect and concentrate algae, and then bring the concentrated biomass onto shore. The second interception approach considered was a 'passive' approach in which booms and skimmers are deployed in a fixed position upstream of spillways to facilitate removal of the algae near the water surface as the water flows past. For a variety of reasons, including lake size, uncertain permitting processes, and research resource considerations, the passive approach was elected. One additional advantage of the passive approach for interception is that it leverages the energy in the water system for algae interception when the spillway is operating. One disadvantage of the fixed interceptor approach is that it requires prediction of where the algae bloom will occur, as well as spillway discharge operations, both of which depend on variable weather patterns.

1.4.2.2 Treatment

For treatment, a key goal was to quickly remove and concentrate the algae into a viscous biomass concentrate, which then makes it a good substrate for the downstream HTL process. DAF has been used successfully with belt press filtration to achieve high levels of algae biomass concentration; AECOM engineering has previously demonstrated the technology for natural algae harvesting. The technical barriers of the DAF approach in the past have included management of the resultant clarified water and the concentrated algae biomass. To facilitate direct discharge of the product water back to the water source, an additional treatment with ozone was applied for destroying potential cyanotoxins in the clarified water stream.

1.4.2.3 Transformation

HTL is a key enabling technology for this project that is used for processing and recovering resources from the highly concentrated algal biomass. Compared to conventional solids treatment systems, like anaerobic digesters, HTL is much faster, making it much more scalable in terms of physical footprint. A typical retention time of an anaerobic digester is about 15-30 days. For HTL, it is about 30 minutes. Remarkably, it can take concentrated organic waste streams from a variety of sources (not just high lipid sources) and create hydrocarbons. It is a brute force method, applying high heat and temperature to drive the water into a sub-critical state, reacting and catalyzing with the organics to transform them in to molecules with high energy content that can be used for fuel. While it is energy intensive, with the proper feed concentration, the process can generate up to two times the energy, making it net energy positive. About 10% of the original biomass volume will be converted to biocrude at about 30-40% energy yield. Importantly, it can treat wet waste streams, eliminating feedstock drying costs. The biocrude can be upgraded to usable fuel through hydrotreating.

1.4.3 Metrics

This research effort inherently requires developing metrics for scalability. Supporting metrics have also been developed based on the HABITATS component technologies and key integration points (Table 1-1). For the first phase of the study, metrics were developed using the case study described in the section 1.5 as a model scenario.

Table 1-1. Scalability metrics for the HABITATS project for a hypothetical system deployed upstream of a spillway.

Attribute	Pilot Scale Metric(s)	Full Scale Metric(s)
Interception	100 gpm	200 cfs
Treatment	100 gpm Cyanotoxin < 1 ppb 50% nutrient removal Algae biomass > 15%	200 cfs Cyanotoxin < 1 ppb 50% nutrient removal Algae biomass > 15%
Transformation	Cyanotoxin destruction 30% oil yield	Cyanotoxin destruction 30% oil yield
Total Algae Removal (from waterway)	Not Applicable (NA)	To be determined
Size/Footprint	NA	200 yd x 200 yd
Energy Consumption	NA	< 1 Wh/gal
Annual Cost	NA	To be determined

The metrics for full scale operations are theoretical at this point and are expected to evolve as additional information is gathered during the study.

- The interception metric for the full scale system envisioned in this study is 200 cubic feet per second (cfs), which represents 5%-10% of the total canal flow for spillway operations during flood control conditions at the Moore Haven site. The interception system is targeted to the water surface where algae tends to be concentrated, particularly during intense bloom conditions, allowing a greater fraction of algae to be removed. For the case of a 2000 cfs discharge, with a 12.5-ft channel depth, the interception metric would equate to the top 1.25 ft of the water column. During periods of lower discharge flow, a greater fraction of the water column could be treated, if significant amounts of algae were present at lower depths.
- The treatment metrics were developed with respect to the desired water quality improvement during the on-shore treatment process. Algae removal, nutrient reductions, and water clarity improvements are expected and required features of the system. The destruction of any microcystin to less than 1 ppb in the product water is also targeted.
- The transformation metrics were developed based on review papers of HTL performance with algae feedstocks (Gollakota et al. 2018). Many of the previous studies of HTL are performed in well controlled environments such as biofuel production facilities or wastewater plants, whereas the present study is in a natural, uncontrolled water source.
- The total algae removal metric is based on the objective to have a significant impact on the water quality in the water body and to remove as much algae as practical. Actual performance will be dependent on the algae distribution in the water column. The HABITATS process is designed for intense bloom scenarios in which algal films are forming at the water surface. In most scenarios, it would not be advisable to treat the whole water column due to high costs and environmental impacts. Targeting the section of the water column where algae tends to concentrate is therefore the current approach.
- The size (or physical footprint) metric will be site specific. The metric shown relates to open area upstream of a spillway at the demonstration test site in the present study.
- The energy consumption metric of 1 Wh/gal is based on typical energy requirements for municipal wastewater treatment processes. While the HABITATS processes are fairly energy intensive (DAF, ozone, and HTL), particularly at small design scales, it is possible that the energy recovery in the form of biocrude could offset these demands and potentially even achieve energy neutrality.

- A cost metric was not developed, though cost minimization is a key objective of the optimization process. Historical costs of large scale HAB events of up to $60M per event have been reported due to economic impacts on tourism, real estate, healthcare, commercial fishing, and disposal of deceased animals. As another costing reference point, the Everglades Agricultural Area (EAA) reservoir project, which is being built to absorb 120 billion gallons per year of discharge from Lake Okeechobee, has an estimated total cost of $2B, which would equate to $67M/yr over a 30-yr period. It includes a stormwater treatment area (STA) to help control contaminants in coordination with other existing STAs that represent additional sunk costs.

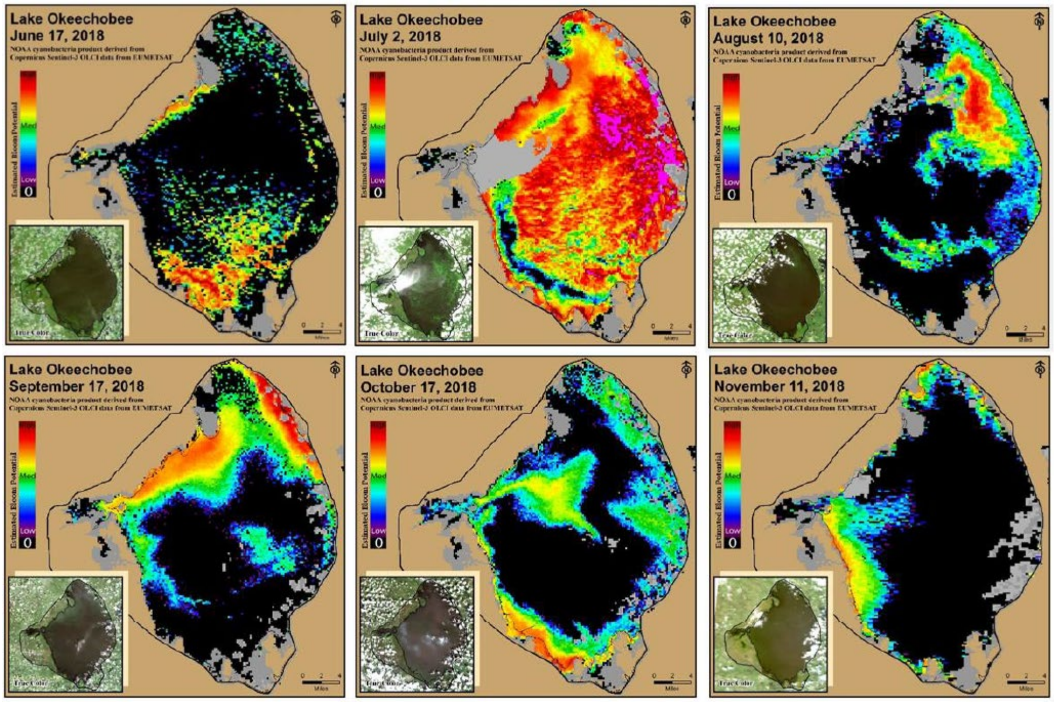
1.5 Case study – Lake Okeechobee

In recent years, particularly intense, large algal blooms have occurred in Lake Okeechobee in southern Florida. In the summers of 2016 and 2018, more than 600 square miles of the lake contained high levels of cyanobacteria. The drivers of bloom formation are complex, but their increasing frequency is likely associated with high nutrient loadings into the water bodies combined with climate and ecological conditions favorable to algae growth. The phosphorous rich sediment in the lake may be another enabling factor. During recent bloom events, there were multiple reports of cyanobacteria toxins such as microcystin being detected in the lake and downstream water bodies.

Lake Okeechobee is a vast, shallow lake with a surface area of about 740 square miles. It plays an important role in natural water flow and contaminant attenuation in the region, and it is also a popular recreational destination and local drinking water source. As part of a broader flood risk management strategy in the region, the lake water levels are carefully controlled. When lake levels get too high, large quantities of water must be discharged downstream. Cyanobacteria bloom formation often occurs during the summer rainy season, at times when the lake has historically needed to discharge water for flood control purposes (Figure 1-2). As such, the lake provides an important case study for the development of HAB mitigation tools. If a scalable method for HAB control could be developed, it may be useful controlling these intense blooms.

Prevention of algal blooms at Lake Okeechobee will likely remain a challenge, as they are fed by diffuse sources of nutrients and sediment. Shovel ready solutions for mitigating the blooms at scale, which can span hundreds of square miles, are also lacking. In responding to regional HAB events, some companies have performed local algae cleanup using skimming technology, but management of the large quantities of potentially toxic biomass waste was a major barrier. Other efforts have focused on destroying algal blooms and toxins using chemicals, but those approaches are not scalable and do not remove the nutrient load from the environment. Furthermore, they can be challenged by high concentrations of organics that can consume the oxidants, resulting in conditions that require more materials and/or energy. For cases such as Lake Okeechobee, which are complex, dynamic, and large in scale, it is important to develop a variety of tools for prevention and mitigation.

Figure 1-2. Dynamics of algae bloom formation on Lake Okeechobee from June-November 2018. The red areas of the heat map indicate high density algae (> 10^6 cells/ml).



2 Materials and Methods

2.1 Water sources for demonstration testing

For reasons described in the previous chapter, the primary case study for the HABITATS demonstration was Lake Okeechobee. Recent years' experience led researchers to the expectation that water from Lake Okeechobee would contain high levels of cyanobacteria. Based on this assumption, a permit was filed with the Florida Department of Environmental Protection (FDEP) to perform a technology demonstration at a specific site near Lake Okeechobee, upstream of one of the primary discharge spillways in Moore Haven, FL. In the summer of 2019, however, the levels of algae in Lake Okeechobee were relatively subdued. Due to a low amount of algae available for challenge testing during the demonstration period, a second water source (Newnans Lake) was used to provide water quality that was representative of cyanobacteria bloom conditions and that would better challenge the HABITATS process (Figure 2-1). Because the permit for the HABITATS project was specific to the site near Lake Okeechobee, the source water from Newnans Lake was transported to the Moore Haven site for on-shore testing of the treatment process.

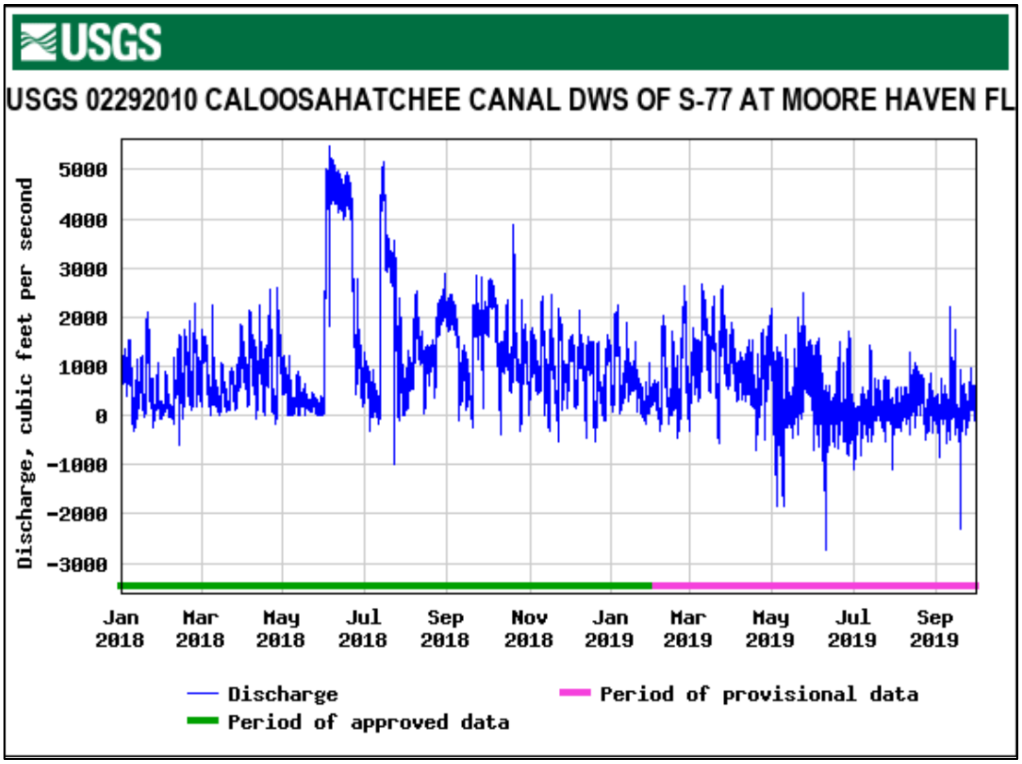
Figure 2-1. Locations of the lake water sources used in the HABITATS research demonstration.

2.1.1 Moore Haven Lock and Dam- Lake Okeechobee

The demonstration was conducted along the shoreline to the northeast of Moore Haven Lock and Dam, located on the west side of Lake Okeechobee at the junction with the Caloosahatchee River (Figure 2-2). The Moore Haven Lock and Dam facility was constructed in 1935 for navigation and flood control purposes. Today it also serves as a recreational gateway to Lake Okeechobee and as a point of discharge (see Figure 2-3) from the lake for flood risk control purposes.

Figure 2-2. Location of the HABITATS demonstration testing site.

Figure 2-3. Examples of discharges from Lake Okeechobee via Moore Haven Spillway (S-77) based on data from a U.S. Geological Survey (USGS) gage station 02292010.



Source: USGS (2019)

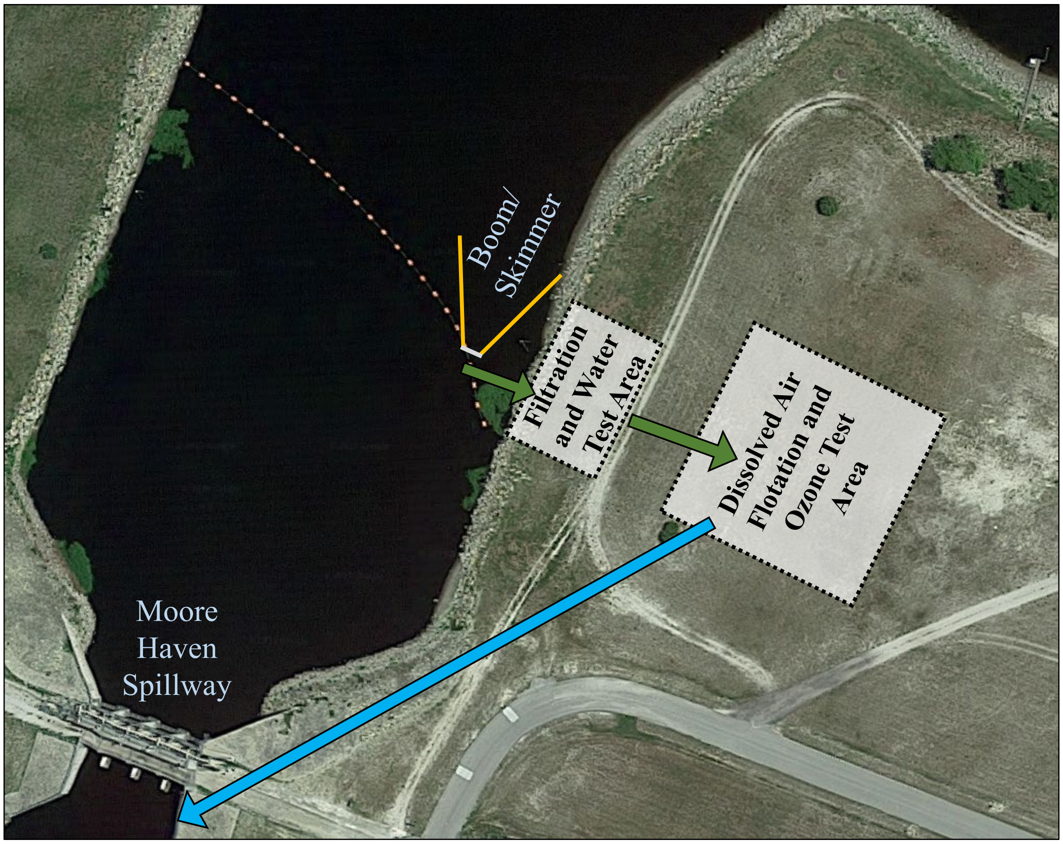
2.1.2 Algae-laden ‘green water’ from Newnans Lake

Newnan’s Lake near Gainesville, Florida was used as an alternate source of algae-laden water. Newnans Lake water was collected in 5,000-gallon tanker trucks at the boat ramp on the southwest side of the lake and transported to the Moore Haven test site and processed within 24 hrs of collection. Samples for water quality analysis and species identification were taken at the point of withdrawal, and subsequently at the Moore Haven site before processing. These samples were analyzed to confirm the absence of any toxins or toxin-generating algal species before the testing at Moore Haven.

2.2 Technology demonstration testing site

The HABITATS technology demonstration testing site was located 200 ft upstream of the Moore Haven spillway (S-77), on the shore at Alvin Ward Park. Water was collected from the canal upstream of the spillway or supplied via tanker trucks from Newnans Lake, and treated on site following permitted protocols. As required by FDEP all treated water was stored on site to confirm treatment efficacy, and then discharged downstream of the spillway into the C-43 canal, a Class III F surface water (Figure 2-4).

Figure 2-4. Pilot Demonstration Site Layout & Temporary Outfall S-77 Moore Haven Lock and Spillway, 1754 Alvin Ward Road.

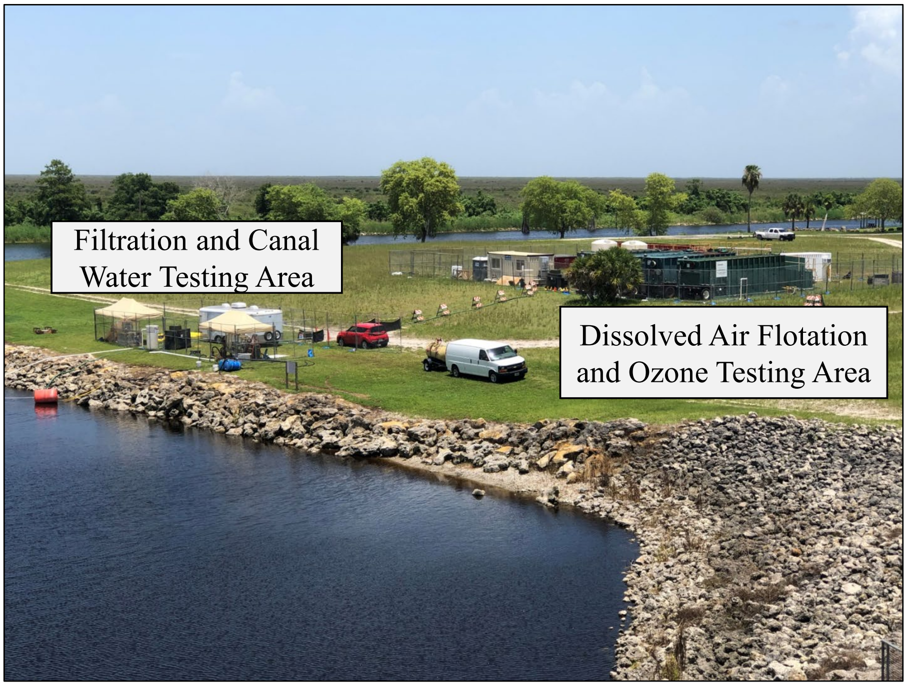


Moore Haven, Florida 33471
Site Location - Lat 26°50’23.35” Long -81°05’02.87”
Outfall Location - Lat 26°50’20.76” Long -81°05’07.36”

Figure 2-5 shows a photograph of water treatment testing area, taken from the top of the spillway. The two on-shore treatment areas were each enclosed in chain link fencing. Above-ground hoses and tanks were used for all water transfer and storage.

