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Optimizing the Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS)

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Abstract

Harmful algal blooms (HABs) continue to affect lakes and waterways across the nation, often resulting in environmental and economic damage at regional scales. The US Army Engineer Research and Development Center (ERDC) and collaborators have continued research on the Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) project to develop a rapidly deployable and scalable system for mitigating large HABs. The second year of the project focused on optimization research, including (1) development of a new organic flocculant formulation for neutralization and flotation of algal cells; (2) testing and initial optimization of a new, high-throughput biomass dewatering system with low power requirements; (3) development, design, assembly, and initial testing of the first shipboard HABITATS prototype; (4) execution of two field pilot studies of interception and treatment systems in coordination with the Florida Department of Environmental Protection and New York State Department of Environmental Conservation; (5) conversion of algal biomass into biocrude fuel at pilot scale with a 33% increase in yield compared to the previous bench scale continuous-flow reactor studies; and (6) refinement of a scalability analysis and optimization model to guide the future development of full-scale prototypes.

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Preface

This study was conducted for Headquarters, US Army Corps of Engineers (HQUSACE) under Funding Account Codes U4370803 and U4370802 and AMSCO Code 485293 under the Aquatic Nuisance Species Research Program (ANSRP) via Civil Works Direct Funding Program 3123, “CW Operations and Maintenance,” “HABITATS” Project. ANSRP is assigned to the US Army Engineer Research and Development Center (ERDC) under the purview of the Environmental Laboratory (EL). Mr. Jeremy Crossland was Acting ANSRP Program Manager, and Dr. Jennifer Seiter-Moser was Technical Director, Environmental Engineering and Sciences, Civil Works.

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

Executive Summary

Nutrient pollution and harmful algal blooms (HABs) cost the nation more than \$1B each year because of their impacts on tourism, health, commerce, and ecosystems (Dodds et al. 2009). The Water Resources Development Act of 2018¹ authorized the Engineer Research and Development Center (ERDC) of the US Army Corps of Engineers to perform research to develop scalable solutions for monitoring, preventing, and managing large harmful algal blooms, and this authorization was recently updated in 2020.² This report describes progress made during the second year of the multiyear Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) research project, which continues to be funded through the Corps' Aquatic Nuisance Species Research Program (ANSRP).

The HABITATS research project seeks to develop and demonstrate a scalable capability to remove algae and nutrients from large water bodies while simultaneously detoxifying and recovering resources from the resulting biomass. By the end of the HABITATS research project, the team intends to validate a rapidly deployable module that can be scaled for mitigating large HABs in an economically viable and sustainable manner. The study will create data-supported designs and models that enable stakeholders to fully assess adoption and implementation at a variety of design scales. As the fundamental unit of the full-scale capability, each HABITATS module will be able to treat up to 2 million gallons per day (MGD) of algae-contaminated water and be transportable on two tractor trailers. It is expected that a single module would be capable of remediating marinas or other confined areas within a week of deployment, whereas multiple modules could be deployed over months for large-scale HAB remediation projects at lakes, rivers, reservoirs, canals, and spillways.

HABs can span hundreds of square kilometers and as such require highly scalable mitigation measures. The key scalability challenges include efficient physical collection of the algae, treatment process throughput, waste

1. Water Resources Development Act of 2018, Pub. L. No. 115-270, 132 Stat. 3774 § 1109 (2018). <https://www.govinfo.gov/content/pkg/PLAW-115publ270/pdf/PLAW-115publ270.pdf>.

2. An Act to Make Technical Corrections to the America's Water Infrastructure Act of 2018, and For Other Purposes, S. 1811, 116th Congress (2020). <https://www.govinfo.gov/content/pkg/BILLS-116s1811eah/pdf/BILLS-116s1811eah.pdf>.

management, and economic feasibility. All these challenges are interconnected. HABITATS addresses the challenges in three complementary steps: interception, treatment, and transformation. In the interception step, algal cells are collected near 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 and then oxidized, creating 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 algal biomass is transformed into biocrude fuel and fertilizer via hydrothermal liquefaction to facilitate efficient resource recovery. A key breakthrough in the HABITATS project is the innovative coupling of high-throughput treatment with a rapid biomass transformation process. 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 the second year of the HABITATS research study, the team performed several pilot-scale field demonstrations aimed at improving the scalability and deployability of HABITATS while focusing on process integration and optimization. These studies provided critical data regarding process optimization and scaling. Key achievements included incorporation of new organic chemicals in the water treatment process to improve downstream fuel conversion as well as the first HABITATS pilot-scale demonstration of algae-to-fuel transformation using hydrothermal liquefaction and a higher-throughput, algae-slurry dewatering process with low power requirements. The majority of testing was performed using an onshore treatment system that was demonstrated in two different climates—Florida and New York. To create a capability to target blooms away from the shoreline, the team also designed and built a mobile shipboard HABITATS prototype and performed preliminary tests of the shipboard system. Economic models for HABITATS performance at full-scale were updated and used to identify priority areas for further improvement.

On the basis of progress made in 2020, the HABITATS team recommends optimization research and testing continue as the systems are deployed and tested at larger scales, including additional research on dewatering and in situ flotation prior to large-scale deployment. In the near term, a trailer-transportable module capable of treating up to 2 MGD could be assembled

and deployed for demonstration testing in parallel to the optimization studies to accelerate technology transfer. While integration is not yet fully optimized, given the success of both the water treatment and transformation portions system for algal biomass removal and transformation, these components could be considered in the near term for small-scale emergency applications where wastewater management infrastructure is available for processing filtrate water from the dewatering process and effluent from the hydrothermal liquefaction (HTL) unit.

Key successes of the 2020 pilot optimization studies

- *Development and validation of a new organic chemical approach for algal cell neutralization that increases the compatibility of the treatment and transformation processes.* In the past, an aluminum-based coagulant was used that is not convertible to fuel. In 2020, a combination of cationic starch coagulant with a low amount of cationic polymer was shown to be effective in water clarification and to be partially convertible to fuel.
- *Confirmation of microcystin toxin and nutrient removal by the dissolved air flotation (DAF) process prior to ozonation.* By physically removing algal cells during treatment, the DAF process also removed 50% of total nitrogen (TN), 90% of total phosphorus (TP), and 90% of total microcystin from the water, resulting in water that is safe for discharge back to the environment. In many cases, HABITATS will meet discharge quality requirements without requiring ozonation, a considerable energy savings.
- *Initial assessment and optimization of a high-throughput algae dewatering process to increase the rate of biomass processing.* A new screw-press approach was studied for dewatering the algal biomass that results from DAF treatment. Dewatering of the algal biomass is critical for fuel conversion efficiency, and previous HABITATS modeling indicated that available algae dewatering systems were a bottleneck with respect to scalability. The new screw-press approach exhibited a higher processing rate and improved energy efficiency compared to previously tested systems. A centrifugation process tested in parallel provided slightly better dewatering performance but at a higher energy cost.
- *First HABITATS demonstration of hydrothermal liquefaction at pilot scale.* The concentrated algal biomass from the demonstration sites was shipped to the Illinois Sustainable Technology Center (ISTC) for processing in a pilot-scale hydrothermal liquefaction reactor. A 33%

improvement in fuel conversion was demonstrated and was consistent or better than yield expectations for the conditions tested. According to the fuel yield data, the HTL process would be energy neutral at the current state and could be improved further if the algal biomass were dewatered further prior to hydrothermal treatment.

- *Expansion of environmental permitting for increased deployability.* In coordination with the Florida Department of Environmental Protection, a newly implemented multisite permitting process increased the ability of the HABITATS team to deploy to those areas most affected by HABs at a given time.
- *Demonstration of HABITATS in a northern climate.* The scope of the HABITATS validation study was expanded in 2020 in coordination with the New York State Department of Environmental Conservation to assess performance in a northern water body. Key water-quality parameters (pH, alkalinity, organic carbon) differed widely from previous studies in Florida, but the HABITATS system still performed well under the different environmental conditions.
- *Development of a shipboard HABITATS system.* ERDC worked with Elastec to design and build the first shipboard HABITATS prototype. Preliminary testing of mobility, flow, and controls was performed at Chautauqua Lake, New York.
- *Refinement of scalability analysis models* to estimate full-scale performance, energy consumption, physical footprint, and cost, including projections for large systems assembled from scalable, rapidly deployable HABITATS modules.

Key project challenges in 2020

- The shift to a new organic chemical formulation coupled with the new high-throughput dewatering process was not fully optimized before or during the field studies, resulting in an algal biomass solids concentration of 7%–10% versus the target of >18%.
- Because of the lower biomass concentration, the hydrothermal liquefaction process achieved a fuel yield of 20% versus a theoretical fuel yield target of >38%. While this was a 33% improvement in fuel conversion compared to the previous year, there remains a need to further optimize dewaterability of the algal biomass.
- The high oxygen content and hydrophilicity of the new organic flocculant materials may also be contributing to the limited fuel yields, as they were not fully convertible to fuel in control tests.

- COVID-19 affected the ability to deploy some of the equipment to project sites at the time of the demonstrations as well as the timeline for delivery of the shipboard prototype. All work was performed carefully using COVID-19 precautions, including masks for personnel at all times, social distancing, and rigorous sanitation.

Year 2 conclusions and recommendations for future research

After the second year of the research project, the data and scalability analyses indicate that HABITATS is approaching readiness for technology transfer. However, further optimization and extended validation studies are still required before a truly optimal solution can be recommended for deployment for large-scale HAB events. In the near term, the technology has applicability for small-scale HAB events, particularly in cases where algae are floating on the surface and where infrastructure is available for disposing of limited waste streams associated with the current dewatering and HTL processes. Those waste streams will be largely eliminated with future developments but must be considered as potentially limiting factors in near-term applications.

A key goal at the outset of the HABITATS project was to achieve energy neutrality for the entire operation, which requires sufficient fuel generation to offset the energy costs of the interception, treatment, and transformation processes. By improving fuel conversion yields this year, considerable progress was made toward this objective. Going forward, the current scalability model indicates energy neutrality is achievable if the influent algae can be preconcentrated to 120 mg/L and if the algal biomass can be dewatered to >18% solids. The following research tasks are recommended to achieve that goal while still scaling up the process:

- Develop an environmentally benign *in situ* flotation method to selectively lift subsurface algae to the surface of a natural water body such that it can be harvested more efficiently. This capability would simultaneously decrease the volume of water requiring treatment and increase the efficiency of the HABITATS process by increasing the concentration of algae in the influent. Ideally, this *in situ* flotation process will be a nonchemical, low-energy approach that leverages the existing HABITATS infrastructure and natural algae-flotation mechanisms.

- Increase biocrude yields from the hydrothermal liquefaction process by optimizing the chemicals used for charge neutralization during DAF and dewatering.
- Develop a mobile 2 MGD onshore HABITATS module to facilitate testing that represents a full-scale emergency response operation.
- Continue development and testing of the shipboard HABITATS capability to treat HABs out on the open water while they are forming. This open-water treatment system will increase capabilities for targeting dynamic bloom formation events and potentially limit bloom progression.
- Execute an extended study that includes on-site algal biomass management with hydrothermal liquefaction at a field site during a HAB response event.
- Make updates to hydrothermal liquefaction technology that include heat recovery, waste heat, and biocrude fuel utilization components as well as on-site treatment of the HTL aqueous stream.
- Demonstrate methods for nutrient recovery from the HTL process for agricultural reuse purposes.

1 Introduction

1.1 Harmful algal bloom (HAB) impacts on the nation

Harmful algal blooms (HABs) form in lakes and inland waterways because of nutrient pollution coupled with favorable thermal, illumination, and hydrodynamic conditions that facilitate rapid overgrowth of cyanobacteria. HABs are a physical manifestation of a process called eutrophication that can devastate the aquatic environment, threaten health, and disrupt economic activity at regional scales. Across the nation, HABs are estimated to cost more than \$1B annually because of impacts on tourism, property values, industry, and potable water supplies. HABs can persist for months, have the potential to produce potent cyanotoxins, and deplete oxygen in the water column when they decay. Unfortunately, the incidence of HABs is increasing across the United States and throughout the world, and the ability to control them is currently limited by economic and practical factors.

HABs would ideally be prevented through the control of nutrient pollution at or near the source such that lakes and waterways could maintain a healthy balance that supports ecosystems and human activities. Many of the key environmental pollution control measures in place today, such as centralized wastewater treatment plants, are designed and optimized for nutrient control, in addition to control of biodegradable matter and pathogens. However, given the growing frequency and intensity of HAB events, not all nutrient pollution sources are being sufficiently controlled. Climate change may also be creating conditions more favorable to HAB formation in some regions. In the near term, as the nation continues working to balance development and environmental protection in an economical and sustainable manner, there is an urgent need for rapidly deployable technologies that will reduce the environmental, health, and economic impacts of HABs.

Conventional approaches for HAB mitigation often involve the use of chemicals that inactivate or sink the algae, potentially reducing the short-term effects at a local scale but not actually removing the entrained nutrients from the water body. These symptom-focused approaches generally do not scale up because of economic or environmental reasons, and generally they do not target the underlying cause of the HABs—the

high levels of phosphorus and nitrogen nutrients in the water and sediment. Given that cyanobacteria can rapidly assimilate nutrients and carbon into their cells, temporarily sequestering those nutrients from the environment, physical removal of HAB biomass represents an opportunity for recovering nutrients and carbon from the water body. And the economic value of those nutrients otherwise being flushed out of the watershed or deposited on the bottom of the water body must be acknowledged.

Historically, economic barriers have hindered the physical removal of algal biomass from water even when performed in controlled settings such as algae raceway farms that use highly controlled algae cultures and recover resources. For HAB mitigation in natural environments via physical removal, management of potential toxins in the biomass presents an additional scalability challenge. Coupling these challenges with the unpredictability and dynamic nature of HABs in natural environments, most technical solutions become impractical because of logistical and economic factors.

The key challenges for large-scale HAB mitigation include efficient harvesting, treatment process throughput, waste management, and economic feasibility. All these challenges are interconnected. The Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) addresses these challenges simultaneously by integrating several high-throughput technologies that have been used individually for other applications. The integration of these technologies for large-scale HAB mitigation is novel and requires research to optimize and validate the approach. 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 employing resource recovery to reduce waste volumes, energy requirements, and cost.

Prior to the HABITATS project, the global engineering service provider AECOM demonstrated a high-throughput process for algae separation from water that uses dissolved air flotation (DAF) technology. While the process was effective and worked well for small-scale cleanup efforts, the scalability and deployability of the technology was limited because of environmental regulations for discharging the treated water back to the environment and limited capabilities for management of the potentially

toxic algal biomass produced by the system. In 2019, the US Army Engineers Research and Development Center (ERDC), AECOM, and Pacific Northwest National Laboratory (PNNL) performed proof-of-concept pilot studies to show that the HABITATS approach has tremendous potential for scalability.

1.2 Capability development requirement

Currently available technologies for HAB mitigation have limited practicality at large scales. However, further development may reduce the impacts of large HAB events through strategic placement of new technologies to facilitate early intervention and high-throughput treatment in key locations. If a mitigation approach could be more practical in terms of cost, labor, and logistics, it would provide an important tool to communities for HAB control that could complement longer-term programs focused on prevention.

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

SEC. 1109. 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.

In the fourth quarter of calendar year 2020, the Water Resources Development Act was updated, and the updates included the continued authorization of HAB mitigation research by the USACE.

1.3 Scope of research

Research conducted during the second year of the HABITATS project was largely guided by results generated in the previous study performed in 2019. The first phase of the HABITATS study took place at Lake Okeechobee in Florida using a combination of pilot-scale systems and laboratory-scale equipment. Results of the 2019 study are detailed in a previous technical report (ERDC TR-20-1, Page et al. 2020). The 2019 effort was a successful baselining and proof-of-concept study that supported technical feasibility of the HABITATS process, but it also highlighted several opportunities for improvement and optimization. At pilot scale, the AECOM DAF technology was coupled with an ozone system to address regulatory concerns about microcystin discharge back to the environment. The treatment system worked very well at pilot scale, clarifying the water, and concentrating the algal biomass effectively. The biomass was dewatered using a belt filter press and tested for conversion to fuel using a bench-scale continuous hydrothermal liquefaction system at PNNL. Biocrude fuel was generated with limited yields and then upgraded to diesel fuel. A preliminary cost and scalability analysis identified some gaps that would need to be addressed to improve the scalability and utility of HABITATS. The 2019 technical report recommendations included the following:

- Modify the DAF process to use naturally derived, organic coagulants instead of inorganic coagulants to increase biocrude yields from the downstream hydrothermal liquefaction process.
- Improve the post-DAF biomass dewatering to increase throughput, reduce energy consumption, and enhance scalability.
- Develop a shipboard HABITATS capability to treat HABs out on the open water while they are forming. Open-water treatment options will increase deployability for dynamic bloom formation events and potentially limit bloom progression.
- Execute an extended pilot study, to include a pilot-scale hydrothermal liquefaction unit in the field during a HAB event.

In 2020, the HABITATS research team performed three pilot-scale field demonstrations aimed at improving the scalability and deployability of

HABITATS while optimizing the integration of the components for interception, treatment, and transformation. Two of the pilot-scale field demonstrations used the onshore treatment approach, in which water was pumped from the water body, treated on the shore, and returned to the water body. The third pilot-scale field study explored a new shipboard approach that pumped water from a lake into a treatment system on a boat and then discharged the clean water back into the lake.

Figure 1-1 provides an example schematic for an onshore, pilot-scale demonstration. Algae-laden water is collected from a lake or waterway using floating skimmers. The contaminated water is pumped through an onshore treatment system that includes DAF and ozonation, with clean water being returned to the water body. The separated algae are concentrated and then transformed to biocrude fuel and fertilizer.

Figure 1-1. Example flow diagram for a pilot-scale, onshore Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) demonstration.

While deployable onshore systems will be appropriate in some HAB remediation scenarios, such as treatment of water upstream of a spillway to remove HAB biomass before it is discharged downstream, onshore systems have a very limited range of operations and cannot target a bloom forming away from the shoreline. An alternative approach is to develop boats or barges that bring the HABITATS capability to the bloom. Figure 1-2 shows a conceptual schematic for this pilot-scale, shipboard HABITATS approach, while Figure 1-3 is a design rendering of the shipboard concept, which includes two lead boats that tow a floating dissolved air flotation barge via two yellow booms that focus algae at the

water surface into the intake weir. A supporting utility barge provides power to the system and facilitates algae dewatering. In the shipboard system, the interception and treatment steps occur on the water body. Only the concentrated algal biomass is returned to the shoreline for conversion to fuel. In the future, for large-scale systems, fuel conversion and fuel utilization would also occur on the water, enabling a self-powered treatment system with a minimal logistical footprint. Only the trace amounts of inorganic solids (nutrients, salts) would need to be ferried to shore.

Figure 1-2. Example flow diagram for a shipboard HABITATS demonstration.

Figure 1-3. Rendering of a pilot-scale shipboard HABITATS prototype with a treatment capacity of 400 gal per minute (gpm).

Whether using an onshore approach or developing the new shipboard approach, most of the design challenges are similar. However, the

shipboard system design is challenged by the impacts of a dynamic water body and may not work well during wavy conditions. The shipboard system also brings additional energy requirements associated with the harvesting operation.

To optimize the onshore approach and to develop the shipboard system, the key research activities during Year 2 of the HABITATS project included the following:

1. Laboratory studies to identify and down select optimal organic flocculants for algae flotation
2. Identification of demonstration sites and preparation of environmental compliance documentation
3. Design and assembly of a new shipboard HABITATS prototype
4. Pilot-scale field demonstrations of onshore and shipboard systems to facilitate data collection.