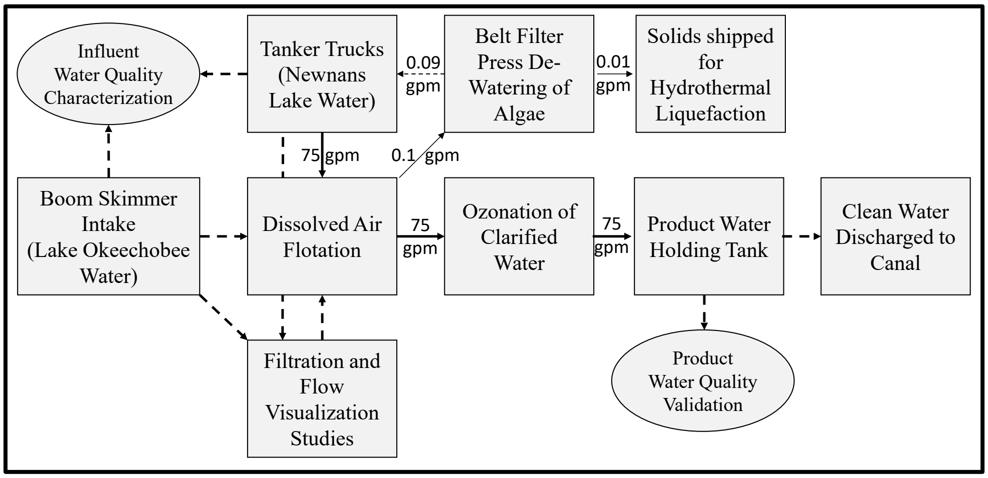
The testing area closest to the shore was used for filtration and canal water characterization studies. It measured 30 ft x 60 ft and was used for testing of pretreatment technologies, described in section 2.7, and to house experimental equipment for canal water characterization. No chemicals were added during testing of any of the pretreatment technologies, and the resulting product and wastewater generated in the pretreatment testing area was sent to a storage tank before being treated by DAF and ozone.

Figure 2-5. View of the HABITATS demonstration testing area, looking north from the top of the Moore Haven spillway.



A larger 100-ft x 130-ft fenced area to the east facilitated testing of the DAF and ozone systems. More than 95% of the water treated in the DAF and ozone systems received no pretreatment. Water was pumped to the DAF unit for clarification. Clarified water was pumped to the ozonation system and then stored on site until verification of water quality before discharge downstream of the spillway. Figure 2-6 provides an overview of the water flow paths for the demonstration test site.

Figure 2-6. Overview of the water flow paths for the demonstration test site. Solid arrows represent the primary flow paths for the demonstration test. Dashed lines represent intermittent flows for research or compliance purposes.



2.3 Water quality test methods

Water quality improvement was a primary focus of the 2019 HABITATS demonstration. Water quality testing was critical to support the concept of a deployable system that can remove water from the environment, clean the water, and return it back to the environment. To this end, the water quality of the influent source water and the treated product water were carefully assessed.

2.3.1 Whole effluent toxicity testing

The U.S. Army Engineer Research and Development Center (ERDC) conducted standard whole effluent toxicity testing (WETT) associated with National Pollution Discharge and Elimination System (NPDES) requirements on product water samples collected during a field demonstration for algae control. A 20-gallon sample of effluent was collected during the middle of the demonstration from an on-site effluent storage tank that contained 5000 gallons of product water.

For ecological hazard testing in compliance with the permitting process of the FDEP, a fresh water hazard assessment of the product water solution was performed using both a cladoceran and a fish species. Acute and chronic toxicity tests were performed with each water sample and prescribed dilutions thereof, and results were compared closely with negative controls. The cladoceran species tested was *Cerciodaphnia dubia* and the fish species was *Pimephales promelas*. *C. dubia* was selected as a more suitable test species because it is expected to be more sensitive, it requires less water volume, and its associated test chronic test method is shorter relative to *Daphnia magna*. For *C. dubia*, acute toxicity assays were performed according methods described in EPA-821-R-02-012 and OECD[*] 202, and chronic toxicity assays were performed in according to EPA-821-R-02-013 and EPA 1002.0. For *P. promelas,* acute toxicity assays were performed according to methods described in EPA-821-R-02-012 and OECD 203, and chronic toxicity assays were performed in according to EPA-821-R-02-013 and EPA 1000.0.

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[*] Organization for Economic Co-operation and Development (OECD)

2.3.2 Grab samples for treatment performance analysis

ERDC set up a field laboratory to facilitate grab sample analyses that were used to assess treatment performance. These analyses were focused on parameters of relevance to HABs, including nutrients, total organics, and solids concentrations. Influent and effluent grab samples, as well as samples from critical control points in the treatment process, were collected daily and analyzed by ERDC researchers within 4 hrs of sample collection. Total Nitrogen and Total Phosphorus were evaluated using commercially available kits (Persulfate Digestion Hach Method 10208 and 10209/10210, respectively). Kits with the appropriate selective range were used depending on the anticipated nitrogen or phosphorus concentration thought to be present in the sample water. Chemical oxygen demand (COD) was determined using the USEPA compliant Hach Method 8000. A field pH meter was used to measure the pH of the sample. Turbidity, total suspended solids (TSS) and volatile suspended solids (VSS) were determined using standard methods. In addition to the field lab measurements, samples were shipped to an independent commercial lab for total nitrogen, total phosphorous, biochemical oxygen demand, TSS, and aluminum using standard methods for water and wastewater analysis (APHA 2012).

2.3.3 *In situ* measurement methods

In situ source water chemistry was assessed using a ProDSS handheld multi-parameter water quality meter (YSI Inc., Yellow Springs, OH) equipped with optical dissolved oxygen, conductivity/temperature, and total algae sensors. Water quality information was collected from each location. The following parameters relevant to this study were collected including: temperature (°C), specific conductance (SPC) (μScm^{-1}), Chlorophyll *a* (μg/L), phycocyanin (μg/L), and optical dissolved oxygen (DO) (mg/L). Data were retrieved using the software KorDSS v 1.6.6.0 (YSI Inc.) and exported to Prism8 v 7.04 (GraphPad, San Diego, CA) for analysis.

A CyanoFluor Handheld HAB Indicator (Turner Designs Inc., San Jose, CA) was used to determine the relative *in vivo* fluorescence of Chlorophyll *a* (Chl *a*) and phycocyanin (PC). For each sample, a 0.2 μm filtrate blank was used to correct for interference from dissolved organic matter (DOM). Three milliliters of raw sample were added to each cuvette and read on the CyanoFluor according to manufacturer's instructions. For each sample, the raw relative fluorescence unit (RFU) of Chl *a* and PC, along with the PC to Chl *a* ratio, were recorded.

2.3.3.1 Chlorophyll and phycocyanin

Chlorophyll pigments were extracted according to USEPA method 546 in 90% acetone. Briefly, samples were filtered onto glass microfiber filters type C (GF/C) pore size 1.2 µm (Whatman, Maidstone, UK) and stored in the dark at -20 °C until pigment extraction. Filters were then homogenized by bead beating using 0.1 mm silica beads at 4.5 m/s (~500 rpm) for 1 minute using a Fast Prep 24 Homogenizer (MP Biomedicals LLC, Santa Ana, CA). After homogenization, the filter/bead slurry and all of the suspension were transferred to a larger vessel where additional extraction buffer was added (10 mL total extraction volume). Samples were allowed to steep overnight at 4 °C in the dark to enhance extraction. Samples were then centrifuged at 1,000 xg for 5 min and the supernatant was transferred to a new scintillation vial for spectrophotometric detection. Absorbance (Abs) was measured on a UV-Vis 1800 spectrophotometer (Shimadzu, Kyoto, Japan) at 750 nm (turbidity), 664 nm (Chl *a*), 647 nm (Chl *b*), and 630 nm (Chl *c1* + *c2*) before acidification to 0.001N hydrogen chloride (HCL) for corrected Chl *a* determination. After acidification absorbance was re-read at 750 nm and 665 nm. For both raw and corrected determinations, the appropriate absorbance at 750 nm was subtracted from each pigment absorbance value. Raw and corrected Chl (mg/L) were determined using the following equations.

Uncorrected

$$[\text{Chl } a] = 11.85\ (\text{Abs } 664) - 1.54\ (\text{Abs } 647) -.08\ (\text{Abs } 630)$$

$$[\text{Chl } b] = 21.03\ (\text{Abs } 647) - 5.43\ (\text{Abs } 664) - 2.66\ (\text{Abs } 630)$$

$$[\text{Chl } c] = 24.52\ (\text{Abs } 630) - 7.60\ (\text{Abs } 647) - 1.67\ (\text{Abs } 664)$$

Corrected

$$[\text{Chl } a] = 26.7(\text{Abs } 664 - \text{Abs } 665\ )$$

$$[\text{Pheophytin } a] = 26.7\ [1.7 \text{ X } (\text{Abs } 665\ ) - (\text{Abs } 664\ )]$$

Total Pigment Concentration (TPC)

$$TPC = \frac{[\text{Chl } a, b \text{ or } c] \text{ X extraction volume (L) X Dilution Factor}}{\text{Sample volume (L) X cuvette cell length (cm)}}$$

Phycocyanin was extracted in much the same way as Chlorophyll a with a different extraction solvent. Rather than using 90% acetone as in the Chlorophyll extraction method, 0.1M sodium phosphate buffer was used. Additionally, absorbance was recorded at 650 nm and 620 nm. Phycocyanin concentration (mg/mL) was determined as follows according to Bennett and Bogorad (1973).

$$PC = \frac{(\text{Abs615} - (0.474 * \text{Abs 652}))}{5.34}$$

2.3.3.2 Molecular methods

Molecular methods were used to help determine if a potentially toxic cyanobacteria bloom was present in the two water sources used in this study. To this end, water samples were filtered onto 0.45 µm (MCE) membranes and preserved at -80 °C until deoxyribonucleic acid (DNA) extraction. Briefly, each filter was homogenized using TRIzol Reagent (Fischer Scientific, Waltham, MA) with sequential freeze thaw cycles in liquid nitrogen. After this, the homogenate was centrifuged and supernatant transferred to a fresh tube. To each field sample, 3M sodium acetate (1/10 total volume) was added, followed by a 2x volume of absolute ethanol to precipitate the DNA. Precipitated DNA was washed twice with 70% ethanol and dissolved in Tris-EDTA (TE) buffer (Fischer Scientific). The genomic DNA concentration was determined using a NanoDrop One microvolume UV-Vis spectrophotometer (Fischer Scientific). For short and long-term storage, extracted DNA was stored at 4 °C and -80 °C, respectively.

To confirm DNA replicability, the extracted DNA template was used in polymerase chain reactions (PCR) with primers targeting the highly conserved broad 16S cyanobacteria rRNA gene, the 16S rRNA gene of the genera *Microcystis, Dolichospermum, Oscillatoria, Nodularia, and Aphanizomenon,* as well as the anatoxin-*a* production gene *anaC.* Product sizes ranged from 205-480 bp. Each PCR was 25 µL and comprised of 100 ng DNA template, 1x Maxima Hot Start *Taq* Master Mix (New England Biolabs, Ipswich, MA), 1.25 µL dimethyl sulfoxide, 0.2 µM forward primer (Table 2-1), 0.2 µM reverse primer (Table 2-1), and PCR-grade water.

Reaction conditions for the 16S Cyanobacteria rRNA gene comprised an initial denaturation at 95 °C for 3 min followed by 45 cycles of 95 °C for 30 s, 53 °C for 30 s, and 72 °C for 1 min, and a single final extension at 72 °C for 5 min.

Table 2-1. Primers used to target the broad cyanobacteria and genus-specific 16S rRNA genes, as well as the anatoxin-a production gene in PCR.

Target	Primer	Sequence
16S rRNA Cyanobacteria	CYA359F	GGGGAATYTTCCGCAATGGG
	CYA781R	GACTACWGGGGTATCTAATCCCWTT
16S rRNA *Microcystis*	micF	ATGTGCCGCGAGGTGAAACCTAAT
	micR	TTACAAYCCAARRRCCTTCCTCCC
16S rRNA *Dolichospermum*	anbF	CCACACTGGGACTGAGACAC
	anbR	TGCATCCTCCGTATTACCGC
16S rRNA *Oscillatoria*	oscLF	AGCTGGTCTGAGAGGACGAT
	oscLR	CGGAGTTAGCCGATGCTGAT
16S rRNA *Nodularia*	nodF	CTGGTGACTGGGGTGAAGTC
	nodR	AGCACTCAGTCTCGAAGCAC
16S rRNA *Aphanizomenon*	aphF	CCACACTGGGACTGAGACAC
	aphR	ACGGCTAGGACTATTGGGGT
anaC	anaCgenF	TCTGGTATTCAGTCCCCTCTAT
	anaCgenR	CCCAATAGCCTGTCATCAA

Reaction conditions for the 16S *Microcystis* rRNA gene were 95 °C for 2 min; 20 cycles of: 95 °C for 30 s, 65 °C for 45 s with a -0.5 °C stepdown per cycle; and 72 °C for 1 min. This was followed by 25 cycles of: 95 °C for 30 s, 55 °C for 45 s, and 72 °C for 1 min; then a one-time extension at 72 °C for 8 min.

Reaction conditions for the 16S rRNA genes of *Dolichospermum, Oscillatoria, Nodularia,* and *Aphanizomenon* comprised 95 °C for 3 min; 40 cycles of: 95 °C for 30 s, 55 °C for 30 s, and 72 °C for 30 s; followed by a final extension of 72 °C for 5 min.

Reaction conditions for the *anaC* gene were as follows: 95 °C for 3 min; 45 cycles of: 95 °C for 30 s, 58 °C for 30 s, and 72 °C for 1 min; followed by a one-time extension of 72 °C for 7 min.

Amplified products were validated via electrophoresis on a 1.5% agarose gel with ethidium bromide in Tris, acetic acid, EDTA (TAE) buffer (100 V, 1 hr). Both 1,000-base pair and 100-base pair ladders were run with the appropriate amplicons, as well as a no template control (NTC).

Total cyanobacterial and toxin presence were further assessed via quantitative PCR (qPCR) using two proprietary CyanoDTec multiplexed primer sets (Phytoxigene, Akron, OH). The total cyanobacteria primer set targeted the 16S rRNA gene and included an internal amplification control. The toxin primer set targeted toxin production genes for microcystin/nodularin, cylindrospermopsin, and saxitoxin. Samples were run with a standard curve of CyanoDTec CyanoNAS nucleic acid standards (Phytoxigene) ranging from 20 to 200,000 copies of target DNA/µL. Both multiplexed primer sets were run under the same reaction conditions, which were as follows: an initial denaturation at 95 °C for 2 min, followed by 40 cycles of 95 °C for 15 s and 60 °C for 30 s.

2.3.3.3 Total and free toxin

Both total and free microcystin were determined using an ADDA-microcystin enzyme-linked immunosorbent assay (ELISA) (Abraxis, Warminster, PA). For total toxin, raw sample was homogenized via bead beating using 0.1 mm silica beads at 4.0 m/s for 1 minute using a Fast Prep 24 Homogenizer. For free toxin, the raw sample was filtered using glass microfiber filters type C (GF/C), pore size 1.2 µm (Whatman, Maidstone, UK). The filtrate was used directly for toxin testing, without any other pre-processing. An aliquot of the filtrate or sample homogenate was then used for the microcystin/nodularin ELISA. Each toxin ELISA was conducted according to USEPA method 546.

2.3.3.4 Microscopic identification and enumeration

Taxonomic identification was determined using conventional microscopic techniques. Briefly, each sample was preserved with 4% formaldehyde and stored at 4 °C until sedimentation. Samples were settled onto counting chambers and then counted.

2.4 Site characterization testing

The water source at Moore Haven spillway, connected to Lake Okeechobee by several canals, was characterized with respect to water quality from May-July 2019. Prior to the demonstration, in June 2019 and early July, 10 sets of samples were collected to characterize the source water quality. During the 2-week demonstration period in July 2019, source water samples were collected and analyzed daily. For the Moore Haven water, samples were primarily withdrawn immediately upstream of the spillway, at depths of 0, 2, 4, and 6 ft, with additional samples taken periodically from the lock channel and a boat ramp area several hundred yards upstream of the spillway (Figure 2-7). Depth samples were collected using a 4-L Van Dorn depth sampler. For the Newnan’s Lake water, samples were taken from a hose connected to the tanker truck once the water was delivered to the Moore Haven site. Water quality parameters were analyzed as described in section 2.3, with a particular focus on algae concentrations, as measured by VSS, relative to TSS, which is a parameter that includes both organic and inorganic particulates.

Figure 2-7. Collection of water using a Van Dorn sampling apparatus to capture water at different depths at the Moore Haven spillway (left) and at a boat ramp upstream of the Moore Haven spillway (right).

2.5 Interception testing

Algae interception testing was performed using a boom and floating weir skimmer. Two 50-ft sections of boom were anchored in a v-shape upstream of the skimmer, with one end of each boom connected near the sides of the skimmer, and the other two ends anchored upstream 50 ft apart (Figure 2-8). The design aimed to focus a 50-ft swath of the surface toward the much narrower skimmer weir inlet.

The stainless steel floating weir skimmer from SkimPak was 4 ft wide, 2 ft long, and 2 ft deep. The floating weir skimmer was ballasted in the water to level the system at the correct depth. The skimmer was rated up to 300 gpm, and the floating weir cut depth was regulated by the rate of flow through the skimmer. The floating weir system contained a 3-hp pump that was encased in the module and pumped the water to shore through a 4-in. rubber hose. The pump was powered by a generator that was positioned on shore.

Figure 2-8. Booms and floating weir skimmer set upstream of the Moore Haven spillway.

To assess skimmer performance, a comparison was made between samples collected upstream and those collected on shore from an equalization (EQ) tank containing water pumped from the skimmer. The sampling events were timed to account for the velocity of water in the canal and retention time within the skimmer collection structure. Surface water samples were collected 200 ft upstream of the skimmer, approximately 150 ft upstream of the boom focusing region.

2.6 Pretreatment testing

Three physical filtration technologies were tested on site for their ability to pre-concentrate algae from the water source. These included two stacked disk filtration systems from SkimPak, which were rated with 5 micron and 200 nm cutoffs, with rated flows of 10 gpm and 5 gpm, respectively; a mechanical self-cleaning screen filter with a 15 micron cutoff; and a ZeeWeed 500 hollow fiber membrane module from Suez, with a 0.04 micron nominal pore size (Figure 2-9).

Figure 2-9. Testing of stacked disk filter (left) and ZeeWeed hollow fiber membranes (middle, right) for algae removal at the Moore Haven demonstration site.

For filter challenge testing, batches of algae-laden water were repeatedly pumped through each filter at the rated filter flow rate. The time for processing each batch was recorded to assess changes in filter flow rate that might occur due to filter fouling by the algae. Each filter was tested through 10 batches of challenge water over the course of about 2 hrs. Midway through each test, samples were taken of the influent, effluent, and filter concentrate to assess water quality impacts and algae concentration performance. Long-term filter performance studies were not conducted due to the limited availability of algae-laden water at the permitted demonstration site.

2.7 Treatment testing

2.7.1 DAF system

A DAF system developed by AECOM (Figure 2-10) for algae harvesting was investigated in this study. The trailer mounted system had a footprint of 12 square yards and a reactor depth of 2 yards.

The DAF system had two chambers. The first chamber was designed to facilitate charge neutralization and flocculation of the algae particles. The coagulant used for surface charge neutralization was aluminum chlorohydrate, dosed at 30-50 mg/L. The second chamber was for flotation, which was achieved by injecting a stream of air-pressurized, recirculated water near the bottom of the chamber. Upon injection of the pressurized water into the chamber, nanoscale bubbles are released into the non-pressurized process water due the sudden drop in pressure. These nanobubbles have high surface area, and the neutralized algae flocs bind to the bubbles and are floated up to the surface.

Figure 2-10. AECOM dissolved air flotation treatment system set up on shore near the Moore Haven spillway.

As the air bubbles release into the atmosphere, a thick slime layer of algae aggregates builds on the surface. A scraper blade periodically harvests the floated, concentrated algae into a hopper. Clarified water was discharged to a holding tank before oxidation. The residence time in the DAF system was 25 minutes for the testing, and the flow rate of incoming water was 75 gpm.

2.7.2 Advanced oxidation system

After DAF treatment, the water was subjected to ozone treatment. Ozone was dosed at a rate of 10 mg/L. This high dosing was required to maintain ozone residual to enable an exposure value of at least 1 mg-min/L, which is sufficient for microtoxin destruction. The ozone was generated using a deployable ozone/hydrogen peroxide unit from HiPOx, Inc. (Figure 2-11). To eliminate the possibility of hydrogen peroxide in the effluent (or the need for on-site chemical quenching), the system was operated in ozone only mode.

Figure 2-11. Containerized ozone advanced oxidation system from HiPOx, Inc. The system is capable of treating with ozone or ozone plus hydrogen peroxide.

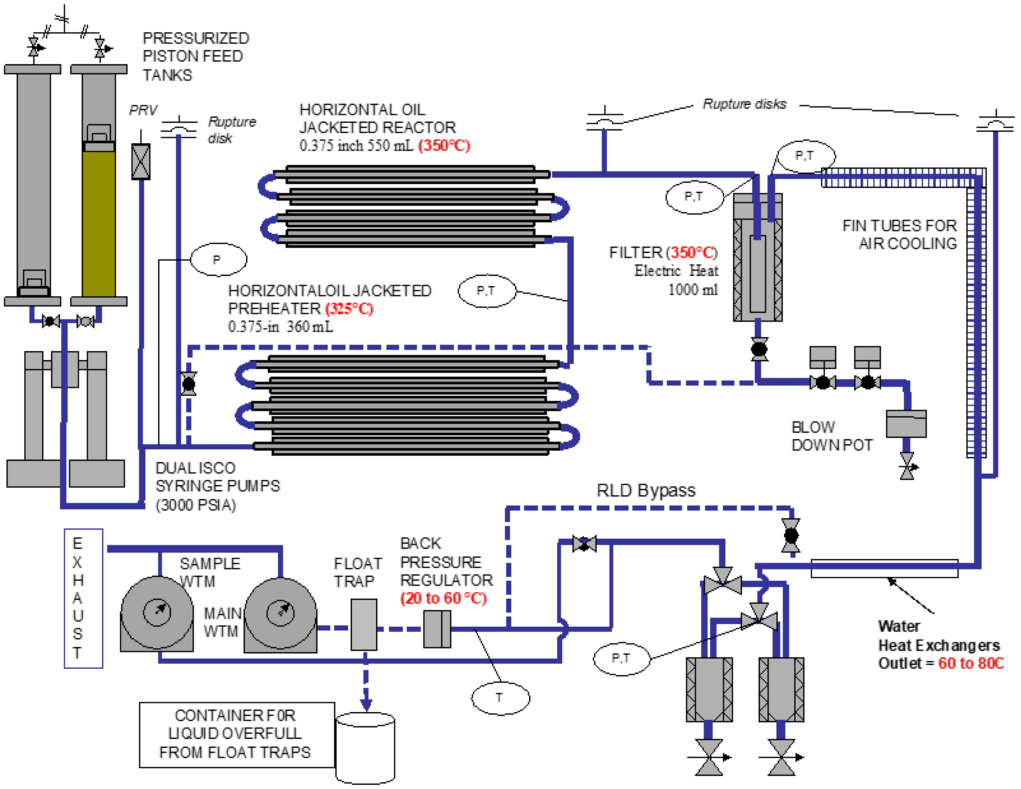
2.8 HTL testing

Hydrothermal Liquefaction testing was performed at bench scale at the Pacific Northwest National Laboratory (PNNL) using concentrated cyanobacteria biomass provided from the HABITATS demonstration site in Moore Haven, Florida. The concentrated algal biomass from the DAF was further dewatered using a belt press. Twelve kilograms of concentrated cyanobacteria at 12.2 wt% solids were shipped to PNNL on July 26, 2019 (Figure 2-12). The viscosity of the solids was atypically high for the mass concentration of algae, potentially due to the high aluminum content. To meet the viscosity requirements of the feed pump for the bench scale HTL reactor, the slurry was diluted to 10% solids and filtered through a 20-mesh screen to remove fibers and seeds prior to hydrothermal processing. Since HTL works best at solids >15%, dilution of the slurry to 10% was a significant setback in terms of biocrude yield potential.

Figure 2-12. Preparation of algal biomass for hydrothermal liquefaction (HTL) testing at the Pacific Northwest National Laboratory (PNNL).

The screened, diluted algae was processed through a continuous flow bench scale HTL system, depicted in the Figure 2-13. The entire batch was passed through in a single run. Influent (algal biomass) and effluent (ash, aqueous, biocrude) streams were characterized for chemical composition and other general parameters.

Figure 2-13. Flow chart for the bench scale hydrothermal liquefaction (HTL) system at the Pacific Northwest National Laboratory (PNNL).



2.9 Post-treatment

Effluent from the HTL reactor contains approximately 1% dissolved organic carbon, as well as high levels of nitrogen, which would need to be treated before discharge. Anaerobic membrane bioreactor technology is being studied for this purpose, as it could recover energy in the form of methane while returning treated water to the headworks of the DAF process at a high volumetric dilution ratio. The post-treatment studies are ongoing at bench scale, and results are not contained in this report.

2.10 Permitting

A 2CS permit was filed with the FDEP on June 2, 2019. The permit was published for public comment and agency review for 45 days before issuance of the permit. The permit application included detailed descriptions of the treatment methods to be used as well as the proposed site operations protocols. Appendix B includes a copy of the issued permit.

2.11 Power monitoring

The on-site electrical generators used in this study were equipped with instantaneous power meters. Power demands in kW were recorded for individual systems (isolated loads) when operating at steady state, and these data were used for calculation of the energy consumption for key components, including the DAF and ozone system, relative to the process flow rate, i.e., Wh/gal. Due to the small scale of the pilot demonstration, the energy efficiency of the treatment systems was non-optimal. As such, published data for larger DAF and ozone treatment systems were considered for scalability analysis.

3 Results

3.1 Demonstration site conditions

3.1.1 Source water suspended solids

A key parameter to assessing the algae harvesting potential of the water samples is the amounts and ratio of TSS and VSS, with the algae comprising the volatile solids. TSS is made up of both inorganic and organic particulates. A high TSS with a low VSS would indicate a water with high amount of inorganic particulate matter, such as sediment or clay. A TSS:VSS ratio of 2 would indicate equal amounts of each, and a TSS:VSS closer to unity would indicate that the sample is comprised primarily of organic particulates, such as algae. The differences between the water from Moore Haven (Lake Okeechobee) and that from Newnans Lake were pronounced (Figure 3-1). The primary difference, of course, was the algae bloom occurring at Newnans Lake. Beyond that, the TSS in Newnans Lake water was four times higher than that in the Moore Haven water, and about 80% of those solids were organic, comprised of algae.

3.1.2 Source water nutrient levels

The nutrient levels in both water sources (i.e., total nitrogen and total phosphorous) were high (Figure 3-2), likely high enough to support bloom formation if the nutrient speciation and supporting environmental factors were suitable. Note that the samples shown in Figure 3-2 were unfiltered, meaning that the nutrients could be in particulate or dissolved form.

Figure 3-1. Comparison of total suspended solids (TSS) and volatile suspended solids (VSS) in water sources from near Lake Okeechobee (Moore Haven) and Newnans Lake (Gainesville).

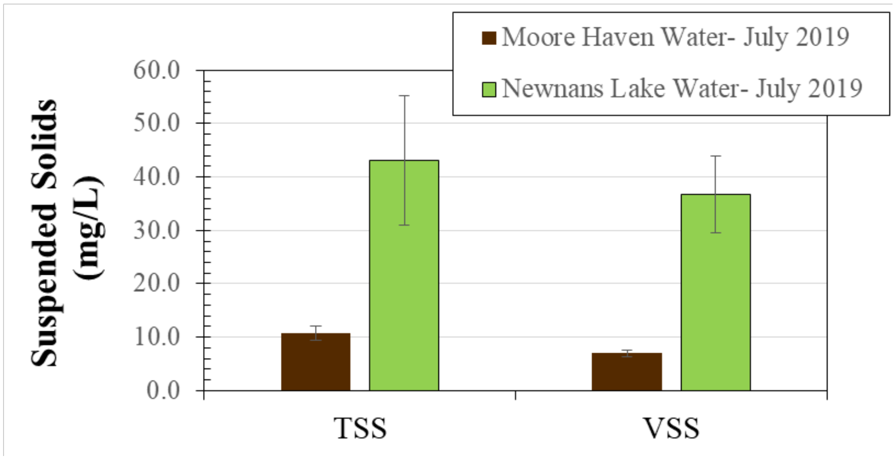
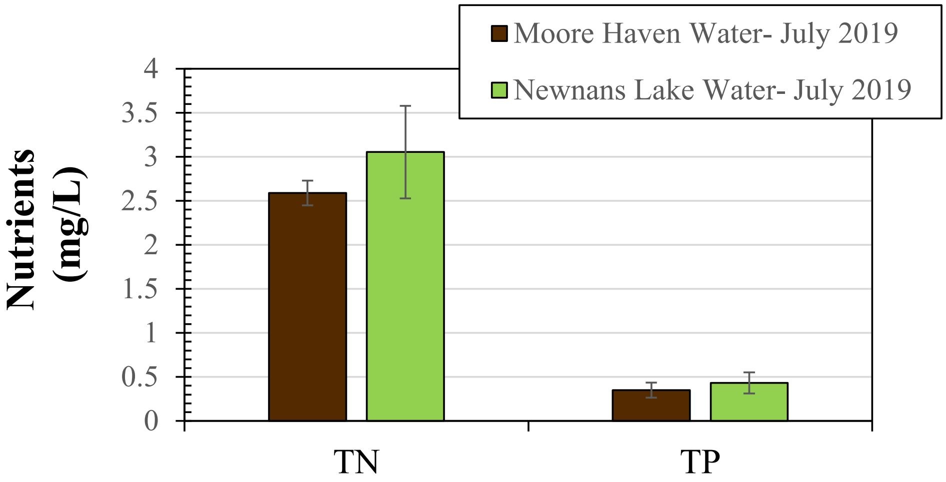


Figure 3-2. Comparison of total nitrogen (TN) and total phosphorous (TP) levels in the two source waters for the HABITATS demonstration project in Florida.



The nutrient analyses were also performed after TSS filtration to assess the level of nutrients present in dissolved form for each sample. The results, shown in Figure 3-3, show some clear differences between the Lake Okeechobee and Newnans Lake water in the case of dissolved nutrients. Despite total nutrient levels being similar, the dissolved nutrient levels in Newnans Lake which had an active algal bloom, were much lower. This indicates that algal blooms can contain a significant fraction of the very same nutrients that cause them. These data support a key hypothesis of the HABITATS approach, which assumes physical removal of the algae will reduce nutrient loads in the water body.

3.1.3 Source water cyanotoxin and microbiology characterization

Because algal blooms can potentially harbor or emit potent toxins, the source waters were monitored carefully for microcystin, a common cyanobacterial toxin in the region, and for cyanobacteria strains with the potential to emit toxins. Microcystin levels were monitored on site using test strips, along with confirmatory analysis of samples in the laboratory. All of the microcystin measurements made in the field, for both the Newnans Lake and Lake Okeechobee source waters, were below the detection limit (1 ppb) of the approved test strip assay. Many of the same samples were analyzed in the laboratory, and the more sensitive ELISA lab methods were completely consistent with the test strip results, with values less than 1 ppb (samples from various water sources shown in Figure 3-4).

Figure 3-3. Comparison of the dissolved nitrogen (TN-F) and dissolved phosphorous (TP-F) levels in the two lake waters considered for challenge testing of HABITATS.

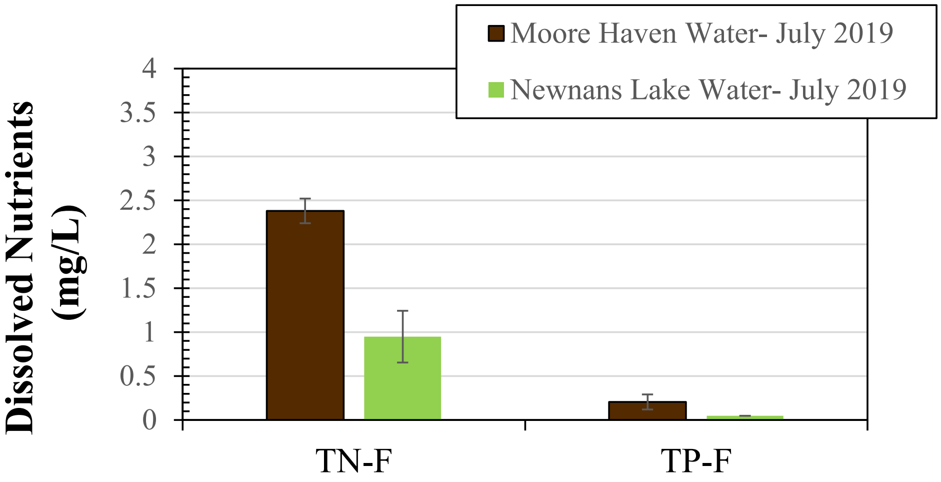
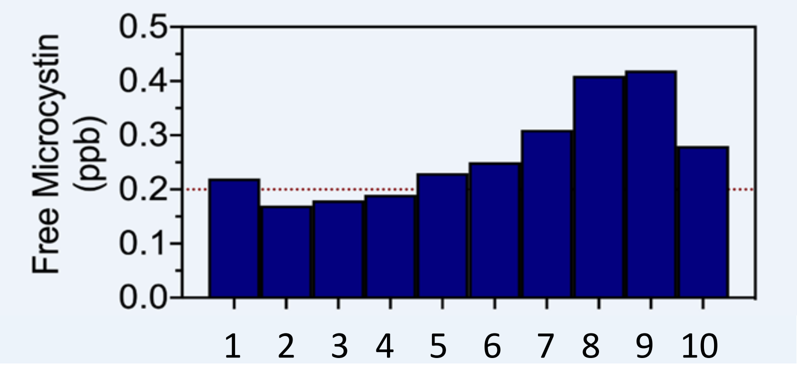
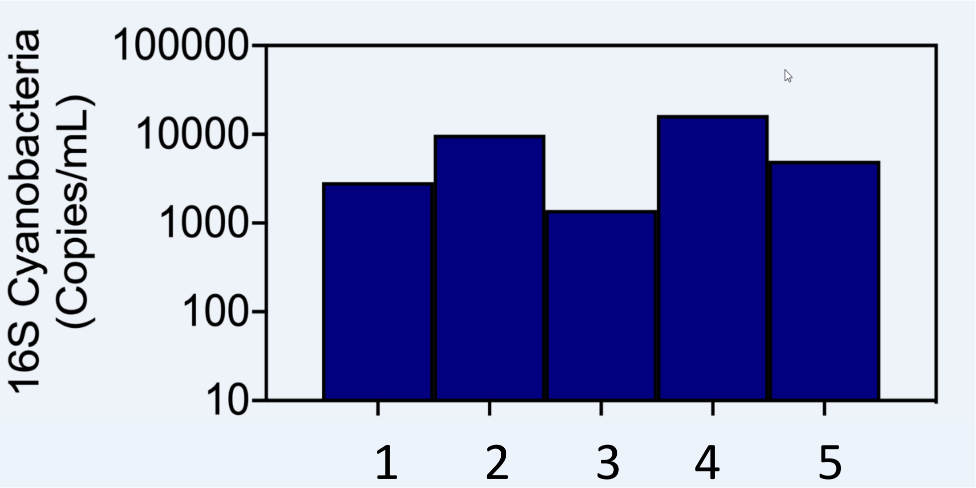


Figure 3-4. Representative microcystin levels in samples collected from the Moore Haven site (1-7, Lake Okeechobee), as well as those from Newnans Lake (8-10), based on enzyme-linked immune sorption assays (ELISA).



Before DAF testing, the research team also took samples for microbial analysis to assess the risk of potential toxin release from the algae. AECOM contracted GreenWater Labs to perform microscopic identification. The samples were predominantly non-toxin-forming filamentous cyanobacteria *Planktolyngbya contorta* sp. (3,603,378 cells/mL) and *Planktolyngbya f. limnetica* (1,055,567 cells/mL). Microcystis species comprised 0.04% of the total sample. Other potentially toxic species were identified at similarly low ratios. ERDC performed additional genetic analysis to confirm these results (Figure 3-5). Tests were done to identify the presence of specific toxin genes but none were found in any of the samples, which is consistent with the lack of toxins observed in the water samples.

Figure 3-5. Representative genetic screening results for Lake Okeechobee (1-3) and Newnans Lake (4-5) water sources used during the demonstration testing.



3.2 Pretreatment testing

Several high rate filtration technologies were evaluated as potential pretreatment systems for deployment downstream of the skimmer and upstream of the DAF. The purpose of these filtration systems could be for screening out large particulates, while allowing algae to pass, or screening the algae as a pre-concentration step before DAF.

3.2.1 Mechanically-cleaned screen filter (15 µm cutoff)

The Eaton DCF 400 mechanically-cleaned screen filter was tested at 20 gpm using algae-laden water from Newnans Lake. The filter flux did not decline after treating 500 gallons of water, and only minor flux decreases were observed between cleaning cycles. The mechanical cleaning cycle restored the filter flux completely. Because the cyanobacteria in Newnans Lake water were dispersed with a diameter much smaller than that of the filter size cutoff, no algae removal was observed with this filter system. Due to its high throughput, it may be a good pretreatment system for removing debris and visible particulates from the water before DAF.

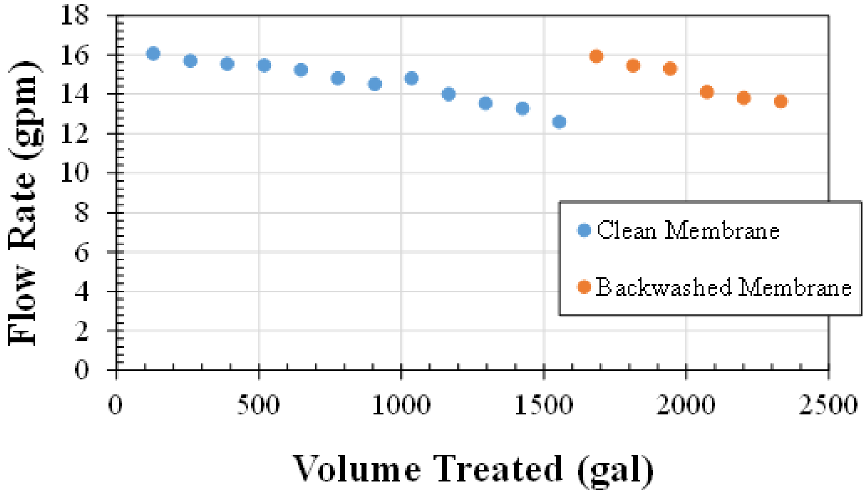
3.2.2 Stacked disc filtration

Two stacked disc filtration systems were tested for algae removal. The filters had size cutoff ratings of 5 and 0.2 microns. Each filter was challenged with 200 gallons of algae-laden water at flow rates of 10 and 5 gpm, respectively. However, neither filter removed or concentrated significant amounts of the microalgae during testing.