1.3.1 Laboratory studies at US Army Engineer Research and Development Center (ERDC)

One of the key gaps identified during Phase I HABITATS testing in 2019 was the need to develop an organic flocculant for DAF that would theoretically increase the convertibility of the resulting algal biomass into fuel during hydrothermal liquefaction treatment. In 2019, the DAF system used an aluminum chlorohydrate (metal salt) coagulant for neutralizing algal cells prior to flotation. The DAF process with aluminum chlorohydrate proved highly effective in removing algal cells and entrained nutrients, producing clean water with no ecological toxicity. However, the added aluminum was adsorbed on the cyanobacterial cells and concentrated within the algal biomass, resulting in a very high inorganic content (30%–35%) within the biomass solids. The high inorganic content decreased fuel yields in the hydrothermal liquefaction process, and the aluminum precipitated out with other inorganic metals and minerals in the reactor, representing a significant solid waste stream that might also limit reuse of the solids and embedded phosphorus.

To increase the organic content of the biomass, the use of organic flocculants was evaluated in 2020 through laboratory-scale DAF testing at ERDC. Several candidate flocculants were identified and tested, and a decision matrix based on activity, ecological toxicity, and practical factors was used to identify an optimal chemical formulation for testing. Because

several of the candidate flocculants were not used previously for algae flotation, and ecological toxicity endpoints had to be generated by the HABITATS project team in many cases, finding a suitable organic flocculant became a challenging and complex task. This challenge was magnified by the COVID-19 pandemic, which reduced the availability of supporting laboratory facilities for extended periods of time. Despite the challenges, sufficient data were generated from these studies to inform pilot-scale designs and associated environmental risk analyses and permit applications.

1.3.2 Demonstration sites and environmental compliance

An additional lesson from the 2019 Phase I HABITATS study in Florida was the need to increase flexibility in demonstration site options for pilot testing. Because of the unpredictable and dynamic nature of HAB events, the research team concluded that a planned deployment to a single site for a specific window of time presents considerable project execution risks. To reduce this risk, the research team worked closely with the Florida Department of Environmental Protection (FDEP) to expand the range of candidate sites so testing could be performed during active HAB conditions.

The fiscal year 2020 (FY20) HABITATS geographical scope was also expanded beyond Florida to include a second demonstration in a northern climate. This northern demonstration was deemed important because of the potential process performance impacts of a colder climate and different water chemistry relative to the highly organic and eutrophic water bodies commonly studied in Florida. The state of New York was identified as a candidate demonstration region because of the large number of recurring HAB events at inland lakes as well as an active HAB mitigation technology demonstration program established by the New York State Department of Environmental Conservation (NYSDEC) at the direction of the State of New York.

1.3.3 COVID-19 impacts

Executing field research demonstrations in two states within a two-month window during the COVID-19 pandemic presented tremendous logistical challenges. Careful safety planning and coordination was implemented to ensure the safety of the team members and communities in which work was performed. No team members contracted COVID-19 before, during, or

after the field demonstrations. COVID-19 affected all the key project tasks in some way, with the most severe impacts on the timelines for the hydrothermal liquefaction (HTL) pilot studies and shipboard system fabrication and testing activities. Because of the seasonality of HABs and limited window for execution, delays in the HABITATS project schedule can hinder technical success. Even with accelerated permitting timelines, the seasonal nature of HABs at the demonstration sites constrained the dates for the demonstration tests. As such, scope adjustments were made as needed to enable completion of as much work as possible in a safe manner. Regional stakeholders played a key role in facilitating demonstration testing in a timely manner under challenging conditions.

As shown in Table 1-1, several of the tasks were pushed back or cancelled because of COVID-19 impacts on lab activities, prototyping, and field testing. Because of COVID travel impacts and laboratory closures, the HTL pilot studies were performed at the Illinois Sustainability Technology Center during October and November 2020 using algal samples collected (and preserved) during the July and August demonstrations. The shipboard system prototyping and testing were also affected significantly.

Table 1-1. Impacts of COVID-19 on project execution schedule.

Task	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Contracting Actions (ERDC)					>	>			
DAF & Ecotox Lab Studies-Flocculant Down-Selection (ERDC)		X	/	>	>				
Site Visits (ERDC)				X		/			
Permit Application and Review-FL (ERDC, FDEP)						>	>		
Permit Application and Review-NY (ERDC, NYSDEC)							>	>	
CRADA-NY (ERDC, NYSDEC)					>	>	>	>	
Boat Assembly (Elastec)							>	>	
Shipboard Treatment Equipment Assembly (ERDC)						X	X	>	

Task	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
On-shore Demonstration-FL (AECOM, ERDC)									
Shipboard System Float and Controls Testing (ERDC)							X		
On-shore Demonstration-NY (AECOM, ERDC)									
Shipboard Demonstration-NY (ERDC)								/	
HTL Pilot Testing (ISTC)							X	X	>

X: Activity Cancelled

>: Activity Delayed Relative to Plan

/: Scope of Activity Decreased Relative to Plan

1.4 Metrics for achieving scalability

Quantitative metrics were updated by the research team to guide optimization of HABITATS towards technical and economic scalability. These metrics are detailed in Table 1-2 and described in subsequent sections. To facilitate technology transfer, the HABITATS research project aims to develop a full-scale modular unit that can be multiplied to address HAB remediation scenarios of varying scale. It was determined through technical analysis of pilot-scale data and market research that the largest possible rapidly deployable module could be built and deployed on two trailers and treat up to 2 million gallons per day (MGD). This modular concept is used as the basis for the updated program metrics. As a reference, the pilot-scale treatment modules tested in 2019 and 2020 are about 10-fold smaller than the target full-scale module.

Table 1-2. Updated scalability metrics for the HABITATS project. (TN: total nitrogen; TP: total phosphorus; TSS: total suspended solids)

Attribute	Pilot scale testing (2019-20)	Full scale module (2021)
Flow rate	130 gpm	1,500 gpm (2 MGD)
Treatment performance	Cyanotoxin <1 ppb 50% TN removal 90% TP removal 95% TSS removal	Cyanotoxin <1 ppb 50% TN removal 90% TP removal 95% TSS removal Separated algae > 2% M/V

Attribute	Pilot scale testing (2019-20)	Full scale module (2021)
	Separated algae > 2% mass/volume (M/V)	
Dewatering	Algae biomass >15% M/V	Algae biomass >15% M/V
Transformation	Cyanotoxin destruction 37% oil yield	Cyanotoxin destruction 37% oil yield
Size or footprint	N/A	8.5 ft × 53 ft (× 2 ft) trailers per 2 MGD module 2,000 sf per module
Energy consumption	N/A	<1 Wh/gal
Annual cost	NA	\$1.5M per module Operations and Maintenance (O&M) to be determined (TBD)

The flow rate metric for a future full-scale module is 2 MGD—equal to three Olympic-sized swimming pools per day. Thus, a single module could clean up small areas such as marinas within a few days. For larger water bodies and higher flows, multiple modules would be required, and in these scenarios, it is not likely to be practical to treat all the water in a large lake or all the water passing through a large spillway. As such, the HABITATS interceptors target only the upper part of the water column, where algae tend to concentrate. Even with this targeted approach, treatment capacity and design footprint would be limiting factors. For example, treating the upper 5% of a water column flowing through a spillway operating at 2,000 cfs would require a treatment flow rate of 100 cfs, or 64 MGD, thus requiring 32 modules. To make this targeted approach even more efficient and also suitable to HAB scenarios in which the algae are uniformly distributed in the water column, research into inducing in situ flotation is ongoing, with the aim of reducing the required volumes of water to be treated.

- The treatment metrics were developed to achieve the water quality improvement required to directly discharge the water back into the environment. Algae removal, nutrient reductions, and water clarity improvements are expected and required features of the system. The destruction of microcystin in the product water to less than 1 ppb was also targeted, which is the guideline level limit for drinking water (WHO 1998) and well below the recreational guideline level limit of 8 ppb (USEPA 2019b).

- The dewatering and transformation metrics were developed using review papers of hydrothermal liquefaction performance with controlled algae feedstocks (Gollakota et al. 2018). Previous studies of hydrothermal liquefaction were performed in well-controlled environments such as biofuel production facilities or wastewater plants, whereas the present study uses algae from a natural, uncontrolled water source. The metrics aim to maximize the energy efficiency of the system by optimizing the HTL process. HTL does not require dry solids, making it favorable relative to other energy conversion or chemical feedstock processes, but it does require partial dewatering to at least 15% solids, preferably >18%.
- The size (or physical footprint) metric will be site specific for a given design scenario, but it is useful to consider the system in a modular manner. A single full-scale 2 MGD HABITATS module will be comprised of two 8.5 ft × 53 ft trailers, which require about 1,500 total square feet per module after considering worker access space and plumbing. Using the previous 2,000 cfs spillway as an example, which required 32 modules for treating the upper 5% of the water column, the site space requirement would be 48,000 ft², or just over 1 ac¹. An additional 0.5 ac would be needed for every 10 modules for supplies, vehicles, chemical storage, and personnel trailers, bringing the total space requirement to 2.5 ac per 100 cfs treatment capacity, which again could support a 2,000 cfs spillway by cleaning the top 5% of the water column where the algae are most concentrated during a HAB event.
- The energy consumption metric of 1 Wh/gal is based on typical energy requirements for municipal wastewater treatment (Department of Energy 2017). While the HABITATS processes demand significant energy (DAF, ozone, and hydrothermal liquefaction), it is expected that the energy recovery in the form of biocrude will largely off-set these demands. The long-term program goal is energy neutrality (0 Wh/gal), which will require preconcentrating the algae prior to interception in most natural settings, and the necessary in situ flotation methods are still in development.
- A preliminary capital cost metric of \$1.5M per deployable 2 MGD module has been developed and is expected to be achievable in the near term. As a reference point, historical costs of large-scale HAB

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

events of up to \$270M per year for a single water body have been reported (Smith et al. 2019), with annual costs of HABs estimated at over \$1B per year (Dodds et al. 2009). Particularly serious examples include HABs in southern Florida and western Lake Erie, which resulted in major economic impacts on tourism, real estate, healthcare, commercial fishing, and disposal of deceased animals. For perspective on costs of currently available solutions, 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. The capital cost alone would equate to \$67M per year over a 30-year period before considering escalation factors. The project includes a storm water treatment area (STA) to help control contaminants, in coordination with other existing STAs that represent additional sunk costs.

2 Materials and Methods

2.1 Site selection and environmental compliance

2.1.1 Florida demonstration site

The HABITATS team worked with FDEP and regional stakeholders to identify several candidate demonstration sites in Florida to ensure that the testing would occur during an active HAB event. To determine which sites should be included in the multisite permit application, a decision matrix was developed to score a large list of candidate locations. The top four candidate sites identified are shown in Table 2-1, along with the scores for each site against a list of site-selection criteria. Many of the decision matrix criteria were specific to a pilot-scale research demonstration at a specific point in time, and as such, the list of criteria and metrics for site selection and associated scores would be different for future deployment scenarios. In addition to HAB formation potential, important site-selection criteria with respect to the ERDC demonstration project included USACE mission relevance, site availability, intake and discharge feasibility, environmental impacts, and other logistical requirements.

Table 2-1. Candidate sites with selection criteria scores.

Site selection criteria	Lake Okeechobee Port Mayaca	Lake Okeechobee Moore Haven	Lake Jesup	Polk County (Saddle Creek)
Criterion 1: [Mission] The site is managed by USACE.	5	5	1	1
Criterion 2: [Site Availability] The site owner is supportive of a HABITATS demonstration at given time.	5	5	4	5
Criterion 3: [Water Quality] Algae is expected to be present at the site at the end of July (based on current Water Quality and discussion with site owner)	5	2	3	4
Criterion 4: [Intake] The water intake area (for the boom skimmer) is accessible by water and land, and the intake will not disrupt boat traffic, and has sufficient locations for the booms.	3	5	2	5
Criterion 5: [Discharge] The effluent discharge area (Class III water body) has sufficient depth to avoid sediment suspension issues, sufficient volume/flow to facilitate effluent dilution, and will not impact the influent/intake quality.	4	5	1	4

Site selection criteria	Lake Okeechobee Port Mayaca	Lake Okeechobee Moore Haven	Lake Jesup	Polk County (Saddle Creek)
Criterion 6: [Space] The site has level, compacted areas for all the equipment- 2 fenced-in areas that are each ~80 ft × 100 ft, and the site setup would not have negative environmental impacts	4	5	1	5
Criterion 7: [Surroundings] Work will not disrupt the public and site access can be controlled.	5	5	3	5
Criterion 8: [Waste] Waste disposal facilities for liquid and solid waste streams are available in the area.	4	5	5	5
Criterion 9: [Logistics] The site is amenable to large equipment (trailer) deliveries	5	5	3	5
Criterion 10: [Boat Access] The site is near a boat ramp.	3	5	1	4
Criterion 11: [Waves, Mixing] The water surface is relatively tranquil.	4	3	1	4
Criterion 12: [Facilities] The site has logistics support facilities available.	5	4	1	3
Criterion 13: [COVID] The site, area lodging, and population density allow for DoD COVID safety compliance measures.	5	3	1	5
Total	57	57	27	55

A multisite 2CS permit for the four sites was filed with FDEP on June 5, 2020. The permit was published for public comment and agency review for 45 days before issuance. The permit application included detailed descriptions of the treatment methods and chemicals to be used, descriptions of the site locations, and demonstration protocols for quality control and assurance. Appendix A includes a copy of the issued permit.

On the basis of environmental surveys during the first half of July 2020, the team decided to set up the onshore system at Port Mayaca Lock and Dam (Figure 2-1). Equipment was set up to the north of the dam during the week of July 19, 2020. However, weather conditions changed, and cyanobacteria were not present at the site during the test period.

Figure 2-1. Candidate demonstration site at Port Mayaca Lock and Dam on the east side of Lake Okeechobee in Florida.

In coordination with FDEP and Southwest Florida Water Management District, the team relocated the equipment to a site adjacent to a spillway on Saddle Creek in Polk County, Florida (Figure 2-2). In addition to an ongoing algal bloom, the Saddle Creek site provided many favorable features for pilot-scale testing, including a secure test area for the equipment, a spillway to separate the intake and discharge locations, and a receiving water body flow rate of up to 100 ft³/s to provide a high level of dilution of the discharge water from the pilot site. AECOM relocated and set up the floating water intake, a 130 gpm DAF and ozone system, a screw press, and supporting equipment to the Saddle Creek site. An ERDC research team was on-site for water quality analysis and performance monitoring. The trailer-mounted, pilot-scale HTL system could not be deployed to the Florida demonstration because of COVID-19 impacts. Biomass material from the Florida demonstration site was preserved and transported to the Illinois Sustainable Technology Center (ISTC) for pilot-scale HTL validation testing.

Figure 2-2. HABITATS demonstration site at Saddle Creek spillway in Polk County, Florida.

2.1.2 New York site down selection and permitting

The HABITATS team worked with the NYSDEC to identify a candidate demonstration site that could facilitate pilot-scale demonstrations of both the onshore and shipboard HABITATS prototypes. The site down selection process leveraged previous work by the state's Water Quality Rapid Response Team that is part of the State of New York's HAB initiative. The initiative identified priority lakes with varying susceptibility to HABs and collaborated with a multitude of experts and stakeholders to draft HAB action plans for each lake (New York State's Water Quality Rapid Response Team n.d.). New York State had also funded and monitored a previous demonstration by AECOM for treatment of HABs with DAF and ozone in 2019. After reviewing the HAB action plans and discussing with NYSDEC, a HABITATS collaboration between USACE and NYSDEC was formalized through the development of a cooperative research and development agreement (CRADA).

Using a similar decision matrix approach, including the requirements for lake depth and water quality representative of northern lakes, USACE and NYSDEC identified Chautauqua Lake as a suitable location. Chautauqua Lake was selected because of the consistency, intensity, and duration of algal bloom formation, the relatively calm surface, and moderate size. The 13,422 ac Chautauqua Lake is used both recreationally and for drinking water by thousands of people in Chautauqua County, New York. The lake has a mean depth of 25.6 ft, length of 16 mi, and shoreline of 42.5 mi. The lake contains a north and a south basin, which act as individual water bodies to some extent because of contrasting depths and the physical

separation by a restricted central channel. The lake, the services it provides, and the ability of residents and visitors to recreate are regularly threatened by HABs that result from excessive nutrients (for example, phosphorus and nitrogen) entering the watershed from a broad range of sources, including wastewater treatment plants, septic systems, runoff from agricultural and urban lands, and more. Since 2012, over 298 HAB sightings have been reported, resulting in 22 beach closures and 286 lost beach days (New York State's Water Quality Rapid Response Team n.d.)

Long Point State Park at Chautauqua Lake served as the USACE base of operations for the HABITATS New York demonstration. The park is located along the southeast shore of the north basin. The park provided slips for five HABITATS boats as well as a level field area where a mobile laboratory and supporting equipment were set up. Initially, the onshore system was to be tested at the park, and the shipboard system was to be tested in the southern basin (Figure 2-3). However, because of unseasonably low algae levels at the park marina during the weeks prior to scheduled testing, the onshore test was relocated to the southern basin and hosted by the Chautauqua Lake Association in Lakewood, New York. AECOM executed the onshore demonstration of water treatment and algae dewatering technology at this location during the week of August 23, 2020, and an ERDC team coordinated water testing and analysis.

The shipboard system was completed later than scheduled because of COVID and other impacts on supply chains for the custom prototype. As a result, initial testing was delayed until the subsequent week (August 30, 2020). Because of unseasonably large waves in the southern basin during the test period, the shipboard system had to be tested in the north basin, where the open-water algae levels were very low. Because of the delays and the environmental conditions, the shipboard system was only subjected to flow and controls optimization testing, and treatment performance could not be validated.

The trailer-mounted, pilot-scale HTL system was also not deployed to the New York demonstration because of COVID-19 impacts. Biomass material from the New York onshore demonstration site was transported to the ISTC for pilot-scale HTL testing at a later time. Because of the low algae levels in the north basin, there was not enough biomass generated in the shipboard test to support HTL testing.

A quality assurance project plan (QAPP) was developed and submitted to the NYSDEC as part of the New York HABITATS demonstration at Lake Chautauqua (see appendix B). The QAPP outlined the background and purpose of the study, the water treatment process plan, data acquisition, and management. The review process included chemical, physical, and biological environmental risk assessments by NYSDEC staff. A public webinar detailing the project and demonstration plan was held on July 21, 2020, to facilitate public review and comment.

Figure 2-3. Locations of HABITATS demonstration sites at Chautauqua Lake in western New York.

2.2 Pilot operations

2.2.1 Onshore testing at Saddle Creek, Florida

The Florida HABITATS demonstration at Saddle Creek occurred from July 24 to 29, 2020. The DAF (Figure 2-4) and ozone systems were operated during the daytime at a flow rate of 130 gpm. The hydraulic residence time of the DAF system was 5 min in the flocculation tank and 15 min in the flotation chamber. The floating intake structure was placed 20 ft upstream of the spillway, and the floating discharge hose was placed 30 ft downstream of the spillway. Jar testing was performed on-site to guide coagulant and flocculant dosing. Volumes of chemicals used and dosing levels were carefully monitored by ERDC for the duration of the testing. The Tramfloc 222 target dose ranged from 0.2 to 0.4 ppm, and the target dose of Greenfloc GFT 5100 ranged from 10 to 100 ppm, depending on the coagulant demand of the water source, with an average dose of 24.6 ppm over the entire demonstration. After DAF treatment and ozonation, the

water was stored in a 20,000-gal frac tank prior to discharge. The frac tank volume provided sufficient hydraulic retention time during which on-site measurement of microcystin levels could be performed to confirm levels were below 1 ppb prior to discharge. Real-time monitoring of effluent pH, flow rate, and ozone concentration was performed by AECOM and its subcontractors. Grab samples were collected by ERDC for on-site analysis of microcystin and turbidity every 90 min of operation. Jar tests were performed at similar intervals to guide coagulant dosing.

Figure 2-4. Onshore dissolved air flotation (DAF) (left) and screw press (right) treatment systems at the Saddle Creek test site in Florida.