3.2.3 ZeeWeed membrane filtration

A 10 gpm microfiltration membrane system from Suez, Inc. was tested over a limited period using algae-laden 'green' water from Newnans Lake. This system was effective in removing and concentrating the algae. Under the conditions tested, limited flux declines were observed, which were recovered with an air scour assisted backwash process (Figure 3-6). Based on the results, long-term testing of the technology in controlled settings is recommended to better characterize potential fouling issues.

Figure 3-6. Changes in water flow rate through the ZeeWeed ultrafiltration membrane module during challenge testing using algae-laden water from Newnans Lake.



A high degree of water quality improvement was observed across the membrane in terms of nutrients, organics, and particulates. The data shown in Figure 3-7 represent a water sample drawn when the amount of permeate was approximately 4X the amount of concentrate, in terms of the water flow mass balance. Nutrients and particulates were concentrated by similar factors, confirming that algal cells contain significant nutrients.

3.3 Treatment testing

3.3.1 DAF system

The DAF system was tested extensively with algae-laden ('green') water from Newnans Lake. Testing was performed intermittently for up to 8 h at a time over a 2-week period. The flow rate was 75 gpm, and the hydraulic retention time ranged from 20-25 minutes. The DAF unit removed high levels of algae, as evidenced by the suspended solids removal and turbidity reduction data shown in Figure 3-8.

Figure 3-7. Water quality in the influent, permeate, and concentrate streams during ultrafiltration membrane challenge testing using algae-laden water from Newnans Lake.

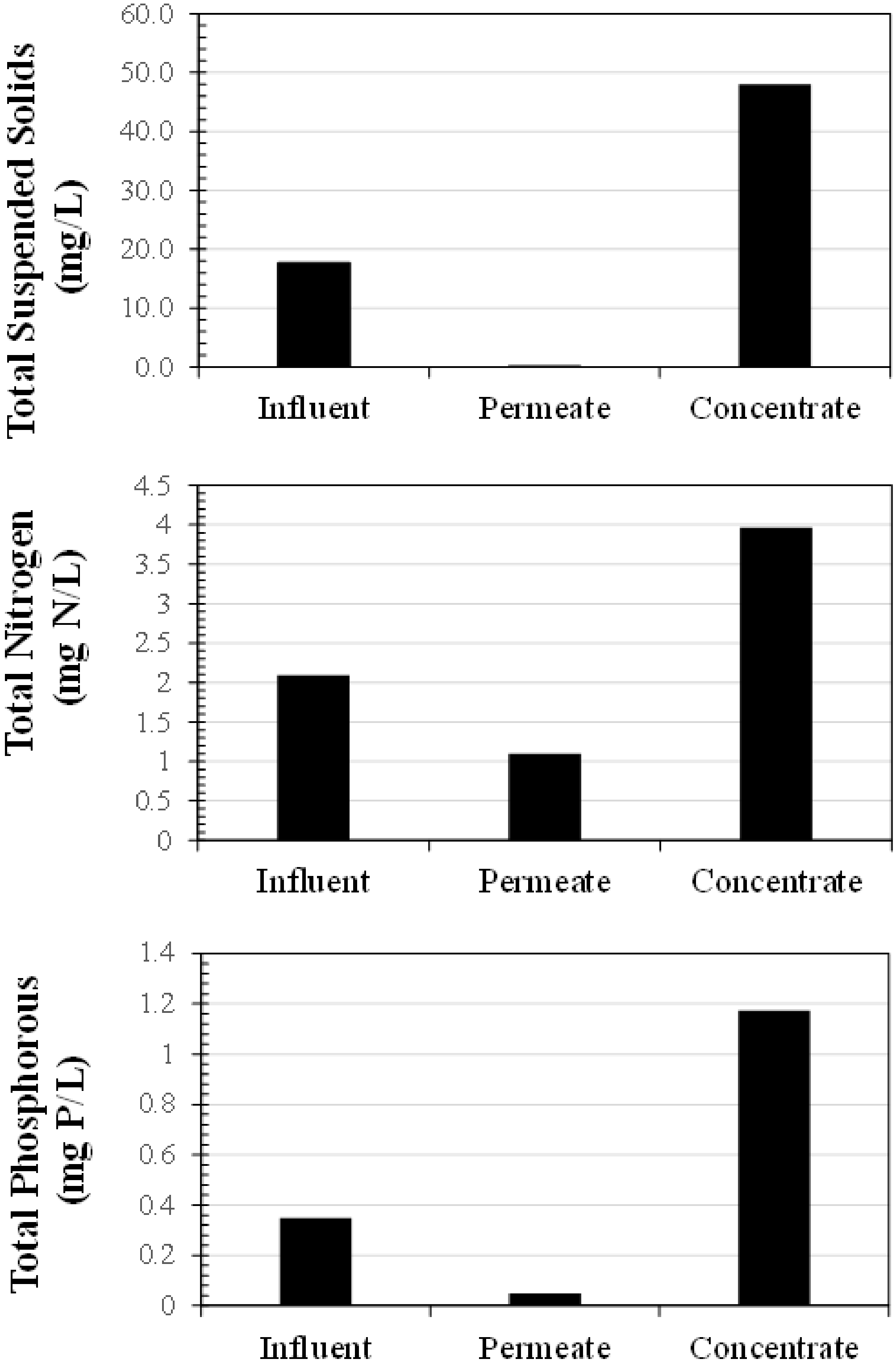
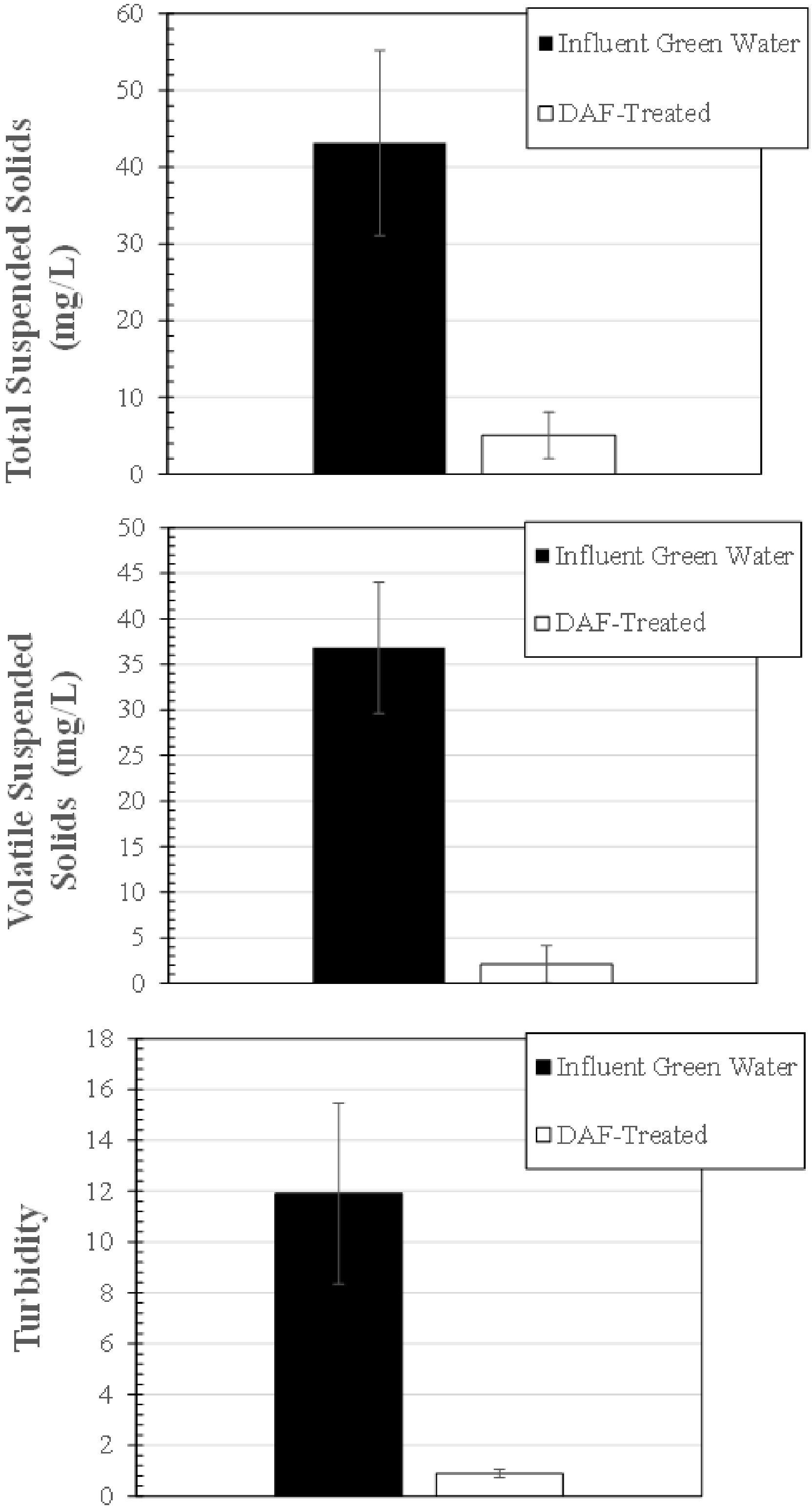


Figure 3-8. Comparison of physical water quality parameters in the influent versus effluent during dissolved air flotation (DAF) challenge testing using algae-laden ‘green water’ from Newnans Lake.



The DAF treatment process also resulted in high levels of nutrient removal from the water, presumably due to the high content of nutrients in the algal biomass. Based on comparisons of DAF versus the solids-free filtered water (TSS Filter Permeate), the removal of dissolved nutrients is likely insignificant (Figure 3-9). These results support the HABITATS hypothesis that removing algae from the water will have a beneficial impact on nutrient loads in the water body being treated or in downstream water bodies.

While DAF may have a limited impact on dissolved nutrients, it appears to have greater impact on reactive fractions of dissolved organics, based on the comparison of DAF to filtration for COD reduction. The levels of COD reduction for DAF were over 80%, whereas COD removal with filtration was closer to 50%. DAF removed about 55% of the total organic carbon (TOC) (Figure 3-10).

Figure 3-9. Removal of nutrients by dissolved air flotation (DAF) during challenge testing with algae-laden 'green water' from Newnans Lake. Total suspended solids (TSS) filtration permeate data are also provided to show the correlation between solids and nutrient removal.

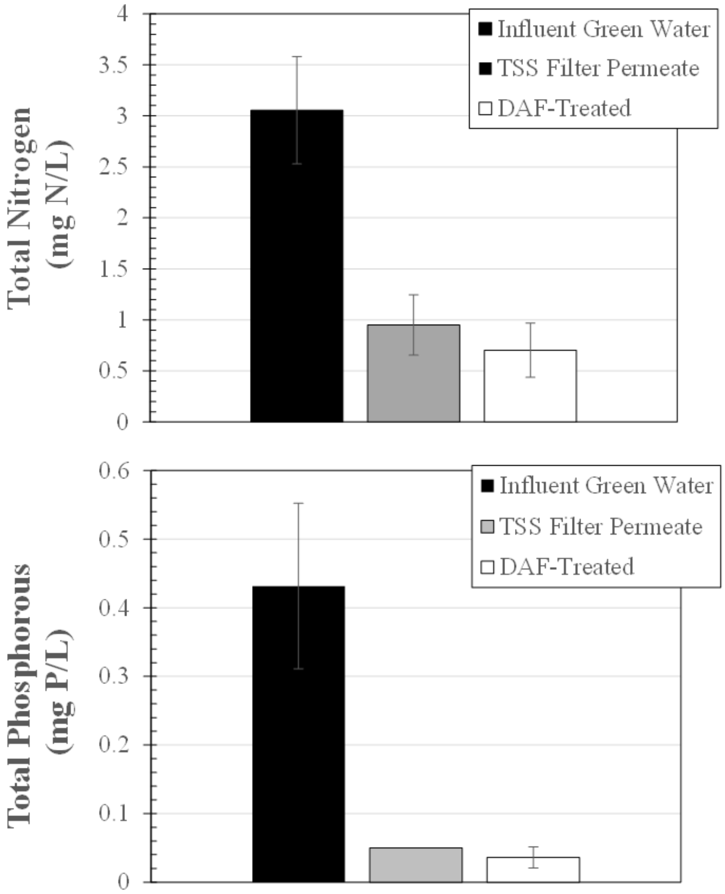
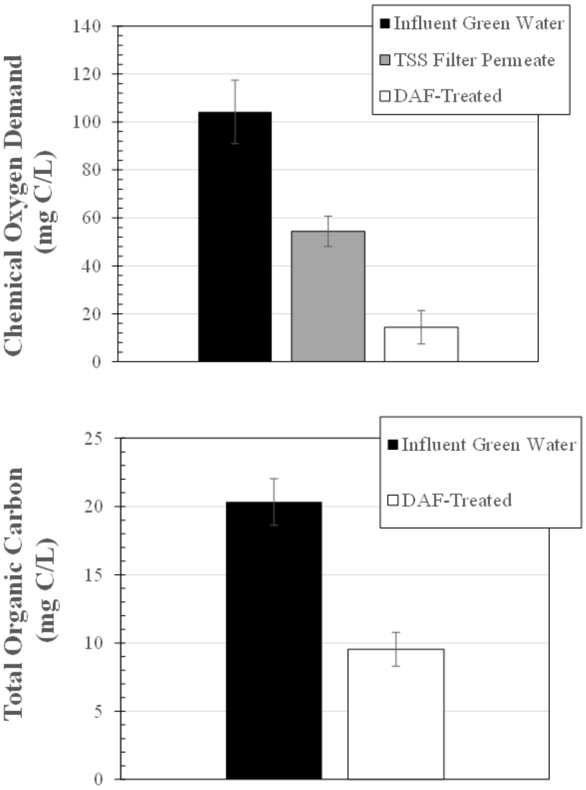


Figure 3-10. Removal of organic compounds by dissolved air flotation, as measured by chemical oxygen demand (COD) and total organic carbon (TOC). Experiments were conducted using algae-laden 'green' water from Newnans Lake.

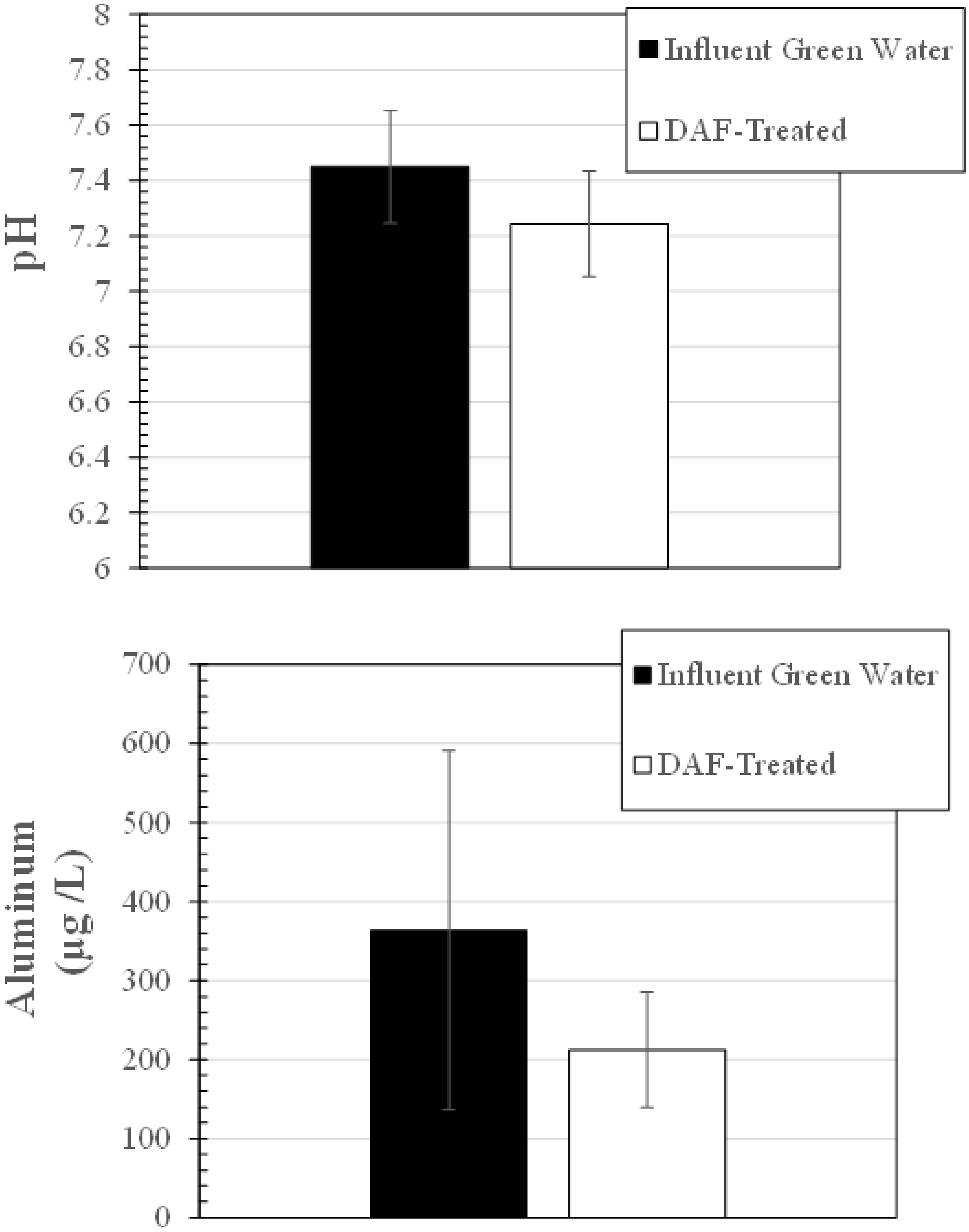


DAF treatment had a slight acidification effect on the water, bringing the pH down from an average of 7.4 (influent) to an average value of 7.2 (effluent). This value is well within the range of pH that is protective of aquatic life. In addition to pH, the influent and effluent were monitored for aluminum, since the coagulant used in the DAF process was aluminum chlorohydrate. Aluminum was detected in the DAF product water at levels similar to or less than the influent water from the lake (Figure 3-11).

3.3.2 Treatment system effluent

The treatment process included an ozone oxidation step downstream of the DAF to ensure destruction of any potential algal toxins before discharge of the effluent to the environment. The ozone system provided brief residual concentrations when set at a target concentration of 15 mg/L for dosing to achieve an ozone dose (CT) of at least 1 mg-min/L. Because algal toxins were not present in the water, it was not possible to validate their destruction by ozone in the demonstration site. However, the ozone doses applied have been shown to be sufficient for greater than 99% destruction of a broad range of algal toxins (USEPA 2016). The effluent water did not contain any detectable ozone, which reacted quickly *in situ*. The effluent also did not contain detectable levels of bromate, a potential byproduct of ozonation.

Figure 3-11. The effect of dissolved air flotation treatment on pH and aluminum levels. Experiments were conducted using algae-laden ‘green’ water from Newnans Lake.



Several effluent parameters were monitored for experimental and compliance purposes. Table 3-1 summarizes water quality of the effluent water, which was stored in holding tanks, with water quality verified before discharge. Effluent toxicity testing with *C. dubia* and *P. Promelas* showed no toxicity, acute or chronic.

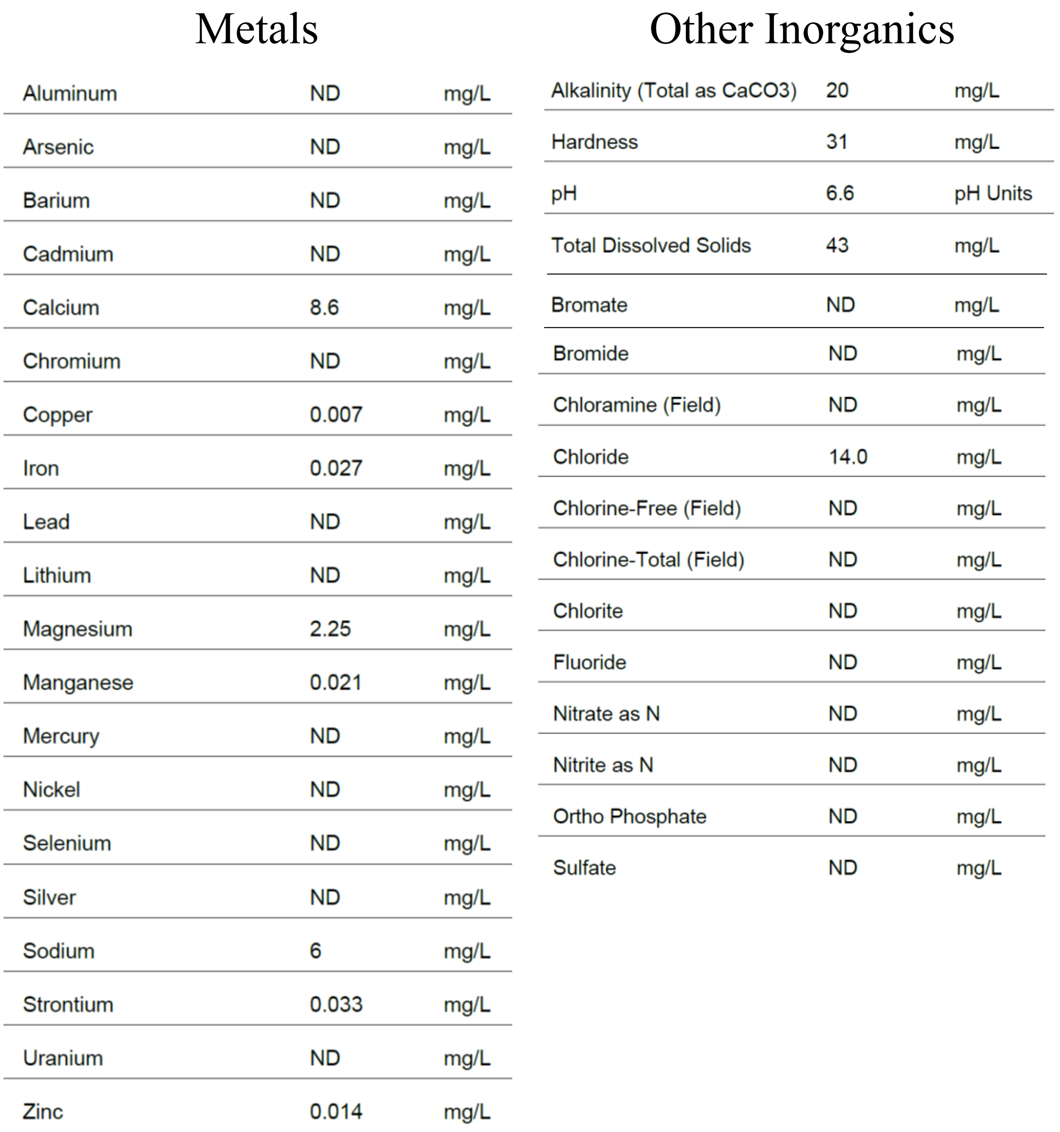
Table 3-1. Results from analysis of HABITATS effluent samples for key parameters relating to organic content, particulates, nutrients, and toxicity.

Compliance Parameters	Units	Reporting Value (Max/Min)	Limit	Demonstration Testing Results July 17-July 31, 2019
Flow	MGD*	Max Max	0.036	< 0.036 Avg. 0.006
Biological Oxygen Demand, Carbonaceous 5 day, 20 °C	mg/L	Max	Report	< 18.2 Avg. 11.3
Solids, Total Suspended	mg/L	Max	Report	< 5.0 Avg. < 5.0
pH	s.u.	Min Max	6 8.5	6.5 < pH < 7.3
Oxygen, Dissolved Percent Saturation	Percent	Min	Report	> 95%
Nitrogen, Total	mg/L	Max	Report	< 0.78 Avg. 0.58
Phosphorus, Total (as P)	mg/L	Max	Report	< 0.206 Avg. 0.078
Acute Whole Effluent Toxicity, 96 hr LC50 (*Ceriodaphnia dubia*)	Percent	Min	100	100
Acute Whole Effluent Toxicity, 96 hr LC50 (*P. promelas*)	Percent	Min	100	100
Chronic Whole Effluent Toxicity, 96 hr LC50 (*C. dubia*)	Percent		Report	100
Chronic Whole Effluent Toxicity, 96 hr LC50 (*P. promelas*)	Percent		Report	100
*million gallons per day (MGD)				

HABITATS effluent samples were also analyzed against a broad array of specific contaminants that are monitored in drinking water (Tables 3-2, 3-3, and 3-4). While the HABITATS design concept is not focused on direct use of the product water for human consumption or other municipal activities, these results indicate that the product water quality is quite high, with no drinking water maximum contaminant levels being exceeded.

However, it should be noted that the organic carbon content of the water (shown in Figure 3-10) is high enough that the chlorine demand and formation of disinfection byproducts (DBP) may present a challenge if considering the effluent as a potential water source.

Table 3-2. Levels of inorganic contaminants in HABITATS effluent after 40 h of operation.



Metals

Aluminum	ND	mg/L
Arsenic	ND	mg/L
Barium	ND	mg/L
Cadmium	ND	mg/L
Calcium	8.6	mg/L
Chromium	ND	mg/L
Copper	0.007	mg/L
Iron	0.027	mg/L
Lead	ND	mg/L
Lithium	ND	mg/L
Magnesium	2.25	mg/L
Manganese	0.021	mg/L
Mercury	ND	mg/L
Nickel	ND	mg/L
Selenium	ND	mg/L
Silver	ND	mg/L
Sodium	6	mg/L
Strontium	0.033	mg/L
Uranium	ND	mg/L
Zinc	0.014	mg/L

Other Inorganics

Alkalinity (Total as CaCO3)	20	mg/L
Hardness	31	mg/L
pH	6.6	pH Units
Total Dissolved Solids	43	mg/L
Bromate	ND	mg/L
Bromide	ND	mg/L
Chloramine (Field)	ND	mg/L
Chloride	14.0	mg/L
Chlorine-Free (Field)	ND	mg/L
Chlorine-Total (Field)	ND	mg/L
Chlorite	ND	mg/L
Fluoride	ND	mg/L
Nitrate as N	ND	mg/L
Nitrite as N	ND	mg/L
Ortho Phosphate	ND	mg/L
Sulfate	ND	mg/L

Table 3-3. Levels of organic contaminants in HABITATS effluent after 40 h of operation.

Halogenated DBPs

Bromodichloromethane	ND	mg/L
Bromoform	ND	mg/L
Chloroform	ND	mg/L
Dibromochloromethane	ND	mg/L
Total THMs	ND	mg/L
Dibromoacetic Acid	ND	mg/L
Dichloroacetic Acid	ND	mg/L
Monobromoacetic Acid	ND	mg/L
Monochloroacetic Acid	ND	mg/L
Trichloroacetic Acid	ND	mg/L
Total HAAs	ND	mg/L

Volatile Organics

1,1,1,2-Tetrachloroethane	ND	mg/L
1,1,1-Trichloroethane	ND	mg/L
1,1,2,2-Tetrachloroethane	ND	mg/L
1,1,2-Trichloroethane	ND	mg/L
1,1-Dichloroethane	ND	mg/L
1,1-Dichloroethene	ND	mg/L
1,1-Dichloropropene	ND	mg/L
1,2,3-Trichlorobenzene	ND	mg/L
1,2,3-Trichloropropane	ND	mg/L
1,2,4-Trichlorobenzene	ND	mg/L

Volatile Organics (cont.)

1,2-Dichlorobenzene	ND	mg/L
1,2-Dichloroethane	ND	mg/L
1,2-Dichloropropane	ND	mg/L
1,3-Dichlorobenzene	ND	mg/L
1,3-Dichloropropane	ND	mg/L
1,4-Dichlorobenzene	ND	mg/L
2,2-Dichloropropane	ND	mg/L
2-Chlorotoluene	ND	mg/L
4-Chlorotoluene	ND	mg/L
Acetone	0.05	mg/L
Benzene	ND	mg/L
Bromobenzene	ND	mg/L
Bromomethane	ND	mg/L
Carbon Tetrachloride	ND	mg/L
Chlorobenzene	ND	mg/L
Chloroethane	ND	mg/L
Chloromethane	ND	mg/L
cis-1,2-Dichloroethene	ND	mg/L
cis-1,3-Dichloropropene	ND	mg/L
DBCP	ND	mg/L
Dibromomethane	ND	mg/L

Table 3-4. Levels of additional organic contaminants in HABITATS effluent after 40 h of operation.

Volatile Organics (cont.)		
Dichlorodifluoromethane	ND	mg/L
Dichloromethane	ND	mg/L
EDB	ND	mg/L
Ethylbenzene	ND	mg/L
Methyl Tert Butyl Ether	ND	mg/L
Methyl-Ethyl Ketone	ND	mg/L
Styrene	ND	mg/L
Tetrachloroethene	ND	mg/L
Tetrahydrofuran	ND	mg/L
Toluene	ND	mg/L
trans-1,2-Dichloroethene	ND	mg/L
trans-1,3-Dichloropropene	ND	mg/L
Trichloroethene	ND	mg/L
Trichlorofluoromethane	ND	mg/L
Vinyl Chloride	ND	mg/L
Xylenes (Total)	ND	mg/L

Other Organics		
2,4-D	ND	mg/L
Alachlor	ND	mg/L
Aldrin	ND	mg/L
Atrazine	ND	mg/L
Chlordane	ND	mg/L
Dichloran	ND	mg/L
Dieldrin	ND	mg/L
Endrin	ND	mg/L
Heptachlor	ND	mg/L
Heptachlor Epoxide	ND	mg/L
Hexachlorocyclopentadiene	ND	mg/L
Lindane	ND	mg/L
Methoxychlor	ND	mg/L
Pentachloronitrobenzene	ND	mg/L
Silvex 2,4,5-TP	ND	mg/L
Simazine	ND	mg/L
Total PCBs	ND	mg/L
Toxaphene	ND	mg/L
Trifluralin	ND	mg/L

3.3.3 Algae biomass characterization

The algae floated and skimmed from the surface of the DAF reactor had a solids concentration between 2%-3% M/V.[*] Given the ambient algae concentration of 50 mg/L in the water source, this represents a concentration factor of 400-600 times. The algae biomass contained nitrogen and phosphorous at similar concentration factors. Table 3-5 lists representative sample values.

The algae slurry from the DAF system was further concentrated using polymer flocculants and a belt press, achieving a final solids concentration of 12%.

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[*] Mass/Volume

Table 3-5. Characterization of key parameters in the algal biomass solids from the DAF process.

DAF Solids			
Parameter	mg/L	+/-	%
TSS	30,200	7,350	3
VSS	21,550	6,804	2.2
TN	1500	422	0.15
TP	144	39	0.01
COD	39,600	7800	39.6

3.4 HTL testing

The conversion of algae into biocrude fuel by HTL was demonstrated at bench scale using the concentrated cyanobacteria biomass provided from the HABITATS demonstration site in Moore Haven, Florida (Figure 3-12). The yield of biocrude was consistent with expectations for the experimental conditions tested, but these conditions were not optimal.

Figure 3-12. Biocrude oil generated via Hydrothermal Liquefaction at PNNL using the concentrated algae biomass collected from the treatment demonstration in Moore Haven, FL.

Upon shipment to PNNL, it was noted that the viscosity of the solids was atypically high for the mass concentration of algae (12.2%), likely due to the high aluminum content. To allow for flow through the bench scale feed pump to the HTL reactor, the slurry had to be diluted to 10% solids. Since HTL works best at solids concentrations greater than 15%, shifting the concentration downward to 10% was a significant setback in terms of biocrude yield potential. Additionally, the inorganic content of the algal biomass was very high (30%) due to the use of an inorganic coagulant in the DAF process, bringing the effective organic solids level to 7%.

In spite of these unfavorable conditions, conversion of the algae into biocrude was achieved, and the experiment provided valuable data for characterizing the chemistry of the influent (algal biomass) and effluent (biocrude, ash, aqueous) streams using inductively coupled plasma mass spectroscopy (ICP-MS). A comparison of the inorganic content in these streams showed that the aluminum did not partition significantly into the biocrude and largely precipitated out, along with phosphate and other minerals, in the ash stream (Table 3-6).

Table 3-6. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) characterization of the inorganic fractions in the influent feed (algal biomass) and effluent streams (ash, biocrude, and aqueous) during the conversion of algae to biocrude by hydrothermal liquefaction (HTL).

		Influent	Effluent		
Analyte	Unit	Feed	Ash	Biocrude	Aqueous
Al	ppm	94440	165750	157.25	< 1
Ba	ppm	< 45	< 45	< 40	< 1
Ca	ppm	2788	6315	163.70	6.60
Cd	ppm	< 45	< 45	< 40	< 1
Co	ppm	< 45	< 45	< 40	< 1
Cr	ppm	< 45	< 45	< 40	< 1
Cu	ppm	69.43	176.80	< 40	< 1
Fe	ppm	6678	11128	154.85	< 1
K	ppm	1155	5499	100.01	72.58
Mg	ppm	618.4	1288	< 40	1.05
Mn	ppm	53.78	165.9	< 40	< 1
Na	ppm	282.8	298.85	77.03	18.67
Ni	ppm	< 45	64.03	< 40	< 1
P	ppm	2804	6798	< 40	< 1
Pb	ppm	< 45	< 45	< 40	< 1
Sr	ppm	< 45	< 45	< 40	< 1
Zn	ppm	85.35	226.7	< 40	< 1
Mo	ppm	< 45	< 45	< 40	< 1
Si	ppm	22150	43015	429.10	101.8
Ti	ppm	123.1	293.9	< 40	< 1
S	ppm	4221	3438	6355	136.5
Zr	ppm	< 45	< 45	< 40	< 1

Additional process stream characterization and fuel upgrading studies, which are ongoing at the time of this report, include characterization of the biocrude organic fractions before and after upgrading via hydrotreating. Studies on the validation of microcystin destruction in the biomass during HTL are also ongoing. Destruction of microcystin by hydrothermal liquefaction in aqueous, controlled conditions has been recently confirmed in collaboration with Dr. Lance Schideman and Kathryn Gunderson of the Illinois Sustainability Technology Center at the University of Illinois.

4 Discussion

Year 1 of the HABITATS demonstration study provided critical data for assessing the baseline performance and scalability of the component technologies for treatment and transformation. More detailed studies of the interception process are required, and some key modifications were identified for the Treatment step that will enable optimal conversion of the algal biomass to biocrude once it is removed from the water. An equally important result was the confirmation of the high degree of nutrient removal that is achieved as a result of the treatment process. By removing the algae and embedded nutrients, the positive impact on the water body and downstream systems should be magnified. Resource recovery opportunities that are inherent to the HABITATS approach are expected to have economic and other sustainability and resiliency benefits as well.

While the analysis of the components for interception, treatment and transformation provided important lessons, discussed in the following sections, the results were also used to build a preliminary model for scalability analysis. This model was used to assess near-term application opportunities as well as priority areas for improvement or additional capabilities that will lead to a truly scalable solution for HAB mitigation.

4.1 Interception

The current interception system is designed for targeting algae that is concentrated at the water surface. The floating boom skimmer design concept is largely driven by visual observations of algal films forming on the water surface in many large and small scale bloom events. The boom skimmer design is similar to those used for oil spill cleanups. However, oil is considerably more buoyant and hydrophobic than cyanobacteria; oil's properties drive it to the water surface and keep it there. Algae, on the other hand, is more miscible and can move up and down in the water column; its flotation is governed by metabolic and environmental conditions. The distribution of algae in the water column is generally not well understood or characterized, even during large bloom events. More work is needed in this area to better determine the magnitude of the problem and to design effective solutions that can apply to any HAB scenarios.

During the demonstration period in July 2019, algal film formation was not prominent in the 'green' water from Newnans Lake, nor in the Lake Okeechobee water at the Moore Haven site. Neither water source had microcystin present above levels of 1 ppb during testing. The algal cells in the 'green' water from Newnans Lake were present at relatively high densities and distributed uniformly in the water column at the collection site. During demonstration testing at Moore Haven in July 2019, the source water algae levels were relatively low and also uniform throughout the water column. In June 2019, sampling as a function of depth was executed at times when algae was present at greater levels, though algae levels were still much lower than previous years. At these lower algae concentrations, the algae was distributed uniformly in the water column, without film formation. During the demonstration, the spillway was operating at low discharge levels, usually less than 200 cfs, so the water velocity in the canal was low.

Efficient interception methods will be key to scalability of the HABITATS approach. The current design will likely work very well for cases when algae is concentrated at the surface. However, due to the environmental conditions at the permitted test site for this particular demonstration, further research is required to validate and optimize the surface interceptor. For cases when algae is distributed in the water column, future research should focus on the use of benign chemicals and low energy nano-flotation systems that can bring more of the algae up to the surface (i.e., an *in situ* DAF process). This would likely be much more practical and environmentally friendly than removing and treating all of the water from a water body. Controlling the environment to trigger or promote the algae's inherent flotation mechanisms may be a more efficient and environmentally sensitive approach. In any case, broader environmental impacts must be considered carefully, including potential impacts on microcystin levels.

4.2 Treatment

The treatment process was largely successful in demonstrating that algae-laden water could be clarified and cleaned rapidly, allowing clean water to be returned to the environment. DAF was particularly effective and should allow HABITATS to have a much smaller footprint than a conventional wastewater treatment plant. With the physically scalable HABITATS approach, the water quality was greatly improved in physical, chemical, and biological respects.

Physical water quality improvement resulted from the clarifying effect of DAF, which was particularly effective in removing the algae during the demonstration. This provided additional benefits of removing high levels of nutrients from the water, and for cases when the algae contain toxins, the DAF would also remove the intracellular toxins along with the biomass. Perhaps as importantly, from a scalability perspective, DAF recovered an extremely high percentage of the process water, generating only 1 gallon of ‘waste’ algae slurry for every 400 gallons of water passing through. This ‘waste’ slurry had a mass concentration of 2%-3% (20,000-30,000 mg/L), whereas the concentration of algae in the influent water was only about 50 mg/L. This ability to concentrate algae quickly in a high throughput (small footprint) manner is a primary reason why DAF is recommended as the key Treatment step in the HABITATS approach.

With regard to HABITATS integration, the only problem observed with the DAF treatment process, as demonstrated, was the use of a metal salt coagulant, aluminum chlorohydrate, for the coagulation process. While the aluminum coagulant was effective for treatment, an alternate organic coagulant should be used in the future to increase compatibility with the HTL process. The coagulant chemical neutralizes the algal cells, allowing them to interact and associate with the nanobubbles in the DAF process, creating the flotation effect. Without the coagulant addition, most of the algal cells remain charge stabilized and dispersed in the water, at least within the range of environmentally acceptable pH conditions. The aluminum chlorohydrate thus necessarily associates with the cells, which means it is also concentrated into the algal biomass.