The algal slurry generated by the DAF system was stored in a large polyethylene tank prior to dewatering. A screw-press method was used for dewatering, and the screw press (MS 600, Press Technology and Manufacturing [PT&M], Springfield, Ohio) was operated at approximately 1 gpm (pictured in Figure 2-4). Because this was the first field test of the screw press for this application, and the performance did not meet design objectives during testing, the filtrate water was collected in a tank and disposed of at an approved wastewater treatment facility rather than being recirculated to the DAF influent line. The algal biomass solids from the screw press were intended to be processed on-site using a pilot-scale HTL unit. However, because of COVID travel restrictions, the biomass was instead collected, chilled, and transported to the Illinois Sustainability Technology Center at the University of Illinois for pilot-scale testing at a later date. The mobile HTL trailer is shown in Figure 2-5 and has a treatment capacity of 0.2 gpm of algal solids.

Figure 2-5. Mobile hydrothermal liquefaction (HTL) system for algal solids transformation, developed by and located at the Illinois Sustainability Technology Center at the University of Illinois–Urbana-Champaign.

2.2.2 Onshore testing at Chautauqua Lake, New York

The onshore test was hosted by the Chautauqua Lake Association in Lakewood, New York, on the south shore of Chautauqua Lake (Figure 2-6 and Figure 2-7). Testing was performed in a manner like the Florida test described in section 2.2.1. However, several operational improvements were made based on the Florida results, including use of a more compact ozonation system and several improvements to the screw-press process that increased its flow rate and the solids recovery ratio. The water treatment flow rate for the test was lower than that of the Florida test, with operations conducted at 89 gpm during the daytime over a five-day period from August 24 to 29, 2020.

Figure 2-6. Pilot scale onshore DAF system at the Chautauqua Lake Association property on the southern shoreline of Chautauqua Lake in Lakeland, New York (August 2020).

Figure 2-7. Panoramic photograph of the AECOM test setup at the Chautauqua Lake Association property on the south shore of Chautauqua Lake in Lakewood, New York. The left tent was used for water quality analysis. The ozonation trailer was under the tent in the middle of the photo. The screw press and the DAF system are shown on the right.

2.2.3 Chautauqua Lake, New York, shipboard system

A first-of-its-kind shipboard HABITATS system was designed, assembled, and subjected to preliminary field testing. Field testing of the shipboard HABITATS prototype followed the onshore HABITATS test on Chautauqua Lake and was conducted from August 30 to September 03, 2020. The testing was limited in scope and duration by climate and environmental conditions during the test period. Because of delays in production supply chains, preliminary tests on boat operability, load balancing, microbubble aeration rates, and pump flow were performed at the field site over the first two days with no chemical addition. After

preliminary operations testing, controls testing was performed at a flow set point of 120 gpm. On the last two days of testing, chemical dosing controls were tested along with integration of the ozonation and UV systems. Because of the limited concentration of algae in the source water, the screw press could not be tested, and quantities of biomass harvested were insufficient for pilot-scale HTL testing.

The shipboard interception system consisted of two lead boats with two 50 ft tow booms connected to a floating weir skimmer intake on the front of a trailing DAF barge (Figure 2-8). The influent skimmer width was 7.5 ft, and the skimmer was protected with a 3/8 in mesh screen to reject aquatic plant material and aquatic organisms. During testing, the top of the weir was typically 1–1.5 in below the waterline, predominantly targeting the surface of the lake. The boats and barges were custom designed by Elastec, a global supplier of oil spill cleanup and environmental remediation equipment. ERDC installed the pumps, floc tubes, DAF equipment, and the electrical and plumbing systems.

Figure 2-8. Aerial photograph of the shipboard HABITATS prototype undergoing initial flow testing in the northern basin of Chautauqua Lake, New York (September 2020). Photo credit: John Kennedy, NYSDEC.

The DAF barge consisted of two pontoons spanned by an equipment deck and a large 7,500-gal bladder submerged in the water between the pontoons. The bladder was retractable, providing a draft of 4.5 ft for launching that extends to 7.5 ft during operation. The DAF barge length was 23 ft, and the beam was 10.5 ft. The pontoons were also retractable onto the top deck to reduce the road-transport width to 8.5 ft for rapid deployability (Figure 2-9).

Figure 2-9. Photographs of the deployable DAF barge equipped with retractable pontoons (left) and pumps and floc tubes above deck (right).

The top deck was equipped by ERDC with a 240 ft serpentine floc tube assembly, including two 3 hp intake suction pumps, flocculant dosing pumps controlled by a Micrometrix streaming current analyzer, static mixers at flocculant injection ports, a 15 hp Rogue-75 whitewater pump, two 3 hp effluent pumps, and a power distribution panel. Magnetic flowmeters were used to continuously measure influent, effluent, and recirculation flow rate. Flow was controlled manually using ball valves. The target recirculation flow rate was 25% of the influent flow rate. The Rogue whitewater pump generates microbubbles without an air compressor and was operated at a backpressure of 75–80 psi. Recirculation flow was blended into the influent flow in the last stage of the floc tube apparatus. A chain-and-flight scraper was installed below the deck to facilitate collection of floated biomass from the top of the DAF

bladder. The scraper was designed to pull algal biomass into a 200 gal hopper at the stern.

2.3 Water quality test methods

Validation of water quality improvement remained a primary focus in the second year of the HABITATS study because of the significant change in treatment chemicals for algae neutralization and flotation. To this end, the water quality of the influent source water and the treated product water were carefully assessed. Water quality testing included measurement of specific contaminants such as nutrients and microcystin, bulk parameters such as total organic carbon and volatile suspended solids, and indirect measurements such as ecological toxicity of the effluent waters and individual chemicals used. While the planned end use of the HABITATS effluent water is direct discharge back to the environment, profiling of drinking water contaminants, including disinfection byproducts, was conducted to identify any potential concerns if the water were to be used as a drinking water source or discharged proximal to a drinking water treatment plant intake.

2.3.1 Whole effluent toxicity (WET) testing

The US Army ERDC and contracted certified laboratories conducted standard whole effluent toxicity (WET) testing associated with National Pollution Discharge and Elimination System (NPDES) requirements on product water samples collected during a field demonstration for algae control. For each demonstration, a 20-gal composite sample of effluent was collected over a 24 h period.

For ecological hazard testing in compliance with the permitting process of the FDEP and NYSEC, a freshwater hazard assessment of the product water solution from each system 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 *Ceriodaphnia dubia*, and the fish species was *Pimephales promelas*. *C. dubia* was selected as a more suitable test species because of its high sensitivity to a diverse range of environmental toxicants, the test requires less water volume, and its associated chronic test method is shorter relative to *Daphnia magna*.

2.3.1.1 *Ceriodaphnia dubia* acute toxicity test

C. dubia (commonly known as the water flea) bioassays were performed in accordance with the standard method for effluent discharges to receiving systems (USEPA 2002a). Bioassays were conducted in an environmentally controlled room (Darwin Environmental Chambers, St. Louis, Missouri) to maintain temperature ($25 \pm 1^\circ\text{C}$) and photoperiod (16 h light:8 h dark). Test organisms were <24 h old neonates, obtained from ERDC–Environmental Laboratory (ERDC-EL) in-house cultures (originally received from ECTesting, Superior, Wisconsin). Neonates were provided a feeding ration of 1:1 algae (*Pseudokirchneriella subcapitata*, formerly *Selenastrum capricornutum*) and yeast-cereal leaves–trout chow mix (YCT) for at least 2 h prior to testing. Each test concentration was replicated four times ($n = 4$), and each experimental replicate was a 20 mL glass scintillation vial containing 20 mL test solution and five organisms. Moderately hard reconstructed water (MHRW) formulated according to EPA-821-R-02-012 was used as the dilution water and control. The assessment endpoint was survival after 48 h of exposure.

2.3.1.2 *C. dubia* chronic toxicity test

C. dubia were exposed to the test waters for 7 d (three brood test), using the standard method for effluent discharges to receiving systems (USEPA 2002b). Bioassays were conducted in an environmentally controlled room to maintain temperature ($25 \pm 1^\circ\text{C}$) and photoperiod (16 h light:8 h dark). Cladocerans were <24 h old neonates, obtained from ERDC-EL in-house cultures (originally received from ECTesting, Superior, Wisconsin). Neonates were provided a feeding ration of 1:1 algae (*P. subcapitata*, formerly *S. capricornutum*) and YCT daily immediately after each 100% daily water exchange. Each daily water exchange consisted of freshly diluted effluent. Each exposure concentration was replicated 10 times ($n = 10$), and each experimental replicate was a 20 mL glass scintillation vial containing 20 mL test solution and one organism. The MHRW formulated according to EPA-821-R-02-013 was used as the dilution water and control. The assessment endpoint was survival and reproduction (average number of neonates) after three broods (7 d).

2.3.1.3 *Pimephales promelas* acute toxicity test

P. promelas (fathead minnow) was exposed to the test waters for 48 to 96 h according to the standard method for effluent discharges to receiving

systems (EPA 2002a). Bioassays were conducted in an environmentally controlled room to maintain temperature ($25 \pm 1^\circ\text{C}$) and photoperiod (16 h light:8 h dark). The fish were shipped as <24 h old larvae from Aquatic Biosystems (Fort Collins, Colorado) and held (receiving a daily feeding ration) and tested as four-day-old fish. During the 96-h acute toxicity test, the fish larvae were provided a feeding ration of brine shrimp (*Artemia nauplii*) at 24 and 72 h. One water exchange was conducted at 48 h of exposure and consisted of freshly diluted effluent. Each test concentration was replicated four times ($n = 4$), and each experimental replicate was a 250 mL glass beaker containing 200 mL test solution and 10 individuals. The MHRW was used as the dilution water and control. The assessment endpoint was survival after 96 h.

2.3.1.4 *P. promelas* chronic toxicity test

P. promelas was exposed to the test waters for 7 d using the standard method for effluent discharges to receiving systems (USEPA 2002b). Bioassays were conducted in an environmentally controlled room to maintain temperature ($25 \pm 1^\circ\text{C}$) and photoperiod (16 h light:8 h dark). Since the fish were shipped as <24 h old larvae from Aquatic Biosystems (Fort Collins, Colorado), and the shipped fish required 24 h acclimation, the age of the test larvae was <48 h. Larvae were provided a feeding ration of brine shrimp (*Artemia nauplii*) after each 100% daily water exchange. Each test concentration was replicated five times ($n = 5$), and each experimental replicate was a 600 mL glass beaker containing 400 mL test solution and 10 individuals. The MHRW was used as the dilution water and control. The assessment endpoints were survival and biomass and growth after 7 d.

2.3.1.5 Reference toxicity tests

The selected reference toxicant for *P. promelas* and *C. dubia* was potassium chloride. In-house *C. dubia* cultures were used for test organisms. Reagent-grade potassium chloride was weighed and completely dissolved in MHRW. Five triplicated concentrations were prepared (100%, 50%, 25%, 12.5%, 6.25%) with the number of organisms in each replicate previously described. For acute tests, the 100% concentration was 2.7 g/L for *P. promelas* and 1.0 g/L for *C. dubia*. For chronic tests, the 100% concentration was 1.0 g/L for *P. promelas* and 0.5 g/L for *C. dubia*. Test endpoints measured were the same as previously described in the acute and chronic testing sections.

2.3.1.6 Toxicity assay water quality monitoring

Water quality during bioassay testing was measured using a YSI Pro Plus multiparameter meter (YSI, Yellow Springs, Ohio) equipped with a model 5560 conductivity cell, a model 1001 automatic temperature compensating pH Triode, and a 2003 Polarographic Dissolved Oxygen Sensor for electrical conductivity, pH, and dissolved oxygen, respectively.

2.3.1.7 Toxicity data analysis

The lethal median concentration producing 50% mortality (LC₅₀) and inhibition concentrations to 50% and 25% of the test organisms (IC₅₀, IC₂₅) for sublethal endpoints were determined by the trimmed Spearman–Karber method (Toxcalc, Version 5.0, Tidepool Scientific Software, McKinleyville, California). The LC₅₀ and IC₂₅ values are presented with 95% confidence limits in parentheses. No observable effect concentrations (NOEC) and lowest observable effect concentrations (LOEC) were also calculated using ToxCalc v5.0. Maximum allowable concentrations (MATC), also known as the chronic value (ChV), were calculated as the geometric mean of the NOEC and LOEC. The acute-to-chronic ratio (ACR) was calculated as the 48 hr LC₅₀ divided by the MATC. The sublethal endpoints for the chronic tests (IC₂₅) included reductions in reproduction, measured as the average number of surviving neonates (*C. dubia*), and growth, measured as post-test biomass (*P. promelas*).

2.3.1.8 Ecological toxicity of individual chemicals

The same methods used for whole effluent toxicity measurement were applied to measure the toxicity of specific chemicals used in the study, including cationic starch (GFT 5100, Dober Chemical) and low charge-density cationic polyacrylamides (TF300 and TF222, Tramfloc). Acute and chronic toxicity measurements were made for a full series of two-fold dilution from 100 ppm to 0.125 ppm for each chemical. Data for other chemicals were already available from manufacturers.

2.3.2 Treatment performance samples

Grab and composite samples were collected one to three times daily on-site, preserved, and shipped to government and contract laboratories. The laboratory analyses were focused on parameters of relevance to HABs, including nutrients, total organics, and solids concentrations. Details on sampling protocols are in the NYSDEC Quality Assurance Plan in

appendix B. An overview of parameters and associated methods is provided in Table 2-2. Testing requirements for the Florida demonstration are described in the associated permit found in appendix A. In addition to monitoring influent and effluent, select samples were taken at critical control points (that is, DAF effluent) to assess performance of specific components of the HABITATS process.

Table 2-2. Testing parameters with their corresponding methods and sample types.

Parameter	Standard method	Sample type
pH	SM 4500 H+ B, 150.2	Influent, DAF effluent, discharge
Conductivity	SM 2510B, 120.1	Influent, DAF effluent, discharge
TSS	SM 2540D	Influent, DAF effluent, discharge
Volatile suspended solids (VSS)	SM 2540E, 160.4	Influent, DAF effluent, discharge
Turbidity	180.1	Influent, DAF effluent, discharge, field samples
TP	SM 4500 PE, 365.4	Influent, DAF effluent, discharge
Orthophosphate	SM 4500 PE	Influent, discharge
TN	350.1, 351.2, 353.2	Influent, DAF effluent, discharge
Nitrate	353.2	Influent, DAF effluent, discharge
Total organic carbon (TOC)	5310C, QBD1200	Influent, DAF effluent, discharge
Whole effluent toxicity	2000.0, 2021.0, 1000.0, 1002.0	Discharge
Biological oxygen demand	5210B	Influent, discharge
Chemical oxygen demand	410.4, 180.1	Influent, DAF effluent, discharge
Chlorophyll-a	SM 10200	Influent, discharge
Microcystin	ELISA	Influent, discharge
Microbial ID	SM 10200	Influent, discharge
Toxin gene ID	SM 10200	Influent, discharge

Process performance monitoring samples were collected every 90 min or more frequently to assess pH, turbidity, and microcystin levels, primarily in the effluent to confirm safety prior to discharge. Ozone was also measured continuously on-site to assess dosing and to confirm its reactive self-destruction prior to effluent discharge.

2.3.3 In situ measurement methods

In-situ source water chemistry was assessed using a ProDSS hand-held multiparameter water quality meter (YSI, Yellow Springs, Ohio) equipped with optical dissolved oxygen, conductivity and temperature, and total algae sensors. Water quality information was collected from each location. The following parameters relevant to this study were collected: temperature (°C), specific conductance (SPC) (μScm^{-1}), chlorophyll *a* (Chl *a*; $\mu\text{g/L}$), phycocyanin (PC; $\mu\text{g/L}$), and optical dissolved oxygen (DO) (mg/L). Data were retrieved using the software KorDSS version 1.6.6.0 (YSI) and exported to Prism8 v 7.04 (GraphPad, San Diego, California) for analysis.

A CyanoFluor Handheld HAB Indicator (Turner Designs, San Jose, California) was used to determine the relative in vivo fluorescence of Chl *a* and 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 (PC)

Chlorophyll pigments were extracted according to US Environmental Protection Agency (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, United Kingdom) 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 min using a Fast Prep 24 Homogenizer (MP Biomedicals, Santa Ana, California). 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 steeped overnight at 4°C in the dark to enhance extraction. Samples were then centrifuged at 1,000g 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 reread 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

$$[\text{Chl } a] = 11.85(\text{Abs } 664) - 1.54(\text{Abs } 647) - .08(\text{Abs } 630) \quad (1)$$

$$[\text{Chl } b] = 21.03(\text{Abs } 647) - 5.43(\text{Abs } 664) - 2.66(\text{Abs } 630) \quad (2)$$

$$[\text{Chl } c] = 24.52(\text{Abs } 630) - 7.60(\text{Abs } 647) - 1.67(\text{Abs } 664) \quad (3)$$

Corrected

$$[\text{Chl } a] = 26.7(\text{Abs } 664 - \text{Abs } 665) \quad (4)$$

$$[\text{Pheophytin } a] = 26.7[1.7 \times (\text{Abs } 665) - (\text{Abs } 664)] \quad (5)$$

Total pigment concentration (TPC)

$$TPC = \frac{[\text{Chl } a, b, \text{ or } c] \times \text{extraction volume (L)} \times \text{Dilution Factor}}{\text{Sample volume (L)} \times \text{cuvette cell length (cm)}} \quad (6)$$

Phycocyanin was extracted in much the same way as Chl *a* but with a different extraction solvent. Rather than using 90% acetone as in the Chl 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):

$$PC = \frac{(\text{Abs } 615 - (0.474 * \text{Abs } 652))}{5.34} \quad (7)$$

2.3.3.2 Molecular methods for cyanobacteria and cyanotoxin measurement

Molecular methods were used to help determine whether 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, Massachusetts) 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 2× volume of absolute ethanol to precipitate the DNA. Precipitated DNA was washed twice with 70% ethanol and dissolved in Tris- ethylenediaminetetraacetic acid (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 to 480 bp. Each PCR was 25 µL and comprised of 100 ng DNA template, 1 × Maxima Hot Start *Taq* Master Mix (New England Biolabs, Ipswich, Massachusetts), 1.25 µL dimethyl sulfoxide, 0.2 µM forward primer (Table 2-3), 0.2 µM reverse primer (Table 2-3), 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 2-3. Primers used to target the broad cyanobacteria and genus-specific 16S rRNA genes as well as the anatoxin-a production gene in polymerase chain reactions (PCR).

Target	Primer	Sequence
16S rRNA Cyanobacteria	CYA359F	GGGGAATYTTCCGCAATGGG
16S rRNA Cyanobacteria	CYA781R	GACTACWGGGGTATCTAATCCCWTT

Target	Primer	Sequence
16S rRNA <i>Microcystis</i>	micF	ATGTGCCGCGAGGTGAAACCTAAT
16S rRNA <i>Microcystis</i>	micR	TTACAAYCCAARRRCCTTCCTCCC
16S rRNA <i>Dolichospermum</i>	anbF	CCACACTGGGACTGAGACAC
16S rRNA <i>Dolichospermum</i>	anbR	TGCATCCTCCGTATTACCGC
16S rRNA <i>Oscillatoria</i>	oscLF	AGCTGGTCTGAGAGGACGAT
16S rRNA <i>Oscillatoria</i>	oscLR	CGGAGTTAGCCGATGCTGAT
16S rRNA <i>Nodularia</i>	nodF	CTGGTGACTGGGGTGAAGTC
16S rRNA <i>Nodularia</i>	nodR	AGCACTCAGTCTCGAAGCAC
16S rRNA <i>Aphanizomenon</i>	aphF	CCACACTGGGACTGAGACAC
16S rRNA <i>Aphanizomenon</i>	aphR	ACGGCTAGGACTATTGGGGT
anaC	anaCgenF	TCTGGTATTCAGTCCCCTCTAT
anaC	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, ethylenediaminetetraacetic acid (TAE) buffer (100 V, 1 h). 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, Ohio). 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 and 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/ μ L. 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 microcystin toxin

For grab and composite samples sent to a laboratory for testing, both total and free microcystin were determined using an ADDA-microcystin enzyme linked immunosorbent assay (ELISA) (Abraxis, Warminster, Pennsylvania). For total toxin, raw sample was homogenized via bead beating using 0.1 mm silica beads at 4.0 m/s for 1 min using a Fast Prep 24 Homogenizer. For free toxin, the raw sample was filtered using GF/C, pore size 1.2 μ m (Whatman, Maidstone, United Kingdom). The filtrate was used directly for toxin testing, without any other preprocessing. 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.

For on-site analysis in the field, a semiquantitative test strip modification of the immunosorbent assay (Abraxis) was used for measuring total toxin levels. This assay was determined previously by FDEP to be highly accurate to determine whether samples contained more or less than 1 ppb of microcystin toxin. Field methods for cell lysis prior to analysis were similar to those described above.

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 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, that is, Wh/gal. Because of the small scale of the pilot demonstration, the energy efficiency of the treatment systems was nonoptimal. As such, published data for larger DAF and ozone treatment systems were considered for scalability analysis.

3 Results

3.1 Flocculant down selection studies (laboratory)

A key task for HABITATS 2020 was the identification and development of organic coagulants or flocculants that neutralized the surface charge and facilitated flocculation of cyanobacterial cells, thereby enabling their adsorption to microbubbles and efficient separation from the water by DAF. These organic chemicals replaced the aluminum chlorohydrate chemical used previously, with the expectation that the organic flocculants would be convertible to fuel during the HTL process. Market research identified several candidate cationic organic molecules with potentially acceptable levels of ecological toxicity. Naturally derived chemicals that were tested included chitosan, cationic starch, and alginate. Synthetic organic chemicals that were tested included PolyDADMAC and two formulations of a cationic polyacrylamide (cPAM) with relatively low charge density to reduce toxicity levels. Strategic combinations of these chemicals were also tested.

ERDC performed DAF jar test studies to assess the performance of these chemicals at various doses, pH levels, and cyanobacteria concentrations. An example jar test is shown in Figure 3-1. The control jar, which received no chemical treatment prior to microbubble flotation, is shown on the left. The second jar received a 0.1 ppm dose of Tramfloc 300 followed by 1.5 ppm of Greenfloc 5100. The third and fourth jars received 3.0 and 6.0 ppm doses of Greenfloc 5100. The combination of Tramfloc 300 with a small amount of Greenfloc 5100 was most optimal in this test.

Figure 3-1. Representative results from a DAF jar test with varying concentrations and types of organic coagulants and flocculants. The left negative control jar received no chemical treatment but was subjected to the same mixing and aeration processes.

In cases of effective neutralization and flotation, a thin layer of concentrated algal biomass forms on the water surface (Figure 3-2). This layer was skimmed from the surface of multiple jars and then squeezed in a loosely woven cotton cloth to assess dewaterability. For the experiment shown, the algal biomass was efficiently separated through flotation, and the solids were dewatered efficiently. The resulting biosolids had a clay-like consistency, and the clear filtrate water was readily released from the solids.

Figure 3-2. (left) Flotation of algal cells after a DAF jar test using organic flocculants, mixing, and microbubbles to generate a thin, dense layer of cells on the water surface. (right) The floated algae were pressed into dewatered solids (left dish) by cloth filtration and separated from the clear filtrate water (right dish). This experiment involved treatment of a 50 ppm suspension of cyanobacteria with 0.1 ppm of TramFloc300 followed by 1.5 ppm of GFT5100 cationic starch and microbubble flotation at pH 7.2 and 25°C.

After a large matrix of jar test experiments, it was determined that the optimal approach for charge neutralization was a sequential treatment of the cyanobacteria suspension with a low dose of Tramfloc 222 or Tramfloc 300 cPAM followed by a 10× higher dose of GreenFloc 5100 cationic starch. A summary of the down selection criteria and relative comparison to the previously utilized aluminum chlorohydrate is shown in Table 3-1. The other candidate formulations were not suitable options according to one or more of these criteria.

Table 3-1. Selection criteria of flocculants.

Criteria	Aluminum salt (2019 benchmark)	Tramfloc 222 plus GreenFloc 5100
Organic (carbon based) to enable conversion of flocculated algal biomass to biocrude	–	+
Low ecological impact of treated water (chemical dose < acute no-observable-effect levels)	~	+
High activity for neutralizing, flocculating, and floating algal cells	+	+
Does not lyse algal cells at treatment dose	+	+

Criteria	Aluminum salt (2019 benchmark)	Tramfloc 222 plus GreenFloc 5100
Available in high concentrations to reduce storage tank size on watercraft	+	+
Cost effective and practical	+	+

While several of the chemicals and formulations tested had acceptable levels of activity, minimizing the ecological toxicity of the formulation was a primary driver of the down selection process. The cPAM formulations (Tramfloc 222 and 300) showed the greatest potency and efficacy for algae separation with the cyanobacteria cultures tested, but they also showed higher toxicity. By combining a small amount of cPAM and cationic starch, an optimal balance of activity and toxicity could be achieved.

Toxicity data for many of the formulations were not available prior to this study, and standard methods in accredited labs were used to determine ecological toxicity endpoints for *C. dubia* (water fleas) and *P. promelas* (minnows), which are used as standards within the industry. These endpoints are provided in Table 3-2. *C. dubia* ecological toxicity endpoint values for various coagulant or flocculant formulations. Endpoint values are provided in mg/L and include the concentrations required for 50% lethality (LC₅₀), for no observable effect (NOEC), for lowest observed effect (LOEC), and for 25% inhibitory effect (IC₂₅). (Table 3-2 and Table 3-3). Using these data, flocculant formulations were developed to achieve effective performance in the laboratory experiments with doses that were below the NOEC. This approach is highly conservative, as more than 90% of the dose material will be recovered from the water with the algae in DAF systems that are operating at appropriate dosing levels (Duggan et al. 2019). However, the dose requirements determined with controlled algae cultures grown in the laboratory may need to be increased in field applications, where other contaminants (inorganic particulates, dissolved organic carbon) can exhibit demand for coagulants and flocculants.

Table 3-2. *C. dubia* ecological toxicity endpoint values for various coagulant or flocculant formulations. Endpoint values are provided in mg/L and include the concentrations required for 50% lethality (LC₅₀), for no observable effect (NOEC), for lowest observed effect (LOEC), and for 25% inhibitory effect (IC₂₅).

Flocculant	Acute LC ₅₀	Acute NOEC	Acute LOEC	Chronic survival LC ₅₀	Chronic survival NOEC	Chronic survival LOEC	Chronic reproduction IC ₂₅	Chronic reproduction NOEC
Tramfloc 222 (97% cPAM)	5.4	0.4	0.8	3.4,3.5 [~]	1.5	3.0	3.1	1.5
Tramfloc 300 (30% cPAM)	0.725	—	—	—	0.375	—	0.117	<0.375
GreenFloc 5100 (22% cStarch)	8.0	6.0	—	—	25	—	3.0	1.5
1% chitosan	1,369*	1,000*	2,000*	—	—	—	—	—
CTAB ^{1,3}	—	—	—	—	0.023 ^x	—	—	—
Aluminum sulfate ²	38.2 ^x	—	—	0.7422 ^x	—	—	—	—
FeCl ₃ ·6H ₂ O ⁴	—	—	—	—	2.51*	5.01*	—	0.63*
Aluminum chlorohydrate (50%) ⁵	>400	—	—	—	>25	—	—	>25

*Daphnia pulex

xDaphnia magna

[~] First value is LC₅₀ (Probit) and the second value is LC₅₀ (Spearman Karber)

Sources: (Columbus Chemical Industries 2015)¹, (United States Environmental Protection Agency 1988)², (ECHA European Chemicals Agency, n.d.-a)³, (ECHA European Chemicals Agency, n.d.-b)⁴, (GEO Specialty Chemicals 2019)⁵

Table 3-3. *Pimephales promelas* ecological toxicity endpoint values for various coagulant or flocculant formulations. Endpoint values are provided in mg/L and include the concentrations required for 50% lethality (LC₅₀), for NOEC, and for LOEC.

Flocculant	Acute LC ₅₀	Acute NOEC	Acute LOEC	Chronic survival LC ₅₀	Chronic survival NOEC	Chronic survival LOEC	Chronic reproduction IC ₂₅	Chronic reproduction NOEC
Tramfloc 222 (97% cPAM)	6.6	3.0	6.0	>0.4*	0.4	>0.4	0.2	0.01
Tramfloc 300 (30% cPAM)	20.2	—	—	—	1.5	—	3.0	6.0
GreenFloc 5100 (22% cStarch)	20.3	12.0	—	—	6.0	—	9.0	6.0
1% chitosan	642	500	750	>1,000	500	1,000	688	500

Flocculant	Acute LC50	Acute NOEC	Acute LOEC	Chronic survival LC50	Chronic survival NOEC	Chronic survival LOEC	Chronic reproduction IC25	Chronic reproduction NOEC
CTAB ³	0.1-0.28 ^x	—	—	—	—	—	—	—
Aluminum sulfate ²	>18.9 to > 49.8	—	—	—	—	—	—	—
FeCl ₃ ·6H ₂ O ⁴	21.8	—	—	3.288	—	—	—	1.0
Aluminum chlorohydrate (50%) ⁵	400	—	—	—	200	—	—	25

*Modeled to be 0.55 mg/L by Probit analysis (note: this is higher than the highest concentration tested)

^xSource said these values were reported in studies of *Oryza latipes* and *P. promelas* but did not specify distinct values for each species

Sources: (Columbus Chemical Industries 2015)¹, (United States Environmental Protection Agency 1988)², (ECHA European Chemicals Agency, n.d.-a)³, (ECHA European Chemicals Agency, n.d.-b)⁴, (GEO Specialty Chemicals 2019)⁵

Some key conclusions and important points of discussion from the laboratory jar test studies included the following:

- Organic coagulants and flocculants could be dosed at lower levels than metal salt flocculants in many cases. However, dosing is limited by ecological toxicity considerations, particularly for the cationic polyacrylamide cPAM.
- Combinations of low doses of cPAM with moderate doses of cationic starch resulted in excellent flotation while reducing total ecological toxicity.
- Some algae cultures grown in open reactors in the laboratory appeared to be sensitive to redispersion (after flotation) or possibly lysis at higher doses of chitosan or cationic starch.
- While an optimal organic coagulant-flocculant formulation was identified and recommended for demonstration testing, further research on reducing ecological toxicity, increasing dewaterability, and enhancing fuel conversion is recommended.

3.2 Demonstration site water source characterization

3.2.1 Saddle Creek, Polk County, Florida

The water source at the Saddle Creek site exhibited a green, opaque appearance across the entire water body, both upstream and downstream of the spillway (Figure 3-3). The cyanobacteria were relatively monodisperse and distributed in the water column, with few visible aggregates and little or no film formation observed on the water surface. The spillway at the site was operating at >50 cfs (>22,400 gpm) throughout the demonstration period, providing a high level of water flow in the area of the intake as well as a high level of dilution (>100×) of the discharge from the pilot scale water treatment system. The green color persisted through the demonstration over days of high flows, indicating that the cyanobacteria bloom was occurring in an upstream water body and simply passing through this site.

Figure 3-3. Representative photos of the green water upstream of the flowing Saddle Creek dam.

3.2.2 Chautauqua Lake, New York

3.2.2.1 South basin during onshore testing

The test site at the Chautauqua Lake Association on the south shoreline of Chautauqua Lake was visibly green but with greater transparency than the Saddle Creek site. On calm days, particularly in the early morning, the lake appeared like a sheet of glass (Figure 3-4, left). These still conditions are highly favorable to bloom formation. Unlike the Saddle Creek site, visible cyanobacteria colonies were present at the Chautauqua Lake site, and a paint-like film of cyanobacteria was present on the surface along much of the shoreline (Figure 3-4, right). The water also contained aquatic plant material on the surface. To reduce collection of the aquatic plant material,

which has a high-water content relative to the algae and could also impact pump performance, the intake was adjusted to collect water 2 in below the surface, rather than directly skimming the surface. Screens with openings of 3/8 in and 1/4 in were used to reject plant material and aquatic organisms.

Figure 3-4. (left) View from the shoreline of still water during the early morning near the DAF intake at Chautauqua Lake, and (right) paint-like film of cyanobacteria mixing with aquatic plants along the shoreline near the demonstration site at Chautauqua Lake Association in Lakewood, New York.

3.2.2.2 North basin during shipboard system testing

At the time of the shipboard HABITATS testing (Figure 3-5), the northern basin of Chautauqua Lake contained disperse visible flecks of cyanobacteria near the surface, but the water was relatively clear. There were sections of water close to the shoreline, particularly near the Long Point State Park marina, where a film of cyanobacteria formed on the surface during portions of the day. However, the cyanobacteria density 20 ft beyond the shoreline, at depths where the shipboard system could be operated, was generally very low. Despite the low algae density, the north basin was the only area available for testing because of high wind and waves in the south basin. Small waves, less than one foot, were also present in the north basin for a significant portion of the test period, but there were intermittent calm periods and a several calmer areas that

allowed for careful assessment of the control systems under more representative hydrodynamic conditions.

Figure 3-5. Mobility testing of the shipboard HABITATS prototype in choppy waters in the southern basin of Chautauqua Lake on August 31, 2020. Testing was subsequently moved to the northern basin because of the wave and wind conditions.

3.2.3 Source water biomass concentrations

Biomass density in the source water was measured as volatile suspended solids (VSS) in the water. The VSS concentration in the water is a measure of the combustible (organic) particulate matter and represents the amount of biomass available from a given water source. VSS is an important parameter for assessing the level of HAB contamination as well as predicting the economic viability of the HABITATS process at a specific site. While VSS is a commonly used parameter in the wastewater treatment industry, it is less commonly used in the characterization of HABs. With respect to HABITATS, if the VSS level is too low, then a relatively large volume of water will need to be treated to generate enough biomass to produce fuel. If influent concentrations are very low, removal by DAF will be less efficient because of decreased collision frequency during flocculation. Models developed as part of the HABITATS 2019 study (ERDC TR 20-1, Page et al. 2020) indicated that HABITATS becomes much more efficient at VSS levels above 30 mg/L, and the process may become net energy positive at levels above 120 mg/L. As seen in Figure 3-6, the four candidate water sources tested during the 2020 demonstration varied widely in VSS concentrations, even though each of these water sources is historically impacted by HABs during the respective test periods. These data highlight the dynamic nature of HABs and the need for response systems and frameworks to be highly mobile.

Figure 3-6. Comparison of volatile suspended solids (VSS) concentrations in water sources studied in the HABITATS 2020 demonstrations. The two candidate Florida demonstration sites are shown on the left. The two New York candidate demonstration sites are shown on the right.

In addition to VSS, TSS values were also measured. TSS includes both organic (combustible) solids such as algae and inorganic (noncombustible) solids such as clay. If the ratio of VSS:TSS = 1, then all the solids are organic, which would be an ideal influent for HABITATS. Previous experience at PNNL indicates that a ratio of at least 0.85 (<15% inorganic solids) in harvested biomass is important for efficient oil production. While the DAF process is partially selective to floatable organic materials, inorganic particulates in suspension can be collected and contaminate the biomass. Table 3-4 provides the ratio of VSS:TSS for the water sources tested in 2020. During HAB events, the VSS:TSS ratio is generally favorable for the HABITATS process. During non-HAB events, the relative levels of inorganic solids would decrease the efficiency of the process.

Table 3-4. VSS:TSS (total suspended solids) ratios of each water source.

Water source	VSS:TSS ratio
Port Mayaca Lock and Dam, East Lake Okeechobee, Florida	0.90
South Branch of Saddle Creek, Florida	>0.95
South Basin, Chautauqua Lake, New York	0.89
North Basin, Chautauqua Lake, New York	>0.95

3.2.4 Source water nutrient levels

The TN levels were highly eutrophic in Saddle Creek (see Figure 3-7) and considerably higher than any of the other candidate sites tested. The TP levels were lower at Saddle Creek compared to Port Mayaca, and both sites far exceeded the TP level of 0.15 for eutrophic designation (USEPA 2019b). Given the higher concentration of cyanobacteria at the Saddle Creek site, higher levels of nutrients would be expected because of cellular uptake.

The New York data from Chautauqua Lake further highlight the assimilation of nutrients in HABs, with total nutrient levels being two-fold higher in the downstream basin in which a HAB was occurring. In Chautauqua Lake, the water in the northern basin contained sufficient dissolved nutrients for bloom formation but lacked optimal conditions of a still, phototrophic environment to bloom prior to flowing into the southern basin.

Figure 3-7. Comparison of total nutrient levels in the four candidate water sources tested. Reference dashed lines indicate eutrophic designation levels for total nitrogen (TN, --- and ---) and total phosphorus (TP, --- and ---) in lakes and streams, respectively (USEPA 2000a, 2000b).

3.2.5 Source water microbiology and toxin characterization

To characterize the microbial ecology at the Saddle Creek site, molecular assays were used as described in the methods section. The dominant group detected were the cyanobacteria, comprising of 90% of species detected. The cyanobacteria group was broken down by taxa, and *Planktolyngbya contorta* was the dominant species throughout the test period, followed closely by *Aphanocapsa*. The genus *Microcystis* was not present in the Saddle Creek water. However, the absence of *Microcystis* does not necessarily reduce the risk of microcystin as there are many other taxa that are known producers of microcystin (for example, *Aphanocapsa*, *Anabaenopsis*, *Dolichospermum*, *Leptolyngbya*, *Merismopedia*, *Pseudanabaena*, *Romeria* and *Aphanocapsa*). Representative data are provided in Figure 3-8.

Figure 3-8. Characterization of the microbial ecology at the Saddle Creek demonstration site in Florida.

At Chautauqua Lake, indirect characterization of cyanobacteria density was measured over the lake using a data sonde equipped with a PC probe. The sonde was mounted over the side of a boat at fixed positions near and

below the surface to facilitate measurements of PC as it traveled around the lake in a grid-like pattern. An example plot of data from one of the algae monitoring trips to the southern basin is shown in Figure 3-9. The gradient in cyanobacteria concentration shows a sharp decrease to the north, consistent with the drastic difference in VSS concentrations in the northern versus southern basins during the demonstration period. While this was a preliminary test of this approach, it represents a powerful tool for mapping blooms on a lake that could potentially provide higher resolution than satellite infrared systems, which primarily detect algae near the surface. In the future, several sensors will be mounted at varying depths to allow construction of a 3D map of the blooms to better understand the total quantities of biomass in a lake.

Figure 3-9. Characterization of the algal bloom through in-situ measurements at Chautauqua Lake, New York on September 1, 2020.

3.3 Saddle Creek onshore treatment results

Over a four-day period from July 31–August 03, 2020, 230,000 gal of water were withdrawn from Saddle Creek and treated by DAF and ozonation by AECOM, removing 430 gal of concentrated algal slurry that was then subjected to dewatering prior to shipment to the Illinois Sustainability Technology Center for HTL testing.

3.3.1 Water quality improvement

3.3.1.1 Clarification

An obvious feature of HABs is their impact on water clarity because of their particulate nature and green color. In treating algae-laden water with a physical removal process, the key performance metric is clarification. Clarification can be observed above in Figure 3-10, where the influent water is visibly greener than the treated effluent water at Saddle Creek, FL. Clarification can be measured using several common parameters from the water and wastewater industry that quantify particulate contamination. Turbidity is a commonly used parameter that measures light reflectance by particles in a water sample, and it can be readily measured in the laboratory or field. VSS is another important parameter that quantifies the amount of organic particulate matter, or biomass. VSS is more difficult to measure but provides critical information for HABITATS.

Figure 3-10. The influent (left) versus effluent (right) of treated Saddle Creek water.