However, this essentially dilutes the algae in the concentrated biomass, taking up valuable mass and volume with inorganic material that is not convertible to fuel. Rather, it forms ash in the HTL process. Given that the inorganic content of the DAF slurry was about 30% of the total solids, this resulted in lower efficiency of the HTL conversion process, which means less fuel production. Going forward, if the HABITATS process is to be successful and scalable, an alternate coagulant that is carbon-based must be used. This will have the effect of increasing fuel yields, as it too will serve as an organic feedstock. Organic coagulants have been successfully used for algae removal in DAF systems, though dosing and chemistry could likely benefit from additional optimization studies. Bench scale jar tests to optimize an organic, low-toxicity coagulation process for DAF are being initiated such that extended pilot studies are being executed and will be optimized in Year 2, pending funding.

For oxidation of the DAF-clarified water to ensure destruction of any algal toxins, the ozone process tested was also effective in delivering a dose sufficient to control microcystin and many other algal toxins in water (USEPA 2016), though microcystin levels were below detection in the test water. Related studies confirming microcystin destruction by ozone in DAF-clarified waters are being conducted to optimize the dose. Ozone is typically effective against trace organic contaminants (TOrCs) when it is applied at concentrations equal to one half of the TOC concentration. This highlights another benefit of DAF, relative to a strictly physical process like microfiltration membranes, because DAF removed 50% of the TOC and over 80% of the COD in the test water, whereas filtration of the algae alone only removed about 50% of COD. Reducing COD results in energy savings due to a lower ozone demand of the process water.

While highly effective against a broad range of algal toxins, ozone is an energy intensive process, particularly when ozone demand of the water is high due to background TOC. Alternative approaches, such low dose ozone/UV, peroxone, or UV-hypochlorite followed by bisulfite addition should be studied in the future as a potential energy- and cost-saving opportunity. One logistical advantage of ozone is its instability, which makes it easier to remove from the water without use of high volumes of chemical quenching agents. Ozone can also be generated on site, reducing volumes of chemicals required for deployment and resupply, though these benefits may be offset by higher fuel requirements for generator-powered operations. Given that HABITATS could potentially generate combustible fuel on site, the fuel resupply issue may have limited impact when algae is abundant. Another opportunity for reducing energy consumption would be to monitor the toxin concentrations in the feed and product waters frequently and only apply the oxidant when microcystin is detected. This approach would entail some risk and is thus not recommended until these systems are validated for long periods of time under various operating conditions.

4.3 Transformation

The HTL process for converting algae to biocrude offers tremendous promise as an efficient means for on-site management of the algae biomass. Some of the HTL studies are ongoing at the time of this report, but to date, this work has demonstrated the ability to rapidly transform algae into biocrude when using a mixed species algae feedstock that was harvested and concentrated from a natural water body. To increase the fuel yield and overall efficiency of the process, some modifications of the algae concentration and dewatering process are needed, but these are expected to be feasible and present low risk. Specifically, the use of an organic coagulant in the DAF process is required, and alternative dewatering processes with higher throughput should be studied.

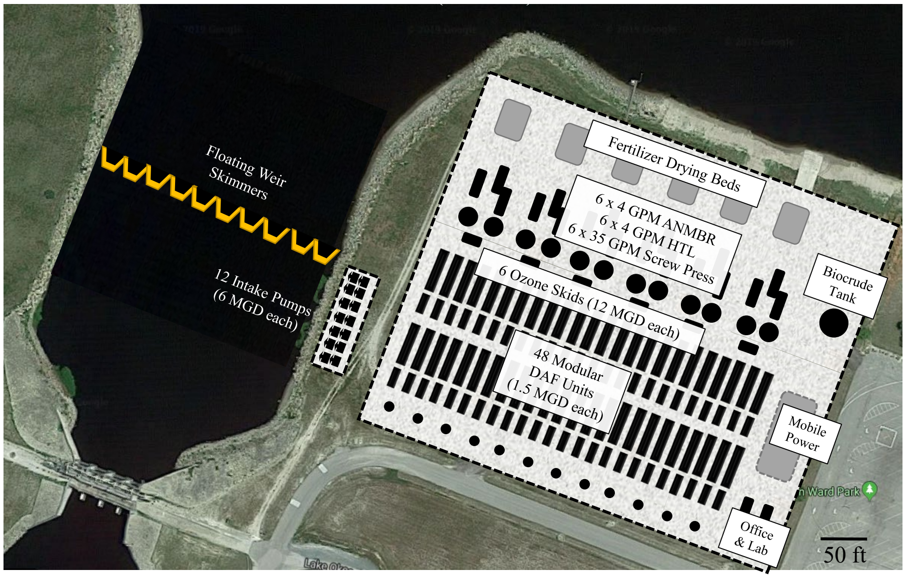
The HTL process creates biocrude, but it also generates other waste streams that need to be processed further. However, due to the high degree of algae concentration by the DAF and dewatering treatment steps, the volumes and flow rates of waste to be processed are orders of magnitude smaller than for the water treatment process. The HTL process also provides a high degree of digestion and stabilization of the resulting aqueous and ash waste streams, making their management less challenging. The data collected in this study showed that, even with high levels of aluminum in the influent biomass, the metals and other organics primarily fall out in the ash stream, along with the phosphate. This could present resource recovery opportunities. The aqueous stream does contain carbon and nitrogen that will require further stabilization treatment. Anaerobic membrane bioreactor technology, which allows for energy recovery in the form of methane and can have high throughput compared to conventional anaerobic systems, could be suitable for this task. The HTL pretreatment should accelerate the anaerobic digestion process as well. Nitrogen recovery methods will need to be explored. For the HTL process, the opportunities for resource recovery are numerous and will help close the loop on the HABITATS process, as well as on regional cycles of nutrients between the natural and built environment.

4.4 Scalability

A preliminary scalability analysis was performed on HABITATS using custom models to estimate footprint, energy consumption, and cost as a function of key variables. To the extent possible, data collected during the pilot demonstration were used to support the model development and analysis. Other sources, such as published water treatment plant cost estimation models based on Engineering News Record data (Plumlee et al. 2014, McGivney et al. 2008), were used as necessary to fill in data gaps and generate cost estimates for different scenarios while considering efficiencies of scale. Published reports and presentations on hydrothermal liquefaction were used to estimate fuel recovery and costs at scale (Snowden-Swan et al. 2016, 2018; Zhang et al. 2017). Any cost estimates cited in this report are general, not site or design specific, and should be considered as range-of-magnitude estimates only. They should not be used for estimating costs of implementation of this technology without further engineering design and site specific analysis. However, the model estimates are helpful for identifying effects and trends through parameter sensitivity analysis, which can help identify priority areas for further research and optimization.

The design scenario used for the scalability analysis was the deployment of HABITATS on shore and upstream of a spillway on a canal or river (Figure 4-1). Potential benefits of this design include leveraging the energy in the existing water infrastructure, creating a barrier to help reduce impacts on downstream communities, and not impeding navigation.

Figure 4-1. Overview of a deployable plant for the HABITATS process that can treat 65 million gallons per day (MGD).



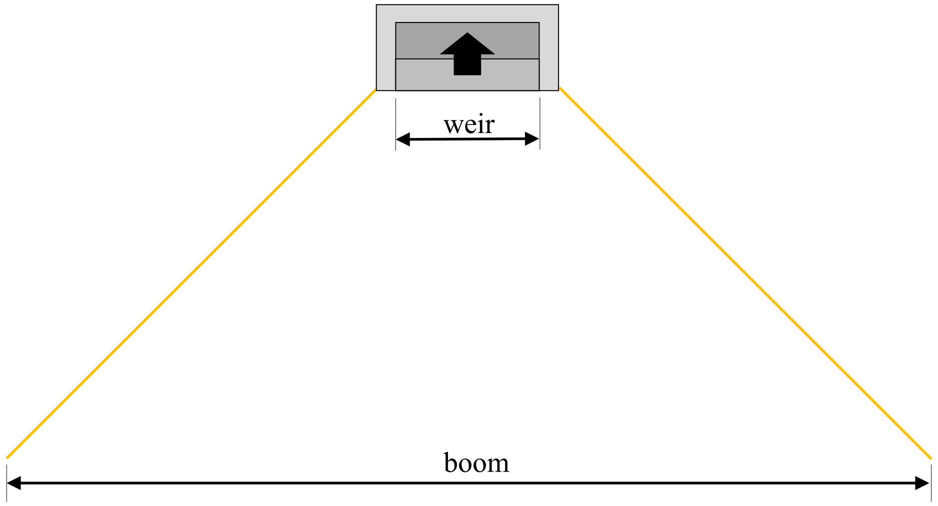
4.4.1 Analysis approach

The estimated engineering performance of a full scale HABITATS deployment is a function of many different parameters. These include design factors such as the treatment capacity and the boom-to-weir ratio of the interception structure, as well as factors dictated by the environmental conditions, such as the ambient algae concentration, the change in algae concentration with depth, the spillway flow rate, and the HABITATS flow rate. Many of these factors are dependent on the interceptor system and site conditions. A key parameter for scalability analysis is the system capacity.

Specifically, it would be helpful to understand the physical footprint of HABITATS relative to the expected algae removal from the water body being treated (in this case, the canal).

The layout and operation of the interception system will affect the expected performance in several ways. First, algae at the water surface can be horizontally concentrated toward the skimmer intake by the booms, which push back on the surface solids as the water passes below. This approach works well with highly buoyant contaminants like oil, but the efficacy with more miscible algae will depend on the algae buoyancy and level of natural aggregation into films or strands at the surface. Mono-disperse algal cells will tend to diffuse quickly and move with the water under the boom, whereas larger particulates and buoyant algae are expected to concentrate and aggregate along the boom. The boom drag ratio compares the velocity of water in the channel to the effective velocity of water impacting the interceptor. It dictates how hard the boom is pushing back on the water. If the ratio is unity, there is minimal drag on the boom, as all the water hitting the boom is being pulled to and through the skimmer. Ratios higher than unity will induce a resistance effect, pushing back on the water flow, allowing slower diffusing algae aggregates and buoyant algae to concentrate. As the ratio increases further, turbulent conditions will also be induced that are not favorable for algae concentration due to the mixing (Figure 4-2). Some of these parameters and relationships are still being developed and tested.

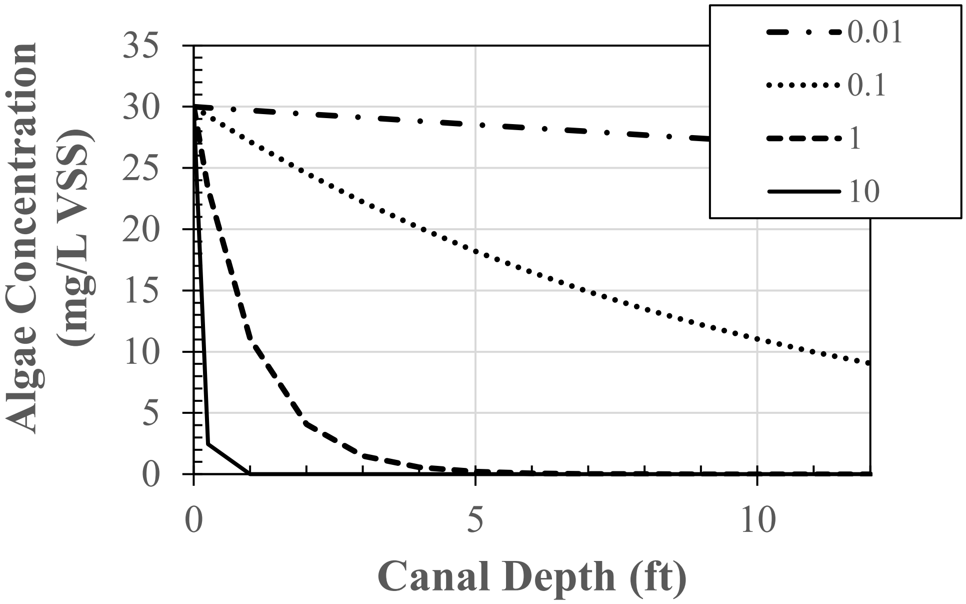
Figure 4-2. The ratio of the boom width to weir width will affect the concentration of algae entering the intake under many conditions.



For the purpose of the model, the term 'ambient algae concentration' refers to the average concentration of algae upstream of the interceptor within the effective cut depth of the skimmer, before any horizontal focusing caused by the boom. Thus, if the boom skimmer is working to concentrate the algae near the surface by compressing it horizontally, the 'influent algae concentration' will be higher than the 'ambient environmental concentration'.

In addition to horizontal concentration effects, it is important to consider the potential natural gradients in algae concentration vertically within the water column, given that algae buoyancy and surface film formation can vary. Figure 4-3 shows some hypothetical algae concentration profiles as a function of depth. In all cases, the surface concentration is 30 mg/L. However, as the algae depth dilution coefficient increases, so does the dilution relative to the surface. For a small depth dilution coefficient, the algae concentration in the entire column is nearly uniform, and removing the algae in the top of the column will have limited impact on total water quality. When the algae is concentrated toward the surface, with the same surface concentration but a larger depth dilution coefficient, there is less algae in the whole column, and removing the algae near the surface will have a greater impact on the total water quality relative to the initial state.

Figure 4-3. Hypothetical profiles of algae concentration versus depth that can be encountered under different environmental conditions. Depth dilution coefficients can be used to model these effects based on field data.



Scalability modeling requires careful consideration of these and other parameters. Some of the parameters are constrained by physical space or other factors, but several of the variables are relatively independent. Many are not within a designer's sphere of control; they are mostly driven by the environment. The key independent variables and arbitrary baseline values used for the HABITATS scalability modeling were:

- Average ambient algae concentration: 50 mg/L (2×10^6 cells/ml)
- Depth dilution coefficient: 0.17 (2X dilution at 4-ft depth)
- Canal water velocity: 0.67 ft/s (equivalent to 2000 cfs discharge).

From this baseline scenario, each of the independent variables was adjusted while the others were held constant. The resulting estimates for physical footprint, energy consumption, and cost were then calculated and plotted as a function of HABITATS processing capacity (in MGD) to identify trends that might aid optimization. The estimated percentages of algae, nitrogen, and phosphorous removed from the canal were also estimated as a function of treatment capacity under each condition. For simplicity at this phase, year-round operation was assumed, given that the system could potentially be deployed at multiple locations as blooms occur.

4.4.2 Effects of ambient algae concentration

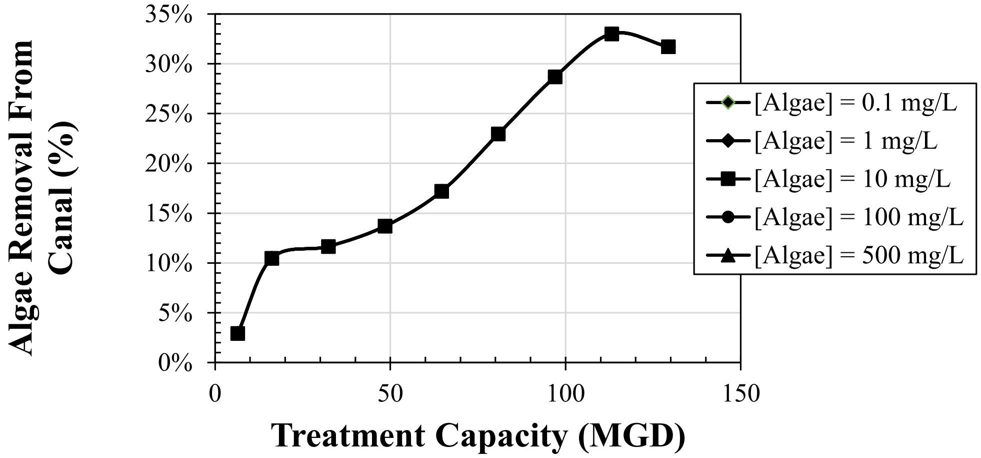
Scalability of HABITATS deployment upstream of a spillway was initially estimated for a baseline condition of 2000 cfs spillway discharge and an algae depth distribution coefficient of 0.17. This would be considered a challenging scenario for HABITATS, since the interceptor is designed for surface recovery. In this case, the algae concentration decreases about 50% every 4 ft, which means a considerable fraction of the algae is below the surface, beyond the reach of the interceptor during high discharge flow conditions.

For modeling purposes, ambient algae concentration ([Algae] = X mg/L) represents the algae concentration near the water surface upstream of the interceptor. The units of cyanobacteria concentration for modeling were mg/L. Based on the molecular weight of a cyanobacteria cell (Hu 2014), 1 mg/L equates to approximately 50,000 cells per mL.

Even under this scenario, in which algae is partially distributed throughout the water column and spillway discharge flow rates are high, HABITATS is estimated to be capable of removing a significant amount of the algae. A 100 MGD system, which is about 150 cfs (compared to the 2000-

cfs spillway discharge rate) could reduce the canal algae concentration by about 30% (Figure 4-4). At smaller design scales, the total algae reduction is expected to decrease rapidly, with a 6 MGD (10 cfs) system only removing about 3%. Under these flow conditions, the current scalability model shows no effect of ambient algae concentration on the percent removal for the range of concentrations modeled.

Figure 4-4. Predicted algae removal from a canal flowing at 2000 cfs and algae depth dilution coefficient of 0.17 (i.e., the algae concentration in the canal decreases by a factor of 2 relative to the surface concentration with every 5 ft of canal depth).



Associated costs were estimated as a function of design capacity (gallons per day [GPD]) for the various ambient algae concentrations are shown in Figure 4-5, which graphs estimated annualized costs, including Operations and Maintenance (O&M) costs with capital costs amortized over 30 yrs. Note that a shorter life cycle would increase annual costs. In this analysis case, the ambient algae concentration has a greater effect. This is due to the ability to recover revenue in the form of biocrude when algae levels are high. Costs of HABITATS are expected to decrease as the ambient algae concentration increases, due to increased resource recovery potential.

The factors driving cost savings with higher ambient algae concentrations are clear when one directly considers the estimated energy consumption (Figure 4-6). It is projected that energy neutral operations will be achieved when algae concentrations reach 100 mg/L, which is not uncommon during major blooms. At higher concentrations, the biocrude fuel becomes a significant energy supply that far exceeds the needs of the treatment operation. A 100 MGD treatment facility could generate in excess of 12,000 gallons of biocrude per day.

Figure 4-5. Effect of the ambient algae concentration on the annualized treatment cost as a function of treatment capacity.