At the Saddle Creek demonstration, the DAF process and associated chemical dosing were guided by turbidity measurements that compared the effluent water to the influent water. These data were initially generated in bench-scale jar tests performed to optimize coagulant and flocculant dosing. The jar testing was performed regularly throughout the demonstration and reinforced by on-site measurements of turbidity before and after treatment in the pilot-scale system. The chemical dosing regimen

for the DAF process is shown in Figure 3-11, with each point representing the average dose during each 8 h period of operation. On the basis of initial jar tests and high VSS present on the first day of the demonstration, a very high average dose was used. After additional jar tests and a slight decrease in VSS over the demonstration period, the cationic starch coagulant dosing was optimized and kept at or below 20 mg/L (ppm).

Figure 3-11. Target coagulant and flocculant dosing during the onshore demonstration at Saddle Creek in Florida. Values shown are averages over 8 h operation periods each day, with cationic starch concentrations on the left axis and cationic polyacrylamide dosing levels on the right axis. All units are in ppm, equivalent to mg/L.

As shown in Figure 3-12, the influent had an average turbidity of 37 NTU, whereas the DAF effluent and discharge waters had turbidity levels below 5 NTU. These data are based on laboratory measurements, but on-site measurements were typically within 5% of these values. The results demonstrate a high level of clarification that was also visibly obvious.

Figure 3-12. Turbidity values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

A similar trend was observed with VSS (Figure 3-13), which are representative of the mass of algal cells in the water. On average the VSS removal level was 90% across the entire treatment process. There did appear to be a difference in VSS before and after ozonation, but it was statistically insignificant on most days. The difference might be due to ozone destroying some of the remaining cells that were not removed in the DAF process.

Figure 3-13. VSS values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

3.3.1.2 Nutrient removal

Nutrients are the primary contaminants that fuel HABs; therefore, reducing their availability in the aqueous environment reduces HAB formation potential in a water body. The concentrations of TN and TP from the Saddle Creek water were measured to assess the effects of clarification and subsequent ozonation on nutrient removal (Figure 3-14 and Figure 3-15). Consistent with the 2019 HABITATS study, in which an aluminum coagulant was used, substantial nutrient removal was achieved through clarification alone. TN levels decreased by an average of 49%, and TP levels decreased by over 85%. TP removal levels were likely higher than reported, as many of the effluent samples were below the method detection limit of 0.06 mg/L. For those samples, the detection limit was used as the effluent value. Nitrate concentrations were also measured (Figure 3-16), and a 37% decrease in nitrate concentration was observed. Given that the HABITATS treatment process is predominantly focused on clarification to remove algal cells, these data indicate that most of the TP in the water is taken up by algal cells during bloom conditions and thus more readily removed from the water. The data also indicate that up to 50% of the nitrogen is cell associated, including a smaller fraction of nitrate. HABITATS is not expected to affect dissolved nutrients.

Figure 3-14. TN values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

Figure 3-15. TP values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

Figure 3-16. Nitrate concentration values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

3.3.1.3 Chlorophyll *a* (Chl *a*), PC, and microcystin removal

Chl *a* and PC are widely used indicators for indirect measurement of cyanobacteria, which contain high levels of these pigment chemicals. As such, it is expected that these pigments will be removed during treatment. Because they are largely intracellular, they can also be considered as a

potential indicator of cell lysis. During the Florida demonstration, the chlorophyll levels decreased in a manner consistent with the VSS (Figure 3-17), indicating that they were removed with the cells and without lysis of the cells. Removal levels for PC, a characteristic pigment of cyanobacteria, were slightly higher (Figure 3-18). Furthermore, significant reductions in microcystin levels were achieved each day after dissolved air flotation and oxidation treatment as shown in Figure 3-19.

Figure 3-17. Chl *a* concentration values for the source water (intake) and after clarification treatment and oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

Figure 3-18. PC concentration values for the source water (intake) and after clarification treatment and oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

Figure 3-19. Total microcystin values for the source water (intake) and after clarification treatment and oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

3.3.1.4 Organics removal

The removal of organic matter, both dissolved and particulate, is shown in Figure 3-20, which depicts the change in total organic carbon (TOC) for influent, DAF effluent, and discharge water. The TOC levels of the influent were very high, consistent with the opaque green color of the water. The TOC levels were only partially decreased by the treatment process, indicating that a large fraction of the TOC was dissolved organic carbon, which is not targeted by DAF. It should also be noted that these high TOC levels likely inhibited the efficiency of the ozonation process in targeting microcystin. This hypothesis is further supported by the chemical oxygen demand (COD) data, which show little change before and after ozonation (that is, comparing DAF effluent and discharge samples) in Figure 3-21. Because ozone is a strong oxidant, it should decrease the COD, which is a measure of oxidant consumption by the organic matter. The large amount of TOC likely overwhelmed the ozone process, resulting in no observable reduction in COD value.

Figure 3-20. Total organic carbon (TOC) values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

Figure 3-21. Chemical oxygen demand (COD) values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Saddle Creek in Polk County, Florida.

3.3.1.5 Water quality parameters required by Florida Department of Environmental Protection (FDEP) permit

The discharge water at the Saddle Creek site was monitored carefully for key parameters of importance to environmental impact. Table 3-5 shows the requirements for discharge monitoring as well as the limits and results from the four-day test period. It should be noted that the discharge water from this pilot study was diluted by a factor of over 1,000 with ample mixing downstream of the spillway, making environmental impacts highly unlikely. However, as design scales are increased in the future and dilution factors decrease, meeting all discharge requirements will be essential. In general, the water quality results were supportive of the environmental safety of the process. However, there was a measurable chronic effect on water flea reproduction rates when testing the undiluted discharge water. A dilution to 64% strength with clean water was needed to bring this effect to 25% or less. The chronic effect observed was likely attributable to the coagulant dose being higher than the demand on the day of sampling, as the sample was collected over an 8 h period in which the coagulant dose was decreased from a high level (100 ppm) to a much lower level (10 ppm), for an average dose of 42 ppm for the composite sample. Some of the discharge pH values were above 8.5, but it should be noted that both the influent water and receiving water had a pH > 9 because of the HAB conditions.

Table 3-5. Florida discharge compliance parameters and measurements.

Compliance parameters	Units	Reporting value (max/min)	Limit	Results
Flow	MGD*	Max avg	0.12 Report	0.11 0.10
BOD, carbonaceous 5 day, 20C	mg/L	Max avg	Report Report	<10 <10
Solids, total suspended	mg/L	Max avg	Report Report	<8.8 avg. 4.31
pH	s.u.	Min max	6 8.5	7.8 < pH < 8.7
Oxygen, dissolved percent saturation	Percent	Min	Report	>95%
Nitrogen, total	mg/L	Max avg	Report Report	<2.44 avg. 1.91
Phosphorus, total (as P)	mg/L	Max avg	Report Report	<0.19 avg. 0.13
Acute whole effluent toxicity, 48 h LC50 (<i>Ceriodaphnia dubia</i>)	Percent	Min	100	100
Acute whole effluent toxicity, 96 h LC50 (<i>Pimephales promelas</i>)	Percent	Min	100	100
Chronic whole effluent toxicity, 7-day IC25 (<i>C. dubia</i>)	Percent	Min	100	64
Chronic whole effluent toxicity, 7-day IC25 (<i>P. promelas</i>)	Percent	Min	100	100

* MGD averaged over 24 h period

3.3.1.6 Other water quality parameters

Composite discharge samples were analyzed to assess the potential presence of other contaminants that might affect the use of product water as a drinking water source (Table 3-6–Table 3-12 summarize results from Florida effluent). These samples were tested for metals, disinfection byproducts, and other contaminants of potential concern from a drinking water perspective. In general, the water quality was very good relative to the standards for these chemicals.

Table 3-6. Inorganic analytes—metals monitored in Florida effluent.

Parameter	Units	8/1/2020	8/2/2020	8/3/2020
Aluminum	mg/L	ND	ND	ND
Arsenic	mg/L	ND	ND	ND
Barium	mg/L	ND	ND	ND
Cadmium	mg/L	ND	ND	ND
Calcium	mg/L	20.2	20.2	19.7
Chromium	mg/L	ND	ND	ND
Copper	mg/L	ND	ND	ND
Iron	mg/L	ND	ND	0.028
Lead	mg/L	ND	ND	ND
Lithium	mg/L	0.001	0.001	0.001
Magnesium	mg/L	4.25	4.14	4.2
Manganese	mg/L	ND	ND	ND
Mercury	mg/L	ND	ND	ND
Nickel	mg/L	ND	ND	ND
Selenium	mg/L	ND	ND	ND
Silver	mg/L	ND	ND	ND
Sodium	mg/L	11	11	11
Strontium	mg/L	0.043	0.042	0.041
Uranium	mg/L	ND	ND	ND
Zinc	mg/L	0.006	0.006	0.009

Table 3-7. Physical factors monitored in Florida effluent.

Parameter	Units	8/1/2020	8/2/2020	8/3/2020
Alkalinity	mg/L	48	46	48
Hardness	mg/L	68	67	66
pH	pH Units	8.3	8.7	8.3
Total dissolved solids	Mg/L	92	91	91

Table 3-8. Inorganic analytes—other monitored in Florida effluent.

Parameter	Units	8/1/2020	8/2/2020	8/3/2020
Bromate	mg/L	ND	ND	ND
Bromide	mg/L	ND	ND	ND
Chloramine as Cl ₂	Mg/L	ND	ND	ND
Chloride	mg/L	17	17	17
Chlorine—free	mg/L	ND	ND	ND
Chlorine—total	mg/L	ND	ND	ND
Chlorite	mg/L	ND	ND	ND
Fluoride	mg/L	0.6	0.6	0.6
Nitrate as N	mg/L	ND	ND	ND
Nitrite as N	mg/L	ND	ND	ND
Ortho phosphate	mg/L	ND	ND	ND
Sulfate	mg/L	6.7	6.7	6.8

Table 3-9. Organic analytes—trihalomethanes monitored in Florida effluent.

Parameter	Units	8/1/2020	8/2/2020	8/3/2020
Bromodichloromethane	mg/L	ND	ND	ND
Bromoform	mg/L	ND	ND	ND
Chloroform	mg/L	ND	ND	ND
Dibromochloromethane	mg/L	ND	ND	ND
Total THMs	mg/L	ND	ND	ND

Table 3-10. Organic analytes—haloacetic acids monitored in Florida effluent.

Parameter	Units	8/1/2020	8/2/2020	8/3/2020
Dibromoacetic acid	mg/L	ND	ND	ND
Dichloroacetic acid	mg/L	ND	ND	ND
Monobromoacetic acid	mg/L	ND	ND	ND
Monochloroacetic acid	mg/L	ND	ND	ND
Trichloroacetic acid	mg/L	ND	ND	ND
Total HAAs	mg/L	ND	ND	ND

Table 3-11. Organic analytes—volatiles monitored in Florida effluent.

Parameter	Units	8/1/2020	8/2/2020	8/3/2020
1,1,1,2-Tetrachloroethane	mg/L	ND	ND	ND
1,1,1-Trichloroethane	mg/L	ND	ND	ND
1,1,2,2-Tetrachloroethane	mg/L	ND	ND	ND
1,1,2-Trichloroethane	mg/L	ND	ND	ND
1,1-Dichloroethane	mg/L	ND	ND	ND
1,1-Dichloroethene	mg/L	ND	ND	ND
1,1-Dichloropropene	mg/L	ND	ND	ND
1,2,3-Trichlorobenzene	mg/L	ND	ND	ND
1,2,3-Trichloropropane	mg/L	ND	ND	ND
1,2,4-Trichlorobenzene	mg/L	ND	ND	ND
1,2-Dichlorobenzene	mg/L	ND	ND	ND

Parameter	Units	8/1/2020	8/2/2020	8/3/2020
1,2-Dichloroethane	mg/L	ND	ND	ND
1,2-Dichloropropane	mg/L	ND	ND	ND
1,3-Dichlorobenzene	mg/L	ND	ND	ND
1,3-Dichloropropane	mg/L	ND	ND	ND
1,4-Dichlorobenzene	mg/L	ND	ND	ND
2,2-Dichloropropane	mg/L	ND	ND	ND
2-Chlorotoluene	mg/L	ND	ND	ND
4-Chlorotoluene	mg/L	ND	ND	ND
Acetone	mg/L	0.01	ND	ND
Benzene	mg/L	ND	ND	ND
Bromobenzene	mg/L	ND	ND	ND
Bromomethane	mg/L	ND	ND	ND
Carbon tetrachloride	mg/L	ND	ND	ND
Chlorobenzene	mg/L	ND	ND	ND
Chloroethane	mg/L	ND	ND	ND
Chloromethane	mg/L	ND	ND	ND
cis-1,2-Dichloroethene	mg/L	ND	ND	ND
cis-1,3-Dichloropropene	mg/L	ND	ND	ND
DBCP	mg/L	ND	ND	ND
Dibromomethane	mg/L	ND	ND	ND
Dichlorodifluoromethane	mg/L	ND	ND	ND
Dichloromethane	mg/L	ND	ND	ND
EDB	mg/L	ND	ND	ND
Ethylbenzene	mg/L	ND	ND	ND
Methyl tert butyl ether	mg/L	ND	ND	ND
Methyl-ethyl ketone	mg/L	ND	ND	ND
Styrene	mg/L	ND	ND	ND
Tetrachloroethene	mg/L	ND	ND	ND
Tetrahydrofuran	mg/L	ND	ND	ND

Parameter	Units	8/1/2020	8/2/2020	8/3/2020
Toluene	mg/L	ND	ND	ND
trans-1,2-Dichloroethene	mg/L	ND	ND	ND
trans-1,3-Dichloropropene	mg/L	ND	ND	ND
Trichloroethene	mg/L	ND	ND	ND
Trichlorofluoromethane	mg/L	ND	ND	ND
Vinyl chloride	mg/L	ND	ND	ND
Xylenes (Total)	mg/L	ND	ND	ND

Table 3-12. Organic analytes—other monitored in Florida effluent.

PARAMETER	UNITS	8/1/2020
2,4-D	mg/L	ND
Alachlor	mg/L	ND
Aldrin	mg/L	ND
Atrazine	mg/L	ND
Chlordane	mg/L	ND
Dichloran	mg/L	ND
Dieldrin	mg/L	ND
Endrin	mg/L	ND
Heptachlor	mg/L	ND
Heptachlor epoxide	mg/L	ND
Hexachlorobenzene	mg/L	ND
Hexachlorocyclopentadiene	mg/L	ND
Lindane	mg/L	ND
Methoxychlor	mg/L	ND
Pentachloronitrobenzene	mg/L	ND
Silvex 2,4,5-TP	mg/L	ND
Simazine	mg/L	ND
Total PCBs	mg/L	ND
Toxaphene	mg/L	ND
Trifluralin	mg/L	ND

3.4 Chautauqua Lake onshore treatment results

Over a five-day test period, 201,000 gal of water were treated by AECOM, generating 350 gal of algal slurry. The average coagulant dose was 32 mg/L during the demonstration. After removal of the algae by DAF and ozonation of the DAF effluent, the resulting water was analyzed for ozone and microcystin levels prior to discharge back into the lake. All samples met the on-site monitoring requirements prior to discharge throughout the demonstration period.

Algal biosolids were processed on-site using a screw press with a modified polymer mixing process developed by AECOM that resulted in an improved solids recovery level. Because of the use of additional polymers in the dewatering process, the press filtrate water was discharged via the local wastewater treatment facility in coordination with NYSDEC and the facility operations staff. The volume of press filtrate water totaled 700 gal over the week.

3.4.1 Water quality improvement

3.4.1.1 Clarification

Water clarification was consistently achieved throughout the demonstration period. Turbidity levels of influent were 47 NTU on average and were decreased to 4 NTU after treatment (Figure 3-22). As anticipated, the clarification was achieved in the DAF step, and no difference was observed between the average values for DAF effluent versus the ozonated discharge water. VSS levels were also decreased during treatment from 37 mg/L in the influent to 7 mg/L after treatment (Figure 3-23).

Figure 3-22. Turbidity values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Chautauqua Lake in New York.

Figure 3-23. VSS values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore demonstration at Chautauqua Lake in New York.

3.4.1.2 Nutrient removal

Total levels of phosphorus and nitrogen nutrients were substantially decreased by the DAF process (Figure 3-24 and Figure 3-25). Average influent values were 0.37 mg/L and 2.65 mg/L for TP and TN respectively, whereas effluent values were 0.04 and 1.1 mg/L. Most of the nutrient removal was achieved in the DAF step rather than the ozonation step. Measurements were also made of dissolved nitrate across the treatment

process (Figure 3-26). There was little change in dissolved nitrate across the treatment process, consistent with the HABITATS mechanisms of clarification and oxidation, neither of which target dissolved nitrate.

Figure 3-24. TP values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Chautauqua Lake in New York.

Figure 3-25. TN values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Chautauqua Lake in New York.

Figure 3-26. Nitrate concentration values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Chautauqua Lake in New York.

3.4.1.3 *Chl a* and microcystin removal

Levels of *chl a* were substantially reduced during the HABITATS treatment process (Figure 3-27). Analysis of select samples indicated that this removal was occurring predominantly during the DAF process. This observation is consistent with the algal cells being separated from the water and retaining their chlorophyll, without any significant lysis of the algal cells.

A very similar trend was observed with microcystin toxin (Figure 3-28). Influent concentrations were decreased from 4 µg/L to 0.25 µg/L just by the DAF process alone, and additional removal of the microcystin by ozone was relatively insignificant. This result indicates that the microcystin was predominantly intracellular in the influent and supports that no lysis was occurring during DAF, as DAF is not expected to target free microcystin. DAF alone was a highly effective barrier against microcystin in this case.

Figure 3-27. Chl *a* values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Chautauqua Lake in New York.

Figure 3-28. Total microcystin values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Chautauqua Lake in New York.

3.4.1.4 Bulk organics removal

The removals of total organic carbon and compounds exhibiting COD were measured to assess the impact of the HABITATS treatment process on the total organic load in the water (Figure 3-29 and Figure 3-30). Modest reductions in TOC were observed, and the removal was primarily associated with the clarification process. The ozone doses applied for microcystin control were not sufficient for conversion of organic carbon to

carbon dioxide, consistent with the system design, and thus ozonation did not affect the TOC levels. When considering COD as an alternate indicator of removal of bulk organics, the differences between COD levels in the influent and effluent were clearly greater than those observed for TOC. Given the high levels of biomass being removed from the water, and the carbon content of the algal cells being removed, it may be that TOC measurements of the influent are not fully capturing the organic load.

Figure 3-29. TOC values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Chautauqua Lake in New York.

Figure 3-30. COD values for the source water (intake), after clarification treatment (DAF effluent), and after oxidation treatment (discharge) during the onshore treatment demonstration at Chautauqua Lake in New York.

3.4.2 WET measurements

Representative composite samples of HABITATS effluent water generated during the demonstration at Chautauqua Lake in New York were analyzed for potential ecological toxicity in compliance with requirements described in the NYSDEC QAPP. As shown in Table 3-13, no measurable ecological toxicity was observed in the collected effluent samples, indicating that the water could be discharged safely into the environment without dilution.

Table 3-13. WET testing results for *C. dubia* and *P. promelas* (acute) and *P. promelas* (chronic) using a composite effluent sample from the onshore HABITATS demonstration at Chautauqua Lake in New York (August 2020).

Acute test results				
Species	NOEC (%)	LOEC (%)	LC ₅₀ (%)	Was a statistically significant difference between control and ACEC shown?
<i>C. dubia</i>	100	>100	>100	No
<i>P. promelas</i>	100	>100	>100	No
Chronic test results				
Species	NOEC (%)	LOEC (%)	IC ₂₅ (%)	
<i>P. promelas</i>	100 ^{a,b}	>100 ^{a,b}	>100	

a. Indicates a statistical outlier was noted

b. Indicates an interrupted dose response

3.5 Shipboard HABITATS testing

The extent of testing for the shipboard HABITATS prototype was limited because of delays in manufacturing and because of challenging weather conditions during the week of the field test at Chautauqua Lake in New York. The field test included two days of mobility and flow testing without any chemical addition followed by two days of controls testing that included chemical dosing. Per Figure 3-6, the VSS levels in the north basin where testing occurred were very low (<10 mg/L), rendering it very difficult to assess performance during the controls test.

3.5.1 Mobility and flow testing

The system mobility test occurred in the northern and southern basins of Chautauqua Lake on August 31, 2020 (Figure 3-31). Winds from the south at 15–20 mph resulted in 2 ft swells in the southern basin that challenged barge navigation and limited flow-testing operations. The DAF pontoon barge and utility barge had been launched and prepositioned at the slips at Long Point State Park marina. After towing the barges into the open water of the southern basin, the bladder retraction system was tested, as were the influent and effluent pumps, which filled and drained the bladder as it expanded or contracted, respectively. At several points during the mobility testing, waves breached the DAF bladder by passing over the bow skimmers and flooding the treatment tank and the algal biomass hopper. While the floating DAF barge was not designed or intended for operation under choppy conditions, this design vulnerability was noted. Also noted were deficiencies in the scraper system for collecting material from the top of the DAF bladder, which were observed on the basis of floating plant material that had entered the system but were not being removed by the scraper. Temporary repairs were made that evening to address the issue. The conclusion of the first day of testing was that the system was generally operable, but the system could not be tested in the southern basin because of the wave intensity. On the second day of testing, the process was repeated in calmer waters of the north basin to confirm the operability of the pumps and larger systems.

Figure 3-31. View from lead boat during mobility and flow testing of the shipboard HABITATS prototype at Chautauqua Lake in New York.

3.5.2 Controls testing

The next stage of the shipboard system testing focused on assessing the function of all the integrated treatment system components, first individually and then collectively. This testing occurred over a two-day period from September 02 to 03, 2020. The influent flow rate was set to 120 gpm for these tests, which included assessment of the chemical dosing pumps, a streaming current analyzer for dose control, DAF whitewater recirculation pump, and the ozone, and UV radiation components.

While significant water quality improvements were not expected during this testing because of the low contamination level of the influent water, grab and composite samples of influent and effluent samples were collected to comply with monitoring requirements established in the QAPP (see appendix B). A summary of the effluent water quality test results is provided in Table 3-14. Water quality was measured using standard methods at certified contract laboratories for at least three samples per parameter. Additional samples were analyzed at ERDC laboratories.

Table 3-14. Effluent water quality test results from shipboard system.

Effluent parameter	Units	Target	Result	Replicates
TSS	mg/L	<10	<5	6
Turbidity	NTU	<5	3.4	8
Biochemical oxygen demand (BOD-5)	mg/L	<30	<2.0	2
COD	mg/L	<60	9.5	6
TN	mg/L	<2	1.1	6
TP	mg/L	<0.2	0.16	6
Microcystin	µg/L	<1	<1	8
TOC	mg/L	N/A	3.4	3
pH	pH units	6–9	8.3	10
<i>C. dubia</i> acute	Percent survival	100%	100%	1

Effluent parameter	Units	Target	Result	Replicates
<i>P. promelas</i> acute	Percent survival	100%	100%	1
<i>P. promelas</i> chronic	Percent survival	100%	ND	1

ND—Not determined because of fungal contamination of water sample.

Because of the low quantities of algae in the surface water during shipboard testing, the biomass harvested was insufficient to support pilot studies on the screw-press or HTL systems. Further, the limited quantities of algae that floated to the surface of the DAF bladder proved susceptible to disruption when ambient waves were greater than 1 ft. Further boat stabilization and wave dampening would be needed for operating in wavy waters. During a brief calm period of testing in which a small HAB was in range of the harvester, the DAF functioned similarly to the onshore system, with algae slurry building up into a mat on the surface inside the flotation tank (Figure 3-32).

Figure 3-32. Algae slurry floating on surface of the DAF bladder below the deck of the shipboard HABITATS prototype during a brief period when a small bloom was within range of the system and lake conditions were calm.

3.6 Solids dewatering results

After the onshore DAF processing, the algal cells formed a slurry with a concentration of 1.8%–2.3% solids. To facilitate efficient processing by

HTL and reduce the volumes of biomass requiring HTL processing, the algae slurry was further concentrated prior to the transformation process using various dewatering methods. The objective for the dewatering process is to increase the organic solids content of the algal biomass from approximately 2% to 15% in an energy-efficient and high-throughput manner. In 2019, a conventional belt filter press proved insufficient for meeting the throughput and energy metrics when analyzed in scalability models (ERDC TR 20-01, Page et al. 2020). Two alternate dewatering processes with potentially higher throughput were therefore studied at pilot scale in 2020.

3.6.1 Screw-press dewatering performance

A new screw-press method was tested for dewatering the algal slurry for both the Florida and New York demonstration sites. This method was a new application for screw press technology, and as such, the earlier demonstration in Florida was not optimal. Lessons learned during the Florida demonstration informed improvements that were tested in the New York demonstration (Figure 3-33).

As seen in Table 3-15, 426 gal of algal slurry were generated at Saddle Creek in Florida, whereas 351 gal were generated at Chautauqua Lake in New York. The lower slurry volume at Chautauqua Lake was due to the lower concentration of cyanobacteria in the DAF influent. The solids content of the DAF slurry at both sites was similar, both being approximately 2%. Prior to dewatering, the fraction of flocculant polymers in the DAF algal slurry was estimated to be 10%–20% according to flocculant dosing levels, influent algae concentration, and algae removal efficiency.

Table 3-15. Total volume and total solids measurements for the algae slurry biosolids and dewatered cakes from the onshore demonstration test sites.

Test site	Screw press process stream	Total volume (gal)	Total solids (% wt.)	Total solids (g/L)
Saddle Creek, FL	Slurry biosolids (influent)	426.0	1.8	18.0
Saddle Creek, FL	Dewatered cake (effluent)	18.5	7.0	70.0
Lake Chautauqua, NY	Slurry biosolids (influent)	351.0	1.9	19.0
Lake Chautauqua, NY	Dewatered cake (effluent)	50.5	9.9	99.0

The primary difference between the two demonstrations was the slurry feed flow rate and the capture efficiency (Table 3-16). At the first

demonstration in Florida, the capture efficiency was very poor, with fewer than 20% of the solids being retained in the process. Process adjustments made by AECOM resulted in an improved capture efficiency of 75% during the New York demonstration and resulted in a larger volume of dewatered solids for HTL testing with slightly higher density. This larger volume was also achieved at a 50% higher flow rate.

Table 3-16. Total dry weight, percent dry solids capture efficiency, slurry flow rate, and screw press run time at the sites.

Test site	Screw press process stream	Total dry weight (lbs)	Dry solids capture efficiency (%)	Average slurry flow rate (gpm)	Total screw press run time (min)
Saddle Creek, FL	Slurry biosolids (influent)	63.9	16.9	0.64	667.0
Saddle Creek, FL	Dewatered cake (effluent)	10.8			
Lake Chautauqua, NY	Slurry biosolids (influent)	55.6	75.0	1.03	305.0
Lake Chautauqua, NY	Dewatered cake (effluent)	41.7			

Figure 3-33. Algal biosolids are generated by the screw-press dewatering process during the onshore demonstration at Chautauqua Lake in New York.

While dewatering improvements were demonstrated at the Chautauqua Lake site, the screw-press process requires additional optimization to meet the project objectives of >15% solids with >95% solids recovery. In both

Florida and New York, high doses of flocculant were required for achieving the dewatering results. Given that these flocculants were in addition to those dosed for DAF treatment, and given the limited recovery levels, the permeate from the screw-press process was disposed of as a municipal waste stream in coordination with local wastewater treatment facilities. Once the dewatering process is fully optimized, the permeate water could be recirculated to DAF intake to reduce waste streams.

3.6.2 Centrifuge dewatering performance

Given some of the challenges observed with the screw press, a dewatering centrifuge was also tested as a second alternative after the onshore demonstration at Chautauqua Lake. Algal solids were diluted in lake water to a concentration of 1% and then concentrated through a sequence of polymer dosing and centrifugation using a centrifuge that could process up to 5 gpm of slurry. This testing showed that, with a few days of optimization, the centrifuge was able to take algae slurry from 0.5%–1.0% solids to a cake in the range of 10%–12% solids. Field optimization time was limited, and additional operational features on larger systems could potentially increase the cake percent solids. These pilot tests were performed by Centrisys (Kenosha, Wisconsin).

3.7 HTL testing results

3.7.1 Feedstock characterization

The feedstocks used for the HTL experiments included algal biomass from the Saddle Creek demonstration, algal biomass from the Chautauqua Lake onshore demonstration, cationic polymers (GFT 5100 and Tramfloc 222), and Spirulina algae powder as a reference standard (Herb Store, Walnut, California). The algal biomass materials harvested from HABITATS demonstration sites were estimated to contain 10%–25% of the cationic polymers on a dry weight basis. Given that the polymers were a significant portion of the harvested biomass, it was important to consider their effects on the HTL process. The main chemical of the GFT 5100 polymer is a cationic starch made from plant material, and solid content is 10%–30 %. The Tramfloc 222 polymer is a more common synthetic acrylamide polymer (CAS No. 69418-26-4), which has a manufacturer-reported

molecular formula of $(C_8H_{16}ClNO_2)_x(C_3H_5NO)_x$.² The complete proximate analysis of the feedstocks was performed by Midwest Laboratories (MWL) in Omaha, Nebraska. The detailed chemical compositions of the algal feedstocks are shown in Table 3-17. The carbohydrate contents of the field biomass samples are higher than the *Spirulina* material due in part to the presence of the cationic starch from the GFT 5100 polymer. Also, any ash content is lumped into the carbohydrate content when it is calculated by difference.

Table 3-17. Proximate analysis of the feedstocks from the Saddle Creek demonstration site (Florida algae) and Chautauqua Lake demonstration site (New York algae). Analyses were conducted by Midwest Laboratories.

Proximate analysis (wt.%) ^a	FL algae ^b	NY algae ^c	<i>Spirulina</i>
Protein (crude)	31.7	36.0	70.2
Fat (crude)	0.47	1.37	0.70
Ash	23.4	28.0	8.62
Carbohydrates (calculated)	44.43	34.63	20.48

a. On a dry basis

b. Florida freeze-dried sample

c. New York freeze-dried sample

CHN elemental analyses of the feedstock were conducted in the University of Illinois–Urbana Champaign (UIUC) School of Chemical Sciences laboratory (SCS) Microanalysis Lab, on an Exeter Analytical-Model CE 440 CHN Analyzer (detection limit 0.1%, error 0.06% on a 2 mg sample). The elemental analysis results with the algae feedstocks are shown in Table 3-18. The samples were measured in duplicate, and the average values $\pm$ standard deviation were reported. After determination of the content of CHN elements in the HTL feed samples, the content of oxygen was determined by difference as shown in equation (8). Note that this calculation method leads to a conservatively high estimate of oxygen content because all ash content is counted as O, but only part of the ash is actually oxygen.

2. For a full list of the spelled-out forms of the chemical elements used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 265, <https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf>.

$$O = 100 - C - H - N, \quad (8)$$

where C, H, N, and O are the mass percentages of carbon, hydrogen, nitrogen, and oxygen, respectively, on a dry weight basis. The higher heating value (HHV) of the samples was computed using the Dulong equation (Vargas-Moreno et al. 2012).

$$HHV = 0.3383C + 1.422\left(H - \frac{O}{8}\right), \quad (9)$$

where HHV is in MJ/kg.

Table 3-18. Elemental analysis of feedstocks and higher heating value (HHV) from algal biomass collected at the Saddle Creek demonstration site (Florida Algae) and a reference standard algae (*Spirulina*).

Elemental analysis (%) ^a	Florida algae ^c	<i>Spirulina</i>
C	37.44 ± 0.04	46.36 ± 0.12
H	5.15 ± 0.00	6.88 ± 0.05
N	4.66 ± 0.01	10.83 ± 0.04
O ^b	52.76 ± 0.05	35.95 ± 0.11
HHV (MJ/kg)	10.6 ± 0.02	19.1 ± 0.01

a. On a dry basis

b. Determined by difference

c. Florida freeze-dried sample

The total solid (TS) and volatile solid (VS) of different feedstocks were also tested, and the results are shown in Table 3-19. The wet feedstocks were mechanically dewatered in a 105°C Yamato Mechanical Convection Oven and measured to determine the TS content. The VS content was tested using a muffle furnace.

Table 3-19. Moisture content, total solid (TS), volatile solid (VS), and VS/TS of algal biomass feedstocks from the demonstration sites before and after various processing methods.

Algal solids samples	Moisture content (wt.%)	TS	VS	VS/TS
Saddle Creek (original)	92.6 ± 0.2	7.4 ± 0.2 %	5.6 ± 0.2 %	74.9 ± 0.3 %
Saddle Creek (air dried)	89.7 ± 1.1	10.3 ± 1.1 %	7.7 ± 0.8 %	74.9 ± 0.1 %
Saddle Creek (freeze dried)	4.2 ± 0.6	95.8 ± 0.6 %	72.8 ± 0.5 %	76.0 ± 0.0 %
Chautauqua Lake (original)	93.4 ± 0.1	6.6 ± 0.1 %	4.8 ± 0.0 %	73.2 ± 1.6 %

Algal solids samples	Moisture content (wt.%)	TS	VS	VS/TS
Chautauqua Lake (freeze dewatered)	84.0 ± 0.7	16.0 ± 0.7 %	NA	NA
GFT5100	72.5 ± 0.2	27.5 ± 0.2 %	NA	NA

3.7.2 Bench-scale batch HTL optimization tests

To explore the effects of different operating conditions on HTL biocrude oil yield, HTL batch tests were conducted in 31.29 mL stainless steel pipe reactors fitted with a needle valve outlet. Reactors were filled with 5–12 g of total reactants, purged with nitrogen gas, and subsequently pressurized to 100 psi with nitrogen gas to ensure that most of the water in the feedstock remained in the liquid phase during HTL. The specific pressures achieved during the batch HTL tests were not monitored.

Once the reactors were prepared, they were then placed in a preheated furnace (Thermo Scientific Lindberg Blue M tubular furnace, model number TF55035A-1). The temperature inside the furnace dropped upon opening the lid, so the retention time did not commence until the temperature equilibrated at the desired reaction temperature. Upon reaching the designated retention time, the reactor was removed from the furnace and immediately cooled using a room-temperature water bath. In order to recover the HTL oil product from the HTL batch reactors and separate it from the aqueous product and solid residuals, dichloromethane (DCM, CH_2Cl_2) was used to rinse out the HTL products. Then, the DCM rinse mixture went through a preweighed vacuum filter paper (Whatman No. 4) to separate the liquid and solid phases. The mass of filterable solids from the reactor were quantified by weighing after drying. The aqueous fraction and biocrude oil with DCM solvent were isolated using a separatory funnel via phase separation, which allowed them to be recovered separately. The weight of the aqueous product could be measured directly after separation. The biocrude oil fraction was collected after evaporating the DCM solvent and then quantified by weight. Additional details of the oil separation procedure laboratory-scale HTL batch tests can be found in Aierzhati et al. (2019). The yield of biocrude oil was calculated as follows:

$$\text{Oil yield (TS based)} = \frac{\text{Weight of biocrude oil}}{\text{TS weight of feedstock}} \times 100\% \quad (10)$$

$$\text{Oil yield (DAF based)} = \frac{\text{Weight of biocrude oil}}{\text{VS weight of feedstock}} \times 100\% \quad (11)$$

All the HTL batch tests conducted using different feedstocks are summarized in Table 3-20.

Table 3-20. HTL laboratory-scale batch test conditions and oil yields.

Feedstock	T (°C)	t (min)	Solid content (wt.%)	Total reactant (g)	TS-based oil yield ^a (wt.%)	DAF-based oil yield (wt.%)
Florida algae						
Hood dried	300	30	20	5	2.5 ± 0.3	NA
Florida big bottle directly	300	45	7.4	5	5.0	6.7
Small bottle directly	300	30	10.3	5	3.0	4.0
Small bottle directly	300	45	10.3	5	5.0	6.7
Florida freeze dried	300	30	15	5	5.0	6.6
Florida freeze dried	300	45	15	5	5.0	6.6
Florida freeze dried	300	30	20	5	4.0	5.3
Florida freeze dried	300	45	20	5	5.0	6.6
1 Freeze dried + 6 big bottle	300	60	20	5	1.2	NA
1 Freeze dried + 6 big bottle	300	90	20	5	2.3	NA
Florida freeze dried	300	60	20	12	2.0	2.6
Freeze dried + glycerol	300	60	20	12	12.0	NA
New York algae						
NY freeze dried	300	60	20	12	7.4	NA
NY directly	300	60	6.6	12	13.2 ± 2.9	18.0 ± 2.9
~15% solid% material	280	60	16	12	6.7 ± 0.9	NA
~15% solid% material	300	60	16	12	8.1 ± 0.1	NA
~15% solid% material	300	30	16	6	9.5	NA
Polymer + Spirulina						
GFT only	300	60	27.5	12	1.8	NA
30%GFT + 14%Spirulina	300	60	22	12	26.3	NA
Spirulina only	300	60	22	12	41.0	44.9
Spirulina only	300	60	14	12	33.5	36.7

Feedstock	T (°C)	t (min)	Solid content (wt.%)	Total reactant (g)	TS-based oil yield ^a (wt.%)	DAF-based oil yield (wt.%)
Spirulina only	320	60	14	12	35.8	39.2
Solid polymer only	300	60	27.5	12	0.9	NA
Solid polymer + Spirulina	300	60	22	12	22.0	NA

a. Oil yields without standard errors were from HTL reactions without replications.

3.7.3 Pilot-scale continuous reactor tests

Algal biomass samples from the field demonstrations were subsequently processed in a pilot-scale HTL system at the University of Illinois campus with a nominal capacity of 1 wet ton per day of feedstock. A schematic drawing and picture of the trailer-mounted HTL pilot reactor is provided in Figure 3-34, which highlights the major equipment items included with the system. The HTL reactor has a volume of 35 L and 7 electrical band heaters for conductive heating of the main reactor core, which has a plug-flow configuration of 1/2 in stainless piping wrapped in a helical coil and surrounded by a black-iron protective housing. The HTL reactor core was operated with temperatures ranging between the 280°C and 300°C with localized temperature variations depending on which heaters were cycling on as the flow moved through the system. The system pressures ranged from 9.7–11 MPa, which was maintained by an air diaphragm back-pressure regulator (BPR). Pressures were fairly constant throughout the system at any time, but variations in pressure occurred during the run as the viscosity of material moving through the BPR was varying with time. The flow rate was controlled by a variable frequency drive on a high-pressure diaphragm pump with a target retention time of 60 min. Additional reactor details are described in Aierzhati et al. (2021).

Figure 3-34. Schematic and photo of the trailer mounted HTL pilot reactor at the University of Illinois.

As shown in Figure 3-35, the HTL pilot runs produced a biocrude oil product that could be partially separated by a metal belt skimmer installed at the first product collection barrel after the BPR (see Figure 3-34). Some additional oil was manually skimmed of the top of the product collection barrel after cooling overnight. These oil products were blended together in a composite sample used for analysis of the amount and characteristics of the bio-oil. The gas product passed through an activated carbon air filter for environmental discharge but was not captured for analysis. The aqueous product was also not collected as it was diluted by water run

through the reactor during the heat up and cooldown of the reactor system. This pilot system does not have an in-line filter to separate solids from the oil and aqueous products. The amounts and basic characteristics of the HTL oil collected during the pilot runs are provided in Table 3-21.

Figure 3-35. A belt skimmer for oil collection on the left, and a sample of the biocrude oil generated from the pilot scale HTL tests on the right.

Table 3-21. Biocrude oil properties from the continuous pilot scale HTL reactor tests.