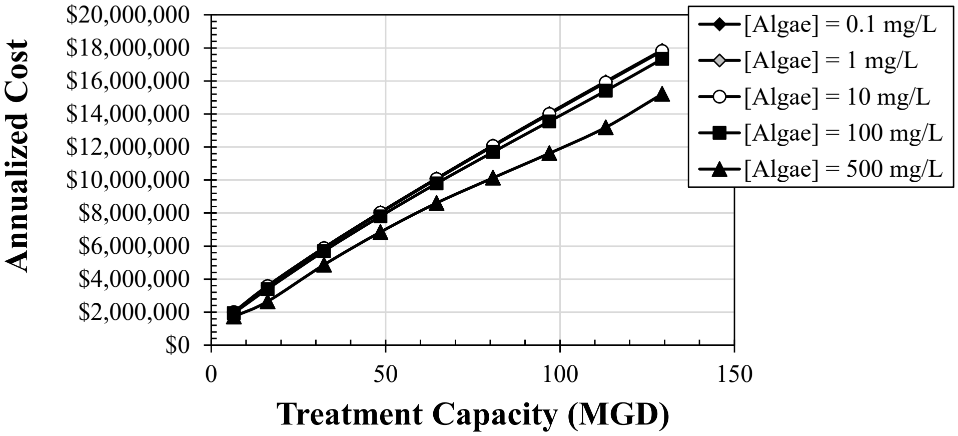
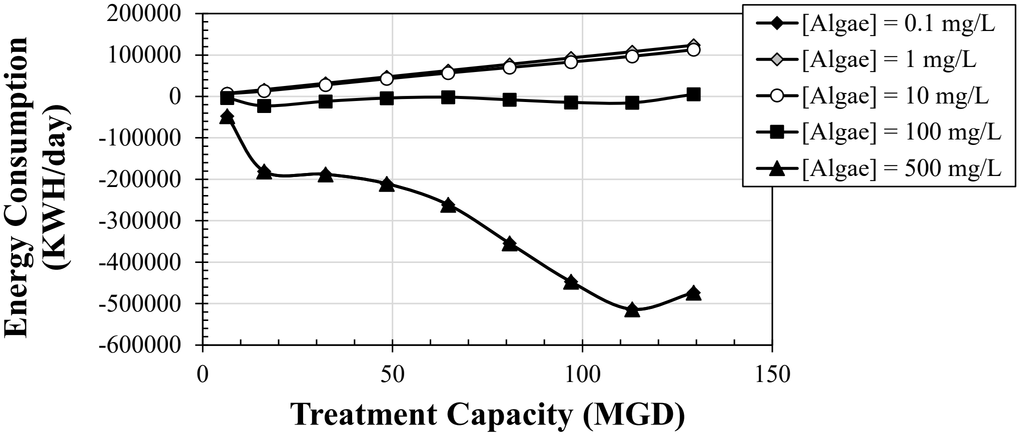
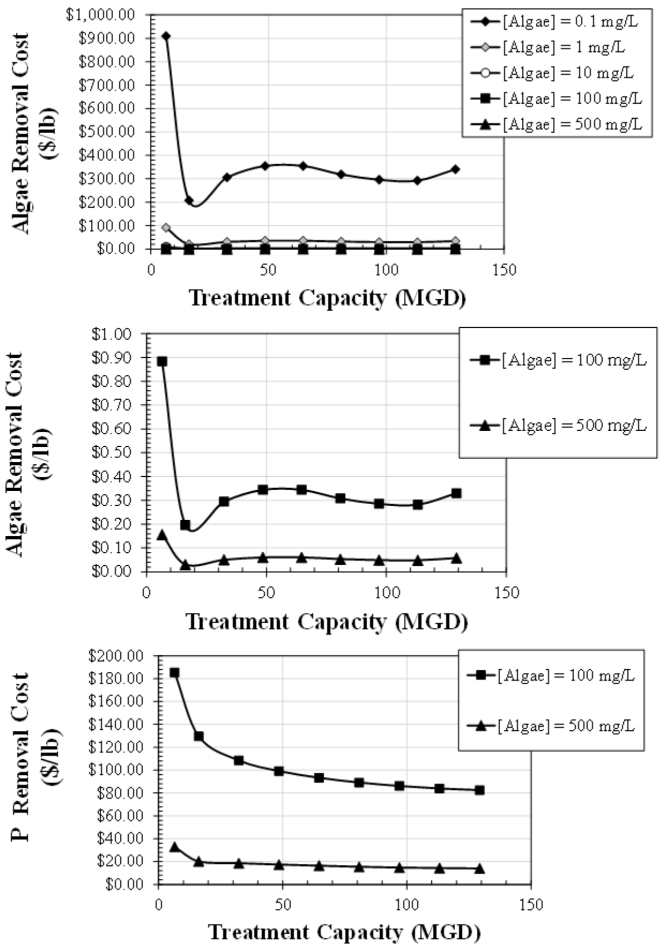


Figure 4-6. Effect of ambient algae concentration on the energy consumption (kWh/day) as a function of treatment system capacity (MGD).



While the biocrude revenues at high ambient algae concentrations only offset a fraction of the annual cost, there are other cost drivers and recovery opportunities. The cost per pound of algae removed is excessive when ambient algae concentrations are low (Figure 4-7), which makes sense given that a large volume of water is required to produce a small amount of algae. At high algae levels, the costs are projected to come down to less than a $1/lb of algae removed due to economies of scale. At 100 mg/L and 100 MGD, the mass of algae removed each day would be almost 40 tons.

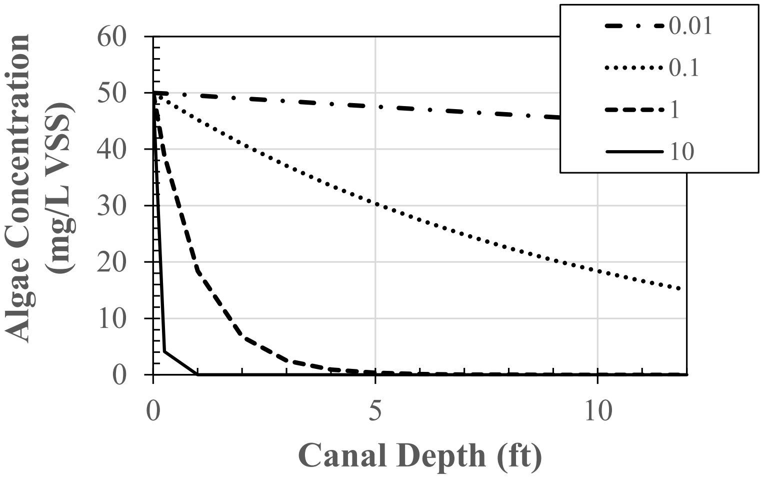
Figure 4-7. Cost estimates per pound of algae or phosphorous removal at varying ambient algae concentrations.



4.4.3 Effects of algae depth distribution

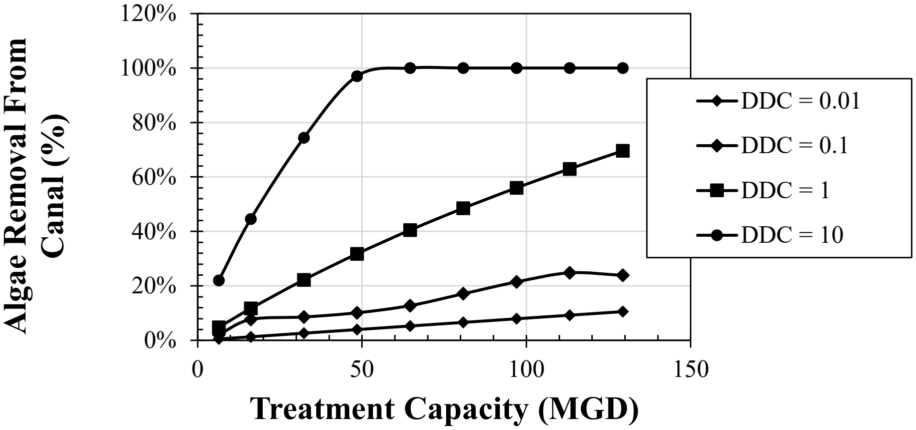
The common picture of HAB incidents typically includes a green slime layer floating on the surface of the water. The degree to which algae becomes concentrated near the surface has significant implications for whether or not it can be efficiently removed. To determine the impacts of the vertical distribution profile of algae in the water column on the predicted HABITATS performance at large scales, various vertical distribution profiles of algae were modeled assuming a fixed surface concentration of 50 mg/L and a spillway discharge rate of 2000 cfs. Figure 4-8 shows the variation in the amount of algae present as a function depth for these different scenarios.

Figure 4-8. Different algae depth distribution scenarios for a fixed surface concentration of 50 mg/L.



The resulting analysis clearly demonstrates the importance of targeting (or creating) environments where the algae is predominantly on the water surface (Figure 4-9), representing a high depth dilution coefficient. For cases when the algae is well distributed in the column, it is very difficult to have a significant impact on the canal water quality. This result is not entirely surprising, given the design of the interceptor system, which targets the surface.

Figure 4-9. Effect of algae depth dilution coefficient on algae removal (from canal) as a function of treatment capacity.



By combining the lessons learned from analyzing the effects of ambient algae concentration and the depth dilution coefficient, a clear path emerges for optimizing the HABITATS deployment. HABITATS will work efficiently and effectively for HAB events in which the algae is predominantly near the water surface at concentrations above 100 mg/L. For cases when the algae is more dilute or distributed, the benefits will be diminished, and the relative costs will increase.

This result from the scalability analysis model provides two key insights. First, for cases when algae predominantly floating at the water surface and not distributed in the water column, the scalability of the HABITATS process increases drastically, and the process will likely be practical in terms of cost, physical footprint, and energy. Second, for cases when algae is distributed throughout the water column, the HABITATS approach is not highly scalable. Achieving scalability in these situations will require new capabilities that can induce algae flotation and be applied efficiently and safely in natural water bodies, prior to interception. The use of benign chemicals and low energy aeration technologies should be explored for this purpose.

5 Conclusions and Path Forward

In July of 2019, key components of the HABITATS system were studied at a pilot test site upstream of Moore Haven Lock and Dam on the west side of Lake Okeechobee in Florida. While the test duration was limited by environmental conditions, several key advancements were made. The DAF process was proven highly effective in both clarifying the water and concentrating the algae, greatly reducing the volume of waste to be managed. The clarified and oxidized water had no measurable toxicity and greatly reduced levels of phosphorous and nitrogen, making it much cleaner and suitable for discharge into the environment. The concentrated algae biomass from the demonstration was then tested for transformation into biocrude fuel stock at PNNL. In addition to the technical advancements, several deficiencies in the current design were noted and will be corrected before the next demonstration. These relate to the type of coagulant used in the DAF process and the type of press used for downstream dewatering. The improved system will be integrated with HTL and validated at pilot scale in Year 2, pending funding.

Using the concepts and data from this study, an initial scalability analysis was performed to highlight potential benefits of HABITATS when deployed at scale. As designed, HABITATS is expected to be able to significantly reduce algae levels when deployed upstream of a spillway, with near complete removal of algae achievable for conditions when the algae is concentrated on the water surface. HABITATS is also projected by the scalability model to be net energy positive for ambient algae concentrations above 100 mg/L. In addition to confirming benefits, the scalability analysis helped to identify priority areas for optimization in future research.

After the first year of the research project, the data and scalability analyses indicate that the HABITATS approach offers great promise. However, further optimization and extended pilot scale validation studies are required before a truly scalable solution is available for deployment. The following research tasks are recommended:

- Modify the DAF process to use organic coagulants instead of inorganic coagulants in order to increase biocrude yields.
- Execute an extended pilot study, to include a pilot scale HTL unit, at a field site during an HAB event.

- Improve the throughput of algae biomass dewatering to enhance scalability by using a screw press instead of a belt press.
- Develop a shipboard HABITATS capability to attack HABs out on the open water while they are forming.
- Develop an efficient, environmentally-friendly capability to float subsurface algae in a natural water body.

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Acronyms and Abbreviations

Term	Definition
Abs	Absorbance
CFS	Cubic Feet per Second
COD	Chemical Oxygen Demand
DAF	Dissolved Air Flotation
DBP	Disinfection byproducts
DNA	Deoxyribonucleic Acid
DO	Dissolved Oxygen
DOM	Dissolved Organic Matter
EAA	Everglades Agricultural Area
EDTA	Ethylenediaminetetraacetic Acid
ELISA	Enzyme-Linked Immunosorbent Assay
EQ	Equalization
ERDC	U.S. Army Engineer Research and Development Center
FDEP	Florida Department of Environmental Protection
GPD	Gallons Per Day
HAB	Harmful Algal Bloom
HABHRCA	Harmful Algal Bloom and Hypoxia Research and Control Act
HABITATS	Harmful Algal Bloom Interception, Treatment, and Transformation System
HCL	Hydrogen Chloride
HTL	Hydrothermal liquefaction
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
M/V	Mass/Volume
MCE	Mixed Cellulose Ester
MGD	Million Gal/Day
NA	Not Applicable
NPDES	National Pollutant Discharge Elimination System
NTC	National Training Center
O&M	Operations and Maintenance
OECD	Organization for Economic Cooperation and Development
PC	Phycocyanin
PCR	Polymerase Chain Reactions
RFU	Relative Fluorescence Unit
SPC	Specific Conductance
STA	Stormwater Treatment Area
TAE	Tris, Acetic acid, EDTA
TE	Tris-EDTA
TN	Total Nitrogen
TOC	Total Organic Carbon

Term	Definition
TOrC	Trace Organic Contaminant
TP	Total Phosphorous
TPC	Total Pigment Concentration
TSS	Total Suspended Solids
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
VSS	Volatile Suspended Solids
WETT	Whole Effluent Toxicity Testing
WLEB	Western Lake Erie Basin

Unit Conversion Factors

Multiply	By	To Obtain
cubic feet	0.02831685	cubic meters
cubic yards	0.7645549	cubic meters
degrees (angle)	0.01745329	Radians
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
Feet	0.3048	Meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
horsepower (550 foot-pounds force per second)	745.6999	Watts
Inches	0.0254	Meters
Knots	0.5144444	meters per second
Microns	1.0 E-06	Meters
miles (U.S. statute)	1,609.347	Meters
pounds (force) per square inch	6.894757	Kilopascals
pounds (mass)	0.45359237	Kilograms
quarts (U.S. liquid)	9.463529 E-04	cubic meters
square feet	0.09290304	square meters
square miles	2.589998 E+06	square meters
square yards	0.8361274	square meters
tons (2,000 pounds, mass)	907.1847	Kilograms
tons (2,000 pounds, mass) per square foot	9,764.856	kilograms per square meter
Yards	0.9144	Meters

Appendix A: Demonstration Site Tour

Authored by Catherine Thomas, ERDC Environmental Laboratory
24 July 2019

Field Demonstration Summary for Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) Field Demonstration at Moore Haven Lock and Dam (Moore Haven, FL)

Collaborators Present: AECOM, South Florida Operations Office (USACE Jacksonville District), Florida Department of Environmental Protection, USACE ERDC (Vicksburg, MS), BLOOM, LLC (subsidiary of Algix)

Project Objective: Strategic removal of algae from water bodies and beneficial use of harvested biomass in a scalable manner.

Treatment Approach: Interception, Treatment, and Stabilization. In the interception process, algae contaminated water is directed into a collection basin. During treatment, the algae is separated and retained while the clarified water is polished via advanced oxidation, and released back into the lake. The stabilization phase involves HTL in which complete degradation of toxins is achieved within a time period between 15 to 30 minutes. The resultant material is a biocrude that can be upgraded to a biofuel, or can be used for other recyclable materials.

A.1 Interception

In the interception process, a boom weir (Figure A-1) is positioned downstream to leverage energy from water movement, focusing water flow into a weir skimmer (Figure A-2) equipped with a grinder pump. The grinder pump breaks up large solid particles (such as clumps of matted algae, hydrilla, etc.) that are pumped up to the treatment module. To control the depth of the box, a liquid ballast system is employed to achieve an appropriate weir height, which maximizes the volume of contaminated water to be collected. The collected water is pumped into a temporary storage tank. The boom skirt used in this application was 18 in. as the maximum concentration of algal growth is generally observed in the water column between 6-12 in. from the water surface. Figure A-3 shows an aerial view of demonstration site.

Figure A-1. Boom weir near canal lock and dam.

Figure A-2. Weir skimmer (silver box) positioned at opening of boom weirs.

Figure A-3. Aerial view of demonstration site.

A.2 Treatment

The treatment phase of the demonstration involved harvesting intact algae cells by way of dissolved air flotation (DAF) to separate the algae from the water. In preparation of the liquid-solid separation, the algae contaminated water is conditioned with an agglomerate (aluminum chlorohydrate) that causes the algal cells to clump into large particles, and a flocculant (polyacrylamide) that binds the finer particles. A stream of white water (non-contaminated water that is pressurized to generate microbubbles) is then introduced into basin. The affinity between the microbubbles and the algae cells drives the attachment of the algal clumps with the bubbles, causing the coagulated algae to float to the top of the treatment basin. After the liquid-solid separation, the top layer is then skimmed off. The concentrated algae is collected, and the clarified water is pumped into a secondary storage tank. From the secondary storage tank, the clarified water is pumped through an oxidation system using ozone and hydrogen peroxide as a polishing step to remove toxins from the effluent. The polished water is pumped into a tertiary storage container, tested for contaminants, and released back into the water body as appropriate. Upon generation of a sufficient volume of polished, clarified effluent, a portion of this water is then recycled into the pressurized system to generate the white water stream required for the liquid-solid separation. The pressurized, processed (oxidized) effluent is circulated back into to system at a rate of 20%-25%. Although scalable, the treatment rate of the demonstration system was 75 gal/min. Figures A-4 to A-15 illustrate a bench scale demonstration of the process taking place in the larger treatment containers.

Figure A-4. AECOM liquid-solid separation specialist adding clarified, processed effluent into a container that was subsequently pressurized using a manual air pump.

Figure A-5. Display of algae contaminated water to be treated in the bench scale demonstration.

Figure A-6. Demonstration of clumping taking place in algae water immediately after conditioning with coagulant and flocculant.

Figure A-7. Visible coagulation of algal cells within 2 minutes of adding reagents.

Figure A-8. AECOM specialist attaching tube from pressurized vessel containing clarified effluent to a separatory funnel before the separation process.

Figure A-9. AECOM specialist adding conditioned algae water into separatory funnel.

Figure A-10. AECOM specialist opening valve on pressurized vessel to introduce a small stream of microbubbles (white water) into the funnel. The volume of water pressurized was 25% of the volume of algae water being treated.

Figure A-11. Visible liquid-solid separation taking place in the funnel with 1 minute of incorporating the mircrobubbles into the algae solution.

Figure A-12. HABITATS liquid-solid separation compartment equipped with skimmer to remove separated algae.

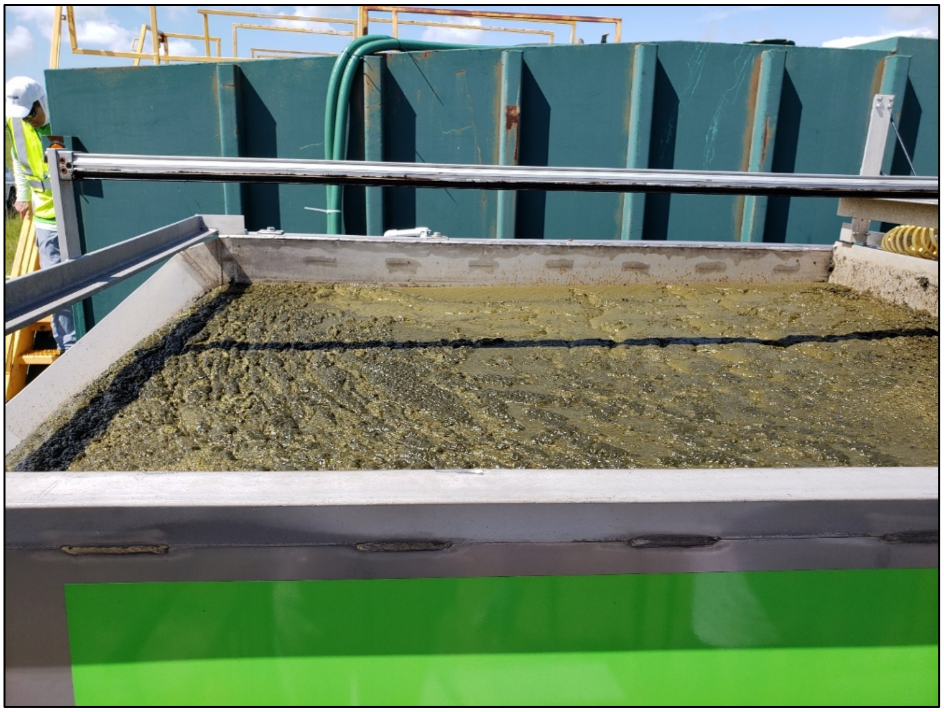


Figure A-13. Conditioning compartment of the HABITATS where coagulants and flocculants are added and mixed into the algae contaminated solution.

Figure A-14. Skimming of the separated algae into a collection tank.