Parameter	Biocrude oil from Saddle Creek algae ^a	Biocrude oil from Chautauqua Lake algae
Raw oil quantity (w/moisture)	1827 g	1917 g
Moisture content (wt.%)	88.7 ± 0.1	41.7 ± 3.0
Dry weight (incl. ash)	207 g	1117 g
Dry oil yield (wt% TS)	5%	19%
C (%)	34.06 ± 0.38	54.34 ± 0.22
H (%)	3.94 ± 0.07	10.96 ± 0.06
N (%)	2.47 ± 0.03	0.77 ± 0.06
O (%) ^b	59.53 ± 0.48	33.93 ± 1.78
HHV (MJ/kg)	6.54 ± 0.32	27.93 ± 0.83
H:C	1.39 ± 0.01	2.42 ± 0.09
O:C	1.31 ± 0.03	0.47 ± 0.04
N:C	0.06 ± 0.00	0.012 ± 0.001

a. Ash Content, HHV, and elemental analyses determined on a dry bio-oil basis (including ash).

b. Moisture content determined by oven drying at 105°C.

c. O content is calculated by difference as per equation (8).

d. Calculated by Dulong formula, equation (9).

The HTL oil produced from the Florida algae sample had an unusually high moisture content and extremely low yield on a dry solids basis, which correlated to the results obtained with HTL batch testing. The very high cationic starch polymer content of this algae sample likely led to the poor oil yield. This observation aligns with the batch scale HTL testing of the polymers by themselves, which had very low oil yields.

The Chautauqua Lake algae sample (77 L wet feedstock) used for HTL pilot testing had a much better bio-oil yield of 19% of total solids (with ash), after correcting for a relatively high moisture content (42%), and a moderate ash content (5%) in the raw wet bio-oil. The calculated heating value of the dry bio-oil with ash was 28 MJ/kg according to the elemental content from CHN analysis. On the basis of these results, the steady-state ratio of heat out:heat in was approximately 1.2, when comparing the heating value of the New York oil to the heating value of the New York algae feedstock and assuming a heat exchange efficiency of 50%. There are

some other minor energy inputs (pumping, odor control), but a net energy-positive HTL process should be achievable at steady state with the pilot performance results noted above. The New York algae oil sample was further analyzed by thermogravimetric analysis (TGA), as shown in Figure 3-36. This figure shows a large weight loss around 100°C corresponding to water in the sample and then most of the remaining oil mass lost between 250°C–300°C, which roughly correlates to the boiling point range of the sample. These data suggest that this oil is on the lighter end of petroleum diesel fuels, which have a typical boiling point range of 200°C–380°C. The primary boiling point range of this oil sample was low in comparison to other algae HTL bio-oils reported in the literature. Possible reasons for this lower range include relatively poor products separation or too long of a residence time, which results in high boiling point compounds being decomposed. This decomposition can also reduce biocrude oil yield. Thus, future testing should evaluate shorter retention times to see if they increase the oil yield and extend the boiling point range to higher temperatures.

Figure 3-36. Thermogravimetric analysis (TGA) curves for biocrude oil generated from HTL processing of algal biomass generated at the Chautauqua Lake demonstration site.

3.7.4 Algal toxin destruction studies

The initial experiments to assess the destruction of microcystin by the HTL process involved spiking a known concentration of an algal toxin mixture into an algae sample and running a reaction on the bench-scale HTL. The aqueous product was collected, and an attempt at different clean up and extraction methods using solid phase extraction (SPE) cartridges was made to quantify the analyte post-HTL process. However, because of the complex nature of the HTL aqueous product, the sample preparation and analysis needed more fine-tuning, and it was decided to first confirm removal in a blank matrix. For the blank matrix experiments, a nanopure sample was spiked with a target concentration of 200 ppb for several algal toxins, which was then added to a static pipe HTL reactor that was sealed and heated to the same temperature and time as a typical HTL reaction (30 min at 300°C). Samples were weighed before and after the reaction to verify sample was not lost during the process. Then analysis of the blank matrix sample on a liquid chromatography–dual mass spectrometry instrument (LC-MS/MS) gave the results in Table 3-22 with the pre-HTL sample for comparison.

All samples were duplicated, and both duplicates had mass spectrometry (MS) signals below the detection limit in the post-HTL sample for all the algal toxins. The detection limit was determined according to the lowest measurable peak area for each toxin in the calibration standards and quality control (QC) samples to ensure a conservative estimate of the percent destruction. QC for the samples was given by two check standards at the beginning and end of the sample run and by an analytical spike on one of the duplicates of the samples. The analytical spike added a known concentration of each toxin into the post-HTL sample just before LC-MS/MS analysis to determine recovery of the analyte by the instrument in the same matrix as the samples. In this case, the recovery of the analytical spike was between 92% and 148% for all compounds tested, which is generally considered adequate for this type of analytical procedure. Thus, these results demonstrate that at least 97% destruction occurred during the HTL process for each of the seven algal toxins in the clean matrix without algae biomass. Several of the toxins had slightly lower detection limits and thus provided quantitative evidence of HTL destruction of more than 99% for some toxins in the clean matrix.

Table 3-22. Algal toxin concentrations and removal in a blank matrix sample before and after HTL (BDL = below detection limit).

Name	Pre-HTL sample (ppb)	Post-HTL sample (ppb)	HTL % destruction
Microcystin RR	209	<1.5 (BDL)	>99%
Microcystin YR	215	<1.3 (BDL)	>99%
Microcystin LR	216	<1.3(BDL)	>99%
Nodularin	202	<1.3(BDL)	>99%
Microcystin LY	238	<4.8 (BDL)	>98%
Microcystin LA	205	<5.6 (BDL)	>97%
Microcystin LW	197	<4.3(BDL)	>98%

After confirming algal toxin destruction in a blank matrix sample, many different methods were tested for the cleanup and extraction of the HTL matrix from algal biomass for subsequent analysis of algal toxins. Experiments involved an initial spike of 100 ppb of each toxin to an HTL aqueous product matrix and then used different types and combinations of SPE cartridges, polarity of elution solvents, and dilution of extracted HTL samples. Initially, three SPE cartridge cleanup processes were identified that gave positive recoveries of blank matrix samples, but the organic

matter in the HTL matrix samples still had too much interference with detection of the analyte on the LC-MS/MS. Subsequent results showed good recovery of known concentrations of analytes in the HTL matrix when aliquots of an HTL sample were first diluted by 2× and processed through a single SPE cartridge before nitrogen sparging of the elution solvent and reconstitution in the reduced amount of solvent. Various other sample dilutions were also tested for comparison with the 2× dilution and extraction results to refine the cleanup and extraction methods, which will be used in further experiments.

In the current sample preparation methods, an Oasis-HLB SPE cartridge was conditioned with 15 mL of methanol followed by 18 mL of nanopure water. Then, the HTL samples were passed through the cartridge, and the sample vial was rinsed with two aliquots of 5 mL of nanopure and poured through the cartridge to ensure the sample was fully transferred into the cartridge. To elute the analyte from the cartridge, 10 mL of a 90:10 solvent blend of methanol:nanopure water was added to the sample vials and then poured through the cartridge and collected. After elution, each sample was evaporated to dryness using nitrogen gas, reconstituted in 1 mL of a 90:10 methanol:nanopure water, and vortexed for 1 minute. Analytical results for three algal toxins using this method are provided in Table 3-23, which showed destruction of microcystins was at least 95% for three of the algal toxins tested. Note that the toxin concentrations in the post-HTL matrix sample were determined using a five-point calibration curve, and the percent removal is calculated using the known spike concentration of 50 ppb. The toxin percent removal levels were slightly lower in the HTL matrix samples (Table 3-23) than the blank matrix samples (Table 3-22), which may be explained by some protective effect of the high organic matter content in the HTL matrix samples. Further research into this difference is needed to better understand the cause.

Table 3-23. Algal toxin concentrations and removal in algae matrix samples before and after HTL.

Name	50 ppb matrix spike measured conc. (ppb)	Avg post-HTL conc. (ppb)	HTL % destruction
Microcystin YR	52.0	2.45	95%
Microcystin LR	47.3	2.05	96%
Nodularin	38.1	1.90	96%

The results for a 50-ppb matrix spike are also shown in Table 3-23, which shows recovery of over 75% for three analytes. The matrix spike determines recovery of the analyte through the cleanup and extraction process. In addition, a 50-ppb analytical spike of the sample just before the LC-MS/MS instrument was also run to determine instrument capability of recovering the analyte in the matrix. The analytical spike recoveries ranged from 88% to 129%, which is also considered adequate. One other toxin (microcystin RR) had a slightly lower recovery, but it was close enough to be able to measure this compound in the HTL matrix samples with some minor method refinements. The other three toxins listed in Table 3-22 (microcystin LY, microcystin LA, microcystin LW) did not have good recovery with the current sample preparation methods for the HTL matrix samples. Further work on a different extraction and cleanup method will likely be needed to measure these other three toxins.

One such approach for improving performance is to perform an initial 2× dilution of the HTL aqueous product with nanopure water, which has shown improved extraction performance when used in conjunction with a more sensitive MS instrument. This work has shown the ability to achieve lower detection limits for several algal toxins and confirm a higher percentage of destruction, as shown in Table 3-24. The initial results with this new sample preparation method are shown below.

Table 3-24. Improved detection limits of microcystin structures in HTL aqueous effluents, allowing for increased quantitation of destruction levels. (MC: microcystin)

	Detection limit (µg/L)	% destruction in HTL
MC-RR	0.05	99.90%
MC-YR	2.5	95%
MC-LR	2.5	95%
NOD	0.5	99%
MC-LY	0.5	99%
MC-LA	0.1	100%
MC-LW	2.5	95%
	Avg	98%

4 Discussion

Several key advancements of the HABITATS technology were achieved in Year 2 of the study, but additional challenges must be overcome prior to deployment at full scale. The treatment and transformation capabilities both saw considerable improvements that increased their compatibility, as evidenced by the increase in fuel yield relative to the first year of the project. The data collected during the second year of the study were essential in updating previous models and identifying opportunities for further improvement in all three areas. The scalability analysis model discussed herein will highlight dewatering as the priority focus area for the final year of the development effort. Improving dewatering will drastically improve energy efficiency of the operation while reducing costs and logistics. The models also indicate that enhancing the interception step can have tremendous benefits in terms of environmental impact and energy efficiency.

4.1 Interception

Several types of interceptors were tested in Year 2 of the study, all revolving around the principle of skimming algae near the water surface using booms and floating weirs. The interceptors in the pilot-scale studies generally performed well in skimming the water at the target depth and in protecting nontarget aquatic species from entering the system. The latter was achieved using 3/8 in screens that rejected both plant matter and aquatic organisms.

It is relatively straight forward to set up a pilot-scale interception system to collect enough algae for the pilot treatment and transformation studies, but concepts for optimal algae interception at full scale to maximize impact on the environment are still in development. Optimizing the interception process to target and preconcentrate the algae will be a key focus in the final year of the HABITATS development effort. Modeling has shown that optimization of how the HABITATS interceptor interfaces with the water body may have drastic implications for success or failure in achieving scalability (ERDC TR 20-1, Page et al. 2020). Equally important is the nature of the HAB itself. HABs in which the biomass is concentrated at the water surface can be targeted effectively by HABITATS. While this is seen in many HABs, it is not always the case, such as the Saddle Creek

scenario, in which the bloom was well dispersed in the water column during the demonstration.

For cases in which the bloom is distributed downward in the water column, or in which the algae are moving up and down in the water column in a diurnal cycle, an active approach for in-situ flotation would strengthen the HABITATS concept. This approach would ideally be a chemical-free process that leverages existing algal flotation mechanisms and is selective for the algal cells. During jar tests in the HABITATS laboratory and field studies, the introduction of microbubbles without chemicals appeared to have some flotation effect, which was thought to be due to extracellular polymers excreted by the algal cells mediating flocculation and flotation. It is possible that natural processes such as excretion of extracellular polymers and cation bridging might promote aggregation and propensity for floatation during mixing with microbubbles, and this phenomenon has been observed in previous studies (Dervaux, Mejean, and Brunet 2015; Druga et al. 2019). Newer technologies that create nanobubbles should also be explored for the purpose of preconcentrating the algae on the water surface prior to interception. This surface concentration would increase the environmental benefit, reduce the volumes of water to be collected, and increase the energy efficiency because of the higher fuel feedstock content of the influent water.

It should also be noted that HABs can be a moving target, even when present on a surface. The newly developed shipboard system provides the ability to target algae in different areas of a water body with an active harvesting approach. While this active harvesting presents an additional energy requirement, a shipboard system would not always need to be moving forward (and using fuel to move through the water) during the treatment process. In areas with surface currents, the lead boats could be anchored strategically into the current to allow the algae to flow towards the interceptor system.

4.2 Treatment

The treatment processes of DAF, ozone, and screw press were studied in detail at the two demonstration sites. Data collection focused on water quality and engineering performance. In general, the water quality improvement was consistent, substantial, and in line with objectives and requirements. In terms of engineering performance, the DAF technology

once again proved itself as a rapid and robust system for clarification, with additional benefits for removing particle-entrained contaminants such as nutrients and toxins. The ozone technology is a robust approach for removal of residual microcystin, but its cost benefit should be analyzed carefully. The screw-press technology (and dewatering technologies in general) remains an important area for improvement.

4.2.1 DAF performance with new organic chemicals

The organic chemicals used for coagulation and flocculation upstream of the DAF process were highly effective in facilitating water clarification, as evidenced by decreases in turbidity and organic particulates (VSS) during the treatment demonstrations. The performance levels were similar to previous studies using aluminum chlorohydrate as a coagulant. In the current study, a combination of cationic starch coupled with a low dose of cationic polyacrylamide polymer provided a balance of effective treatment performance and reduced ecological toxicity. At the higher doses applied in Florida, the effluent required environmental dilution by a ratio of 2 parts effluent to 1 part receiving water to achieve toxicity compliance with respect to water flea reproduction. In the demonstration, the ratio was approximately 1,000:1, resulting in no environmental risk, but larger-scale systems could be constrained by discharge limitations. Further research should be conducted to decrease the potential for effluent toxicity and to develop on-site monitoring methods for coagulant and flocculant materials.

By switching to an organic chemical for coagulation and flocculation upstream of the DAF, there seemed to be a limited change in the nutrient removal levels relative to the previous HABITATS study, which used aluminum chlorohydrate. Even though aluminum salts can remove dissolved phosphate directly, most of the phosphorus removal observed in the previous study appeared to be cell associated. This observation is consistent with phosphate being a growth-limiting nutrient for HABs. The high levels of TP and TN that accumulate relative to the dissolved ionic nutrient species exemplifies how cyanobacteria can act as nutrient accumulators in the environment.

4.2.2 Ozonation for residual microcystin control: is it needed?

Ozone is an advanced oxidation process that is an effective tool for destruction of many trace organics, including residual microcystin and

other cyanotoxins in water. It is also highly reactive and therefore dissipates in the water without needing to be quenched in many cases. Despite the high general reactivity, it preferentially reacts with microcystin with a rate constant above $10^5 \text{ M}^{-1} \text{ sec}^{-1}$ (Kim and Lee 2019) even when other organics are present. As such, an ozone dose approaching 20% of the mass concentration of TOC in the water will provide microcystin reductions of >90% in many cases (Lee et al. 2013).

Ozone is a relatively energy-intensive chemical oxidation process, though it offers the advantages described above in addition to logistical advantages of being generated on-site. Ozone generation requires equipment and electricity for oxygen purification and ozone generation. To apply an ozone dose of 2 ppm to a 2 MGD module process stream would require oxygen generation and purification at a rate of 150 lpm and ozone generation at a rate of about 700 grams per hour. This equipment would require about 7.5 kW for the oxygen generator and 25 kW for the ozone generation, which equates to 0.36 Wh/gal. To put this quantity into perspective, the energy requirement for the influent pumps, entire DAF system, and effluent pumps is 1.02 Wh/gal. Thus, the ozone unit increases energy consumption of the entire treatment process by 35%.

In the present study, ozone was effective in removing residual microcystin present after DAF treatment of water from Chautauqua Lake. However, the DAF treatment itself removed most of the microcystin from the influent, making it difficult to assess the full potential of ozone for controlling high levels of microcystin. Further, on the basis of these data, the benefit of ozone relative to the cost and energy requirement is questionable. While the target level for microcystin in the HABITATS discharge water is less than 1 ppb, the recreational guideline for microcystin is actually 8 ppb. Using this limit, the Chautauqua Lake water with microcystin at 4 ppb would already be deemed compliant with recreational use guidelines. After DAF treatment, the residual microcystin in the water was about an order of magnitude lower, or about 0.3–0.4 ppb, which is below the drinking water guideline level. Thus, the application of ozone after DAF seems to have limited benefit in this case. A more plausible and efficient approach would be to have an ozone unit available but to only operate the ozone system when microcystin is present in the DAF effluent at levels deemed unsuitable for discharge.

To further assess the need for ozone, a review of HAB data should be conducted to assess the level of microcystin commonly present and whether the microcystin is in the free dissolved form or whether it is predominantly intracellular (within the cells). In the latter case, DAF should remove most of the microcystin along with the cells. If influent microcystin is predominantly free dissolved microcystin, it is unlikely that DAF will have much impact, and ozone would be needed if influent levels exceed discharge requirement levels. On the basis of the data in this study, ozone use would likely be limited to scenarios in which free microcystin is present at levels of concern in the source water. If intracellular microcystin is present, it will be removed with the algal cells during DAF treatment.

4.2.3 Dewatering challenges

The screw-press method for dewatering offers great promise in terms of throughput and energy efficiency, but it did not meet performance targets for solids concentration (7%–10% versus 18% target), solids recovery (75% versus 95% target), or flow rate (1 gpm versus 2.5 gpm target). Engineering optimization by AECOM with input from ERDC and ISTC during the three-week period between the Florida and New York demonstrations resulted in improved performance, but the improvements were limited relative to objectives. While it would be convenient to ascribe the shortcomings to the screw-press method technology itself, it is possible that the organic chemicals used for coagulation and flocculation were not optimal for dewatering of the algal slurry after DAF separation. This notion is supported by several observations. First, additional flocculant material with higher charge density was required to facilitate dewatering by the screw press, with chemistry drastically affecting performance. Second, processing the same solids with a centrifuge that had previously dewatered algal slurry to 18% solids yielded only 10% with these samples. Lastly, early laboratory results that used a slightly different chemical formulation resulted in more extensive dewatering and a powder-like appearance of the solids versus the high sheen solids observed in the field. In the future, the organic chemicals used for coagulation and flocculation must be down selected according to dewaterability in addition to the previously established criteria for low toxicity and jar-testing performance (clarification). Fuel conversion potential should be an additional criterion for down selection.

Another shortcoming during the screw-press testing was the need to dispose of the filtrate as wastewater because of additional flocculant material that was required to increase solids separation and retention. For environmental

compliance reasons, this additional flocculant material prohibited recirculating the filtrate water generated by the screw press back into the DAF feed. While the wastewater volumes that resulted were limited—being 300-fold lower than the volumes of water that passed through the DAF and ozonation prior to discharge—the wastewater generation would still represent a logistical burden for a full-scale operation.

4.3 Transformation

A key milestone in the second year of the HABITATS study was the first pilot-scale test of HTL technology for converting algae into biocrude oil. Because of limitations in the dewatering process, it was expected that the fuel yields would be significantly impaired. However, biocrude yields up to 20% were achieved, which should be sufficient for energy neutrality for the HTL process itself when heat recovery is practiced in a continuous-flow reactor. The 20% yield was a 33% improvement compared to the bench-scale continuous-flow reactor study performed during the first year of the study. This improvement is likely due to the increased organic content of the algal biomass, as biomass from the previous year contained high levels of aluminum. While the improvement was significant, the fuel yields were still lower than theoretical projections and controlled experiments have shown is possible. Two issues need to be addressed to realize maximal fuel yields. First, the coagulants and flocculants could be improved by selecting polymers with lower oxygen content. Second, the algal biomass must be dewatered to at least 15% dry solids, preferably 18% or more. Both improvements are expected to be achievable through optimization of the chemistry of the treatment and dewatering processes. This optimization is a focus of ongoing laboratory research.