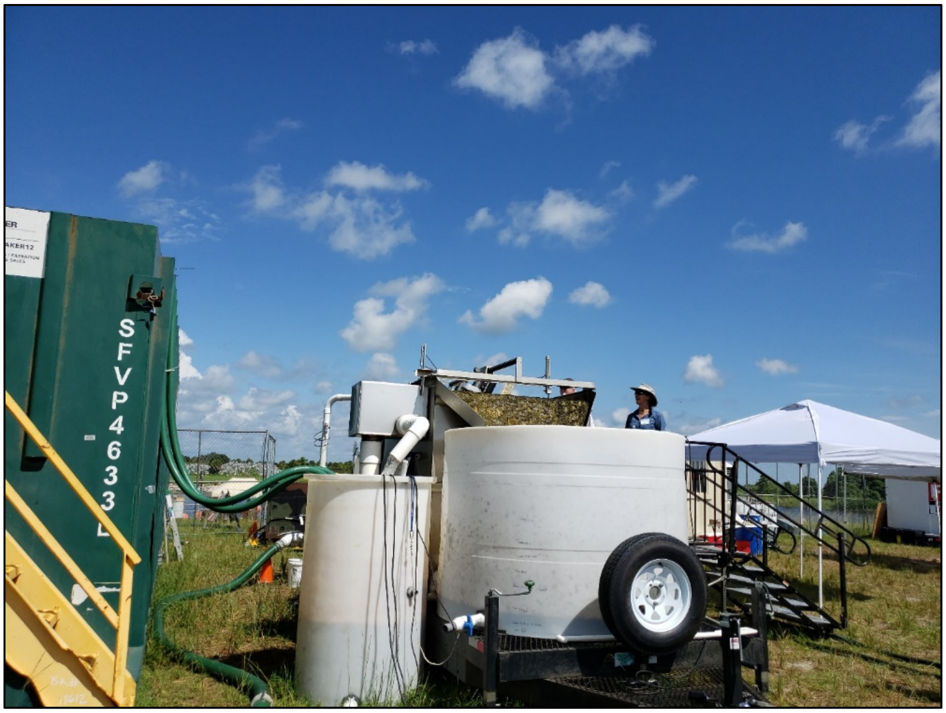


Figure A-15. Water treatment module where clarified water is oxidized to remove toxins from the solution.

A.3 Stabilization

HTL is performed to generate biocrude that can be upgraded into diesel, gasoline, and jet fuel and simultaneously stabilize the concentrated algae. HTL can also generate solids that can be recycled as fertilizers (containing iron, potassium, phosphorus, and nitrogen). Although HTL generally involves heating a wet biomass moderate temperatures (such as 350 °C) at high pressures (2900 psig), it has been found that the thermal deploymerization of the harvested algae can be achieved at a temperature of 250 °C, with no external means of pressurization as the pressure generated from the heated water inside the treatment digester is sufficient.

Other beneficial uses of the stabilized byproduct include the generation an activated solid, as well as the production of a wide range of recyclable polymers. Activated solids can be used for contaminant sorption. In the development of recyclable polymers, various types of products can be manufactured (Figures A-16 and A-17). Currently the company BLOOM, LLC is marketing footwear, sporting goods, and foams made with the stabilized algae in the United States. In the manufacturing process, the stabilized algae is dried at less than 10% moisture, and milled down to fine powder. The powder is then compounded or blended at 1:1 (algae: resin) ratio with various type of polymers depending on the end use application. The algae blended resins can then be converted via compression molding or injection molding to make a wide range of products.

Figure A-16. Dr. Edith Martinez-Guerra discusses the HTL process of algae depolymerization to generate usable feedstock materials.

Figure A-17. Sample products marketed by BLOOM, LLC made with stabilized algae recovered from the HABITATS. Demo products included footwear and foams.

A.4 Results

The two products yielded as a result of the interception and treatment process are the harvested algae, and the processed effluent (Figure A-18). The harvested biomass is further converted into usable and/or recyclable products, and the processed effluent is released back into the water body. The process ultimately yields no net waste material.

Figure A-18. Display of clarified, processed effluent (left container), algae water collected from the water body (center container), concentrated algal biomass recovered from the liquid-solid separation process (right container).

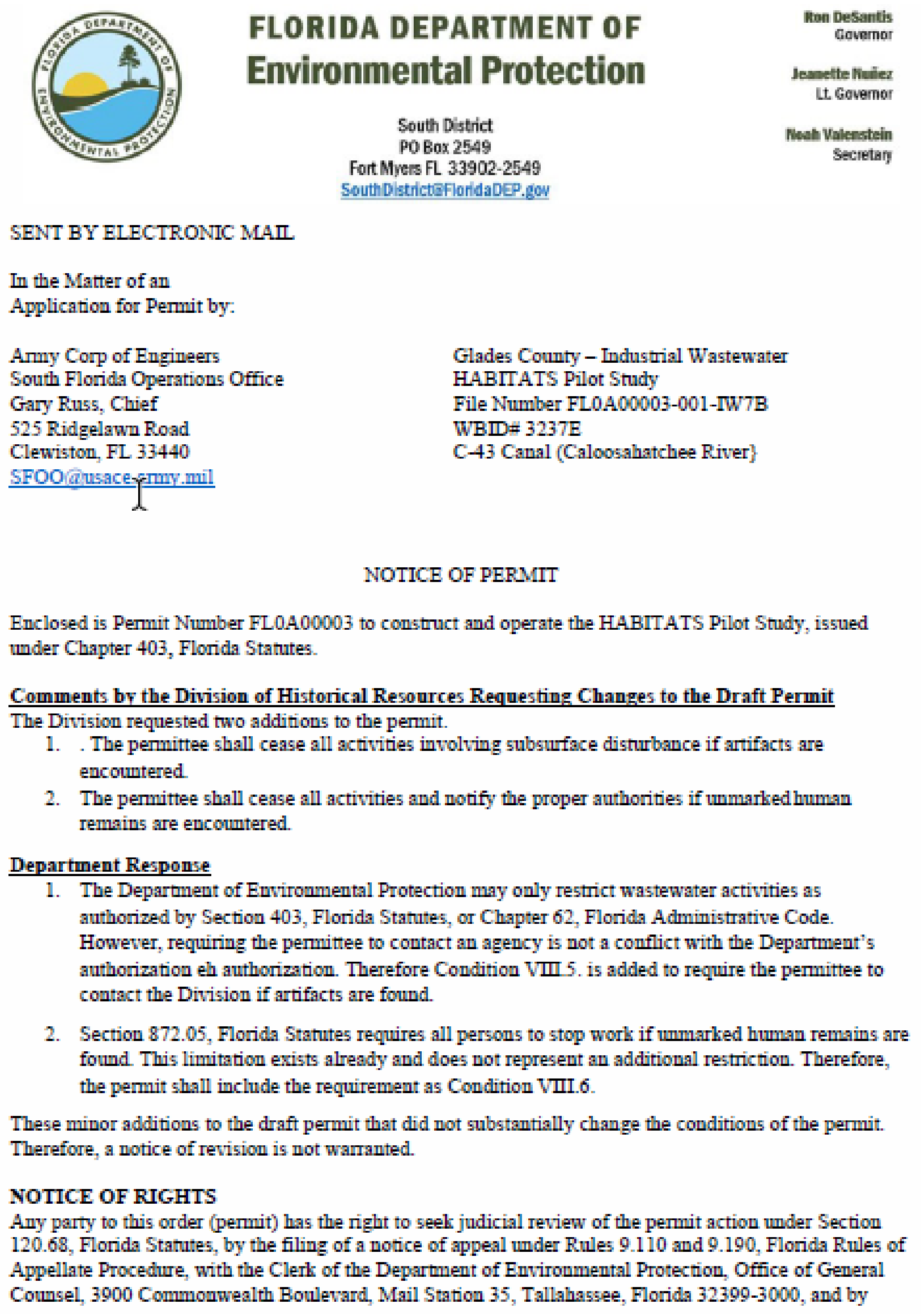
A.5 Conclusion

In conclusion, HABITATS can be considered as an energy neutral process in that it separates and recycles nutrients and produces a stabilized biomass that can be used as feedstock in the development of other materials. The benefits of this system include:

- The removal of HABs in the affected water body without introducing harmful chemicals into the environment
- The reduction in nitrogen and phosphorus concentrations from the treated water body as nutrients are harvested within the intact algal cells collected
- Stabilization and recycling of the harvested biomass, which eliminates costly disposal (Note that toxins present within the harmful algae would cause the material to be classified as a hazardous waste if not stabilized via HTL.)
- Scalability of the treatment system
- Small footprint of the system.

Appendix B: Environmental Discharge Permit

Figure B-1. Notice of 2CS permit for surface discharge of clean product water from the HABITATS project site, filed with the Florida Department of Environmental Protection.



FLORIDA DEPARTMENT OF
Environmental Protection

South District
PO Box 2549
Fort Myers FL 33902-2549
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Ron DeSantis
Governor

Jeanette Nuñez
Lt. Governor

Noah Valenstein
Secretary

SENT BY ELECTRONIC MAIL

In the Matter of an
Application for Permit by:

Army Corp of Engineers
South Florida Operations Office
Gary Russ, Chief
525 Ridgelawn Road
Clewiston, FL 33440
SFOO@usace.army.mil

Glades County – Industrial Wastewater
HABITATS Pilot Study
File Number FL0A00003-001-IW7B
WBID# 3237E
C-43 Canal (Caloosahatchee River}

NOTICE OF PERMIT

Enclosed is Permit Number FL0A00003 to construct and operate the HABITATS Pilot Study, issued under Chapter 403, Florida Statutes.

Comments by the Division of Historical Resources Requesting Changes to the Draft Permit
The Division requested two additions to the permit.

1. . The permittee shall cease all activities involving subsurface disturbance if artifacts are encountered.
2. The permittee shall cease all activities and notify the proper authorities if unmarked human remains are encountered.

Department Response

1. The Department of Environmental Protection may only restrict wastewater activities as authorized by Section 403, Florida Statutes, or Chapter 62, Florida Administrative Code. However, requiring the permittee to contact an agency is not a conflict with the Department's authorization eh authorization. Therefore Condition VIII.5. is added to require the permittee to contact the Division if artifacts are found.

2. Section 872.05, Florida Statutes requires all persons to stop work if unmarked human remains are found. This limitation exists already and does not represent an additional restriction. Therefore, the permit shall include the requirement as Condition VIII.6.

These minor additions to the draft permit that did not substantially change the conditions of the permit. Therefore, a notice of revision is not warranted.

NOTICE OF RIGHTS
Any party to this order (permit) has the right to seek judicial review of the permit action under Section 120.68, Florida Statutes, by the filing of a notice of appeal under Rules 9.110 and 9.190, Florida Rules of Appellate Procedure, with the Clerk of the Department of Environmental Protection, Office of General Counsel, 3900 Commonwealth Boulevard, Mail Station 35, Tallahassee, Florida 32399-3000, and by

Mr. Gary Russ
July 16, 2019
Page 2 of 2

filing a copy of the notice of appeal accompanied by the applicable filing fees with the appropriate distric court of appeal. The notice of appeal must be filed within 30 days from the date when this document is filed with the Clerk of the Department.

EXECUTION AND CLERKING

Executed in Fort Myers, Florida.
STATE OF FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

Jon M. Iglehart
Director of District Management

Attachment:
Permit FL0A00003

CERTIFICATE OF SERVICE

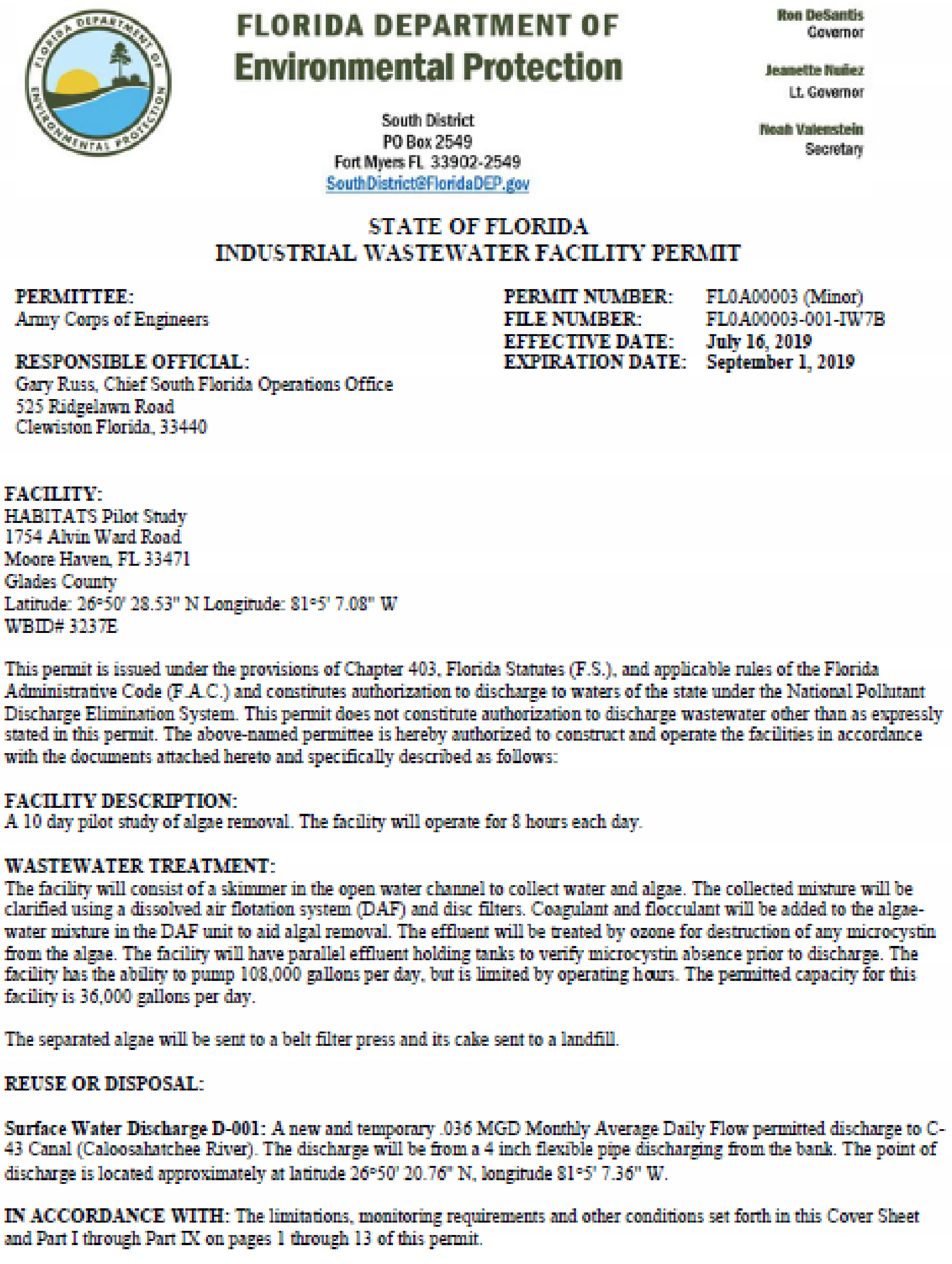
The undersigned duly designated deputy clerk hereby certifies that this document and all attachments were sent on the filing date below to the following listed persons:

Martin Page, Ph.D. (Martin.A.Page@usace.army.mil)
William Colona (william.colona@aecom.com)
Division of Historic Resources (Kristen.Hall@dos.myflorida.com)

FILING AND ACKNOWLEDGMENT

FILED, on this date, pursuant to Section 120.52, F. S., with the designated Department Clerk, receipt of which is hereby acknowledged.

Regina C. Dick July 16, 2019
Clerk **Date**



FLORIDA DEPARTMENT OF
Environmental Protection

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Governor

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Lt. Governor

Noah Valenstein
Secretary

STATE OF FLORIDA
INDUSTRIAL WASTEWATER FACILITY PERMIT

PERMITTEE:
Army Corps of Engineers

RESPONSIBLE OFFICIAL:
Gary Russ, Chief South Florida Operations Office
525 Ridgelawn Road
Clewiston Florida, 33440

PERMIT NUMBER:	FL0A00003 (Minor)
FILE NUMBER:	FL0A00003-001-IW7B
EFFECTIVE DATE:	**July 16, 2019**
EXPIRATION DATE:	**September 1, 2019**

FACILITY:
HABITATS Pilot Study
1754 Alvin Ward Road
Moore Haven, FL 33471
Glades County
Latitude: 26°50' 28.53" N Longitude: 81°5' 7.08" W
WBID# 3237E

This permit is issued under the provisions of Chapter 403, Florida Statutes (F.S.), and applicable rules of the Florida Administrative Code (F.A.C.) and constitutes authorization to discharge to waters of the state under the National Pollutant Discharge Elimination System. This permit does not constitute authorization to discharge wastewater other than as expressly stated in this permit. The above-named permittee is hereby authorized to construct and operate the facilities in accordance with the documents attached hereto and specifically described as follows:

FACILITY DESCRIPTION:
A 10 day pilot study of algae removal. The facility will operate for 8 hours each day.

WASTEWATER TREATMENT:
The facility will consist of a skimmer in the open water channel to collect water and algae. The collected mixture will be clarified using a dissolved air flotation system (DAF) and disc filters. Coagulant and flocculant will be added to the algae-water mixture in the DAF unit to aid algal removal. The effluent will be treated by ozone for destruction of any microcystin from the algae. The facility will have parallel effluent holding tanks to verify microcystin absence prior to discharge. The facility has the ability to pump 108,000 gallons per day, but is limited by operating hours. The permitted capacity for this facility is 36,000 gallons per day.

The separated algae will be sent to a belt filter press and its cake sent to a landfill.

REUSE OR DISPOSAL:

Surface Water Discharge D-001: A new and temporary .036 MGD Monthly Average Daily Flow permitted discharge to C-43 Canal (Caloosahatchee River). The discharge will be from a 4 inch flexible pipe discharging from the bank. The point of discharge is located approximately at latitude 26°50' 20.76" N, longitude 81°5' 7.36" W.

IN ACCORDANCE WITH: The limitations, monitoring requirements and other conditions set forth in this Cover Sheet and Part I through Part IX on pages 1 through 13 of this permit.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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01/01/2020

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Final Technical Report (TR)

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Harmful Algal Bloom Interception, Treatment, and Transformation System, “HABITATS”: Pilot Research Study Phase I- Summer 2019

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5b. GRANT NUMBER

5c. PROGRAM ELEMENT
96 x 3123; AMSCO 008284

6. AUTHOR(S)
Martin Page, Bruce MacAllister, Angela Urban, Chris Veinotte, Irene MacAllister, Kaytee Pokrzywinski, Jim Riley, Edith Martinez-Guerra, Craig White, Chris Grasso, Al Kennedy, Catherine Thomas, Justin Billing, Andrew Schmidt, Dan Levy, Bill Colona, David Pinelli, and Chandy John

5d. PROJECT NUMBER
476546

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Engineer Research and Development Center (ERDC)
Construction Engineering Research Laboratory (CERL)
2902 Newmark Drive
Champaign, IL 61824

8. PERFORMING ORGANIZATION REPORT NUMBER
ERDC TR-20-1

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Engineer Research and Development Center (ERDC)
Environmental Laboratory (EL)
3909 Halls Ferry Road
Vicksburg, MS 39180-6199

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Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Nutrient pollution and harmful algal blooms cost the Nation an estimated $1B each year. The U.S. Army Engineer Research and Development Center (ERDC) began research in the Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) project to develop scalable solutions for managing large harmful algal blooms (HABs), with the objective to develop a rapidly deployable system for mitigating large HABs at various design scales. The first year’s progress includes: (1) development and deployment of an interception technology that efficiently collects algae at the water surface; (2) validation of high throughput treatment using dissolved air flotation (DAF) technology to clarify algae-laden water; (3) oxidation of the DAF effluent using ozonation for removing microcystin and other potential cyanotoxins; (4) successful permitting with the Florida Department of Environmental Protection for discharging the treated water back to a surface water body at the demonstration site; (5) demonstration of rapid concentration of algae from a natural water source; (6) transformation of concentrated algae from the study site into biocrude oil at bench scale, and (7) development of a scalability analysis model to establish baseline estimates for full scale performance and cost.

15. SUBJECT TERMS
Algal blooms, Nutrient pollution of water, Water quality, Water quality management, Environmental protection, Environmental management

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER (include area code)**
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