In addition to improving fuel yields, the second year of the project continued to demonstrate destruction of microcystin by the HTL process. To date, multiple confirmatory experiments have been performed at the ISTC in clean water and highly organic water. In algal biomass matrices, it is more difficult to measure and differentiate microcystin relative to the abundance of organic compounds, though extraction methods are being optimized to mitigate this issue in the future. In the aqueous experiments, spikes of high levels of microcystin allowed for accurate measurement of the destruction of various forms of microcystin and analogous structures.

Another important focus area for future optimization of the HTL process is process heat recovery and incorporation of waste heat from the

HABITATS electrical power generators. Heat recovery will be the last step in achieving net energy neutrality and possibly net energy production for the HABITATS system. Specifically, hot fuel and aqueous waste exiting the reactor should be used to preheat algal biomass entering the reactor. For heating the reactor itself, glycol heat transfer loops should capture the high-temperature waste heat exhausted from electrical generators. By leveraging these heat sources, very little electrical heating energy would be required. Importantly, these concepts could further the sustainable on-site use of the biocrude generated from the algae.

4.4 Scalability analysis of onshore system

The scalability analysis developed and described in the previous HABITATS report (ERDC TR 20-1, Page et al. 2020) was updated using data and market research collected during the second year of the project. Revised estimates of footprint, energy consumption, and cost as a function of key variables such as influent algae concentration are presented herein. To the extent possible, data collected during the pilot demonstration were used to support the model and analysis. Other sources, such as published water treatment plant cost estimation models using Engineering News Record data (Plumlee et al. 2014; McGivney and Kawamura 2008) and informal market research, 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 HTL were used to estimate fuel recovery and costs at scale (Snowden-Swan et al. 2016, 2018; Zhang et al. 2017).

A key update to the scalability analysis and HABITATS project vision is the definition of a full-scale module that can serve as the fundamental building block for various design scales. The size of the base module was constrained primarily by the maximum DAF unit that could be road transportable without special wide-load or other permits. A road-transportable base module would allow for rapid deployment and flexibility with respect to where and when modules could be deployed. The form factor could be a low-boy trailer or modified frac-tank trailer that would not require specialized transport. It was determined that a trailer DAF system could treat 2 MGD (that is, 1,500 gpm or 4 cfs). A second trailer would contain all the supporting equipment, including ozonator, screw press, HTL reactor, and a membrane bioreactor for HTL aqueous effluent. The system could be fully automated and remotely supported, enabling one on-site trained technician having the capability to operate

multiple modules aided by remote engineering support and performance monitoring.

4.4.1 Analysis approach

The previous HABITATS scalability analysis (ERDC TR20-01, Page et al 2020) was updated to further incorporate data from field testing and equipment manufacturers in support of a more narrow focus on deployable modules that could provide an onshore HAB response capability for deployment upstream of critical spillways, along canals, or near critical shoreline areas on lakes. Each HABITATS module is comprised of two interstate-transportable equipment trailers capable of treating up to 2 MGD of algae-laden water and transforming the biomass into fuel. It is envisioned that multiple modules could be deployed to achieve desired design capacities and that modules could be moved from site to site as HABs occur around the nation. For clarity in the present discussion, two cases of spillway discharge rates of 200 and 2000 cfs will be analyzed. Variations in influent algae concentration, algae depth distribution, influent microcystin concentrations, and operation schedules will be assessed in terms of cost, land requirements, energy, and water-body impact.

Some of the key physical components of the model are shown in Figure 4-1. Key input parameters for the model include water flow rate, surface algae concentration and depth distribution coefficient, process throughput and energy consumption for each component, operation schedule, and capital cost per module. Output parameters include capital cost, operation and maintenance costs, total system cost, annualized cost over a 20-year life cycle, system energy consumption and production, labor and chemical costs for operations, costs per pound of phosphorous and nitrogen removed, and cost per ton of algae removed.

Figure 4-1. Key physical components of the HABITATS model.

The updated model also reduces the complexity of assumptions made previously for the interception process. Because HABs can be well dispersed in some water bodies, as observed at the Saddle Creek site, no claims of preconcentration of the algae by the floating booms are made in the updated model, and the influent algae are assumed to be the ambient algae concentration. However, the depth coefficients developed previously are still used to describe the biomass distribution in the water column for assessing various cases. Preconcentration of algae at the surface will remain a focus in future work, and the scalability model will guide development of the associated metrics.

4.4.2 Energy consumption

A key focus of the HABITATS approach is to reduce the energy requirements for HAB mitigation through energy recovery in the form of fuel. An important observation in the previous report was that energy consumption by HABITATS is strongly dependent on the influent algae concentration. The general conclusion was that a higher influent algae concentration would reduce net energy consumption because of the ability to recover more fuel from a given volume of water being processed. However, this conclusion was based solely on dewatering efficacy (to 18% solids) and the theoretical biocrude yields of 37% projected at that time based on controlled laboratory studies reported in the literature. The analysis was repeated in Year 2 of the study using actual data from the pilot studies (that is, dewatered solids concentration of 8%; fuel yield of 20%) as well as specifications for a deployable 2 MGD treatment module. Modeled results are presented in Figure 4-2 and show that the net energy requirement increases with influent algae concentration when the algal solids are 8% and the fuel yield is 20% (current energy consumption). For

comparison, the theoretical future energy consumption for a fully optimized system is also shown.

Figure 4-2. Modeled results of energy consumption as a function of influent algae concentration.

The data show that the current HABITATS metric of 1 Wh/gal, which is based on typical wastewater treatment energy requirements (Department of Energy 2016), would not be achieved, and higher influent algae concentrations would push performance further away from the target. This result is driven primarily by the shortcoming in dewatering efficiency. Reducing the solids concentration decreases fuel yields, but it also increases the volume of biomass to be processed by the energy-intensive HTL step. If HABITATS were deployed at scale without first improving the dewatering process, energy objectives would not be met. However, if the dewatering process can be improved to increase the algal biomass concentration prior to HTL, the project metrics will be met and even exceeded at higher influent algae concentrations. Improving dewatering performance will be the key research focus area going forward.

4.4.3 Cost efficiency

The capital cost of a HABITATS module will be a fixed quantity, but cost efficiency will vary as a function of influent algae concentration and operation schedule. From an engineering perspective, cost efficiency in water treatment is typically determined relative to the volume of water treated. From an environmental perspective, cost efficiency could be considered relative to the amounts of carbon, nitrogen, and phosphorus

removed. From a business perspective, costs could be normalized to the fuel and nutrient resources recovered. It is important to understand how variations in parameters such as influent algae concentration will affect each of these cost perspectives, as stakeholders may have different priorities based on their specific situation.

As shown in Figure 4-3, the cost model developed for HABITATS modules estimates that the operations and maintenance costs (power, chemicals, labor) are almost two- to four-fold greater than the 20-year annualized capital cost for the systems. The annual cost is therefore strongly dependent on the uptime over a given year because of the increased operating costs. Because of capital invested, the first 10% of uptime (5.2 weeks) is expensive relative to higher levels of uptime.

Figure 4-3. Projected annual cost of a HABITATS system over a 20-year period as a function of treatment capacity with varying uptimes.

The cost efficiencies become more apparent when looking at the cost for treating 1,000 gal of water as a function of uptime (Figure 4-4). Increasing the uptime reduces the cost for each gallon of water treatment, especially in the lower uptime range because of the capital costs not being utilized efficiently. There are diminishing returns for very high uptimes, as capital costs become less significant relative to the operating costs. The key takeaway from this analysis is that the systems need to be deployed to one or multiple sites with HAB activity for at least a few months per year to optimize return on the capital investment.

The treatment cost is also dependent on the design capacity, with the labor costs for small deployments (<8 modules, 16 MGD) increasing because of economies of scale that are labor specific.

Figure 4-4. Estimated cost for treating 1,000 gal of water as a function of treatment capacity with varying uptimes.

The economics of a HABITATS system are also highly dependent on the influent algae concentration, as is apparent when looking at the costs for removing algae (cost per dry ton in Figure 4-5), removing nutrients (per pound in Figure 4-6), or the rate of generating biocrude fuel (Figure 4-7).

Figure 4-5. Estimated cost for removing algae per dry ton as a function of treatment capacity with varying algae concentrations.

Figure 4-6. Estimated cost for removing phosphorus and nitrogen per pound as a function of influent algae concentration.

Figure 4-7. Estimated yield of biocrude in barrels per day as a function of treatment capacity with varying influent algae concentrations.

4.4.4 Environmental impact—spillway scenario

HABs can be difficult to predict, and research on bloom triggers and environmental conditions that promote bloom formation continues. Regardless of the trigger, a HAB event is difficult to stop once it begins if environmental conditions are favorable. In the near term, communities might consider strategic application of mitigation technologies to limit the

impacts at specific locations, such as upstream of a spillway, near a drinking water treatment plant intake, or near a public beach area.

Remediation goals for each water body will likely be specific to local requirements. Previous work by the EPA has identified levels for total nitrogen and total phosphorus above which represent eutrophic conditions, and a reasonable goal would be to restore total nutrient levels to those below eutrophic conditions. Because most of the total nutrient content is absorbed into the algal biomass during a bloom event, removing the algal cells from the water provides a direct approach for reducing total nutrient levels in the water.

Microcystin is also a contaminant of concern, and it is often present inside cyanobacteria. It can also be freely dissolved in the water when cells lyse. The EPA reports that anatoxin-a and the microcystin variants are found intracellularly approximately 95% of the time during the growth stage of the bloom, but some other types of cyanotoxins can be released by viable cells (EPA-810F11001, 2019). Removing algal cells would remove most of the total cyanotoxin load in many cases, though there may be some cases in which additional treatment of free toxins in the water would be needed.

An overgrowth of cyanobacteria also creates environmental problems when the algae decays in the water. This process can deplete the oxygen levels in the water column, creating anoxic or hypoxic conditions that cannot facilitate a healthy ecosystem. Cyanobacteria can sequester carbon from the atmosphere at much higher rates and greater efficiency per unit area than plants (Sayre 2010), but their decay after overgrowth can cause considerable harm.

Some general targets for the water body after treatment might include the recreational guideline of <8 ppb for microcystin (USEPA 2019b), biochemical oxygen demand (BOD-5) and TSS of less than 10 ppm, TN of less than 2 ppm, and TP of less than 0.1 ppm. These would be target levels for the water body after treatment and not the targets for the HABITATS discharge water. Because HABITATS cannot treat the entire water body in many cases, it must selectively target parts of the water column where the contaminants are most concentrated and remove them to greater levels in order to have the intended impact on the whole water column.

One example for a potential HABITATS deployment scenario is an onshore system deployed upstream of a spillway to reduce the impact of the HAB occurring in a lake or reservoir on a downstream community by treating some or all of the water being discharged. Due to the clear separation between the contaminated water source and the receiving water body, this scenario provides a manageable starting point for assessing environmental impact and system scalability.

The previous HABITATS report identified several critical parameters for assessing the environmental impact of HABITATS for the spillway scenario, but one of the most impactful parameters identified was the algae depth dilution coefficient (DDC), which was an exponential coefficient used to describe the change in algae concentration with depth. For cases where algae are perfectly distributed in the water column, meaning the concentration at the water surface is equal to the concentration at the bottom of the water column, the DDC is equal to zero. In the previous report, a DDC of 0.17 was selected as a representative scenario for analysis. In this case, the algae concentration at the surface was two-fold higher than that at a depth of 4 ft. A model was developed to compare HABITATS performance for various DDCs and a fixed surface concentration of 50 mg/L (Figure 4-8). A high DDC indicates that most of the algae is concentrated at the water surface, and at greater depths, very few algae are present. A high DDC would therefore represent a surface HAB in an otherwise clear water body. Conversely, a low DDC would represent the Saddle Creek scenario, in which the algae was well dispersed in the water column. Thus, two water bodies with similar surface concentrations could have vastly different amounts of algae in the water body, and deployment of HABITATS would also have very different impacts because it targets water near the surface.

Figure 4-8. Example of changes in algae concentration with depth for various dilution coefficient (DDC) values (0.01, 0.1, 1, and 10) for a fixed surface concentration of 50 mg/L.

The associated HABITATS performance analysis demonstrated the importance of targeting (or creating) environments where the algae are predominantly on the water surface (Figure 4-9), representing a high DDC. For cases when the algae are evenly 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. However, this analysis was performed with a fixed surface concentration, meaning the total algae load in the water column was different for each DDC scenario.

Figure 4-9. Effect of algae DDC on algae removal from a canal discharging at 2,000 cfs as a function of HABITATS treatment capacity. (2,000 cfs = 1,080 MGD.)

This analysis was expanded further for a specific scenario of a 200 cfs (or 129 MGD) capacity HABITATS deployment and used the updated model that incorporated data from the 2020 pilot studies. Instead of assuming a

fixed algae concentration at the surface, it was assumed that the total algae in the water body was the same for each scenario, and two DDCs were compared (0.17 and 1.0). The surface concentrations were then set at 65 and 300 ppm, respectively, to achieve the same average biomass density in the water column (35 ppm). The resultant percentages of biomass removal from the water body were then calculated as a function of the spillway flow rate. Consistent with the previous report, the results indicate that the DDC is pivotal in determining environmental impact, even when the total biomass in the spillway is the same (Figure 4-10). For the higher DDC of 1.0, which implies 75% of the algae is in the top 1.5 ft of the water column, total algae removal levels of 50% or more would be expected at spillway discharge rates of up to 2400 cfs. For the lower DDC of 0.17, which implies 27% of the algae is in the top 1.5 ft of the water column, total algae removals of 50% or more were only achievable for spillway flow rates of less than 600 cfs.

Figure 4-10. Effect of algae DDC on algae removal (from water column) by a 200 cfs HABITATS system as a function of spillway flow rate. (200 CFS = 108 MGD.)

While these results present a challenge for high-flow systems in which algae is distributed in the water column, there are other cases where the water flow requirements would not be nearly as high. Spillway flow rates at the Saddle Creek site in Florida ranged from 50–100 cfs during the demonstration, or about 32 MGD. In theory, 16 HABITATS modules could treat all the water passing over the spillway at 50 cfs and turn the creek from green on the upstream side to clear on the downstream side. The environmental implications of treating a large fraction of the total water body would need to be considered carefully, as there would be little dilution of the discharge water.

The Chautauqua Lake case study presents a more complicated design scenario, because the objective is to improve the lake, which spans thousands of acres, rather than just improving a portion of water that is passing over a spillway. Assuming a bloom density of 30 ppm in the top 2 ft of the water column for the southern basin, the amount of water and algae to be processed would be quite large. The surface area of the southern basin is approximately 6,500 ac, which translates to a HAB water volume of 4.25 billion gallons for a HAB depth of 2 ft. Processing 4.25 billion gallons over a three-month period would require 16 HABITATS modules to treat 32 MGD, which is about 25% lower than the lake discharge rate to the Chadakoin River during HAB season. However, rather than discharging clean water directly downstream, which may not aid the lake in the near term, the clean water could be discharged at a strategic location away from the intakes and away from the lake outlet to the Chadakoin River. This different discharge location would dilute the nutrients entering from the north basin and local watershed and decrease bloom formation potential in the southern basin. Intake and discharge structures would need to be positioned optimally with respect to environmental and navigational impacts. To extend the reach of the HABITATS intake structures, several shipboard modules could be deployed to target the upper part of the water column in strategic locations. To support the onshore and shipboard operations, an accessible site would be needed to provide 2,000 f² per module, or about 0.7 ac in total, as well as access for vehicles and supporting utilities.

On the basis of the three scenarios assessed herein, HABITATS has potential applicability at all three locations (high-flow spillways, moderate-flow spillways, and in-lake treatment). However, consistent with findings from modeling efforts published previously, the scalability analysis highlights two key opportunities. First, for cases when algae predominantly float at the water surface and not distributed in the water column, the scalability of the HABITATS process increases drastically, and the process will be more practical in terms of cost, physical footprint, and energy. For this case, improving algae dewatering is still needed to realize energy-efficiency objectives and optimize costs. For the second case, when algae are distributed evenly in the water column, the HABITATS approach is not highly scalable and may not be useful for large HAB events or high-flow spillways. Achieving scalability in these situations will require new capabilities that can induce algae flotation in situ and be applied efficiently and safely in natural water bodies prior to interception. This topic is being

researched at ERDC, and concepts for optimal integration of in situ flotation with the HABITATS approach are being developed in order to expand the scope of scenarios for which HABITATS can be scalable.

5 Conclusions and Path Forward

The HABITATS 2020 pilot research demonstrations provided critical data for assessing the current maturity and scalability of the system for full-scale applications. The data and scalability analyses indicate that HABITATS is approaching readiness for technology transfer. However, further optimization and extended validation studies are still required before a truly optimal solution can be recommended for deployment for large-scale HAB events. In the near term, the technology has applicability for small-scale HAB events, particularly in cases where algae are floating on the surface and where infrastructure is available for disposing of limited waste streams associated with the current dewatering and HTL processes. Those waste streams will be largely eliminated with future developments but must be considered in the near term.

In addition to physical and logistical scalability, a key goal at the outset of the HABITATS project was to achieve energy neutrality for the entire operation, which requires sufficient fuel generation to offset the energy costs of the interception, treatment, and transformation processes. By improving fuel conversion yields this year, considerable progress was made toward this objective. Going forward, the current scalability model indicates energy neutrality is achievable if the influent algae can be preconcentrated to 120 mg/L and if the algal biomass can be dewatered to >18% solids.

The key advancements made in 2020 studies included the following:

- Development and demonstration of a combination of organic chemicals for the DAF process that can be converted into fuel in HTL. These chemicals were effective for algae removal as well as removal of nutrients and microcystin contained within the algae. The new formulation resulted in 20% biocrude yield in the first pilot-scale studies, which was a 33% improvement over the bench-scale studies conducted during the first year with aluminum-based DAF chemicals.
- Execution of two onshore field demonstrations with data showing HABITATS can improve water quality when treating algae-laden water in southern and northern climates with varying water chemistry.
- Design and assembly of the first shipboard HABITATS prototype, including flow and controls testing, for open-water algae harvesting

- and treatment. This system will increase operational reach and allow for targeting of HABs at strategic locations.
- Confirmation at pilot scale that the DAF process can remove microcystin from algae-laden water prior to the ozonation step. While a standby ozonation capability is recommended, its use could potentially be limited to cases when microcystin is in the free state rather than the more common intracellular state. Eliminating the ozonation step could reduce energy costs by 25%–33% and operational costs by 10%.
 - Development of a design for the full-scale HABITATS module that can treat up to 2 MGD and be transportable on two 53 ft trailers.
 - Updating scalability models to reflect the full-scale modular concept and analysis of several case studies of importance to stakeholders.

The key challenges and associated recommendations for future research are as follows:

- The dewatering process did not meet performance objectives, despite significant improvements made during the field studies. Improving dewatering is critical to optimizing HTL and meeting energy-efficiency targets for the system. Full-scale deployment of HABITATS is not recommended until this issue is resolved.
- For cases when algae are evenly dispersed in a water column, the scalability of HABITATS will be limited. Models indicate that HABITATS will be most effective for treating surface blooms. Given that blooms are generally only characterized at the water surface through sampling and satellite observation, more research is needed to understand algae concentrations as a function of depth. To target HABs below the surface, the development of in situ flotation technology will be key to increasing the scalability of HABITATS. In situ flotation would also allow for smaller treatment systems and increased energy efficiency.

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Acronyms and Abbreviations

Term	Definition
ABS	Absorbance
ACR	Acute-to-chronic Ratio
ANSRP	Aquatic Nuisance Species Research Program
BPR	Back-pressure Regulator
C	Carbon
CFS	Cubic Feet per Second
CHv	Chronic Value
COD	Chemical Oxygen Demand
cPAM	Cationic Polyacrylamide
CRADA	Cooperative Research and Development Agreement
DAF	Dissolved Air Flotation
DCM	Dichloromethane
DDC	Depth Dilution Coefficient
DNA	Deoxyribonucleic Acid
DO	Dissolved Oxygen
DOM	Dissolved Organic Matter
EAA	Everglades Agricultural Area
ELISA	Enzyme Linked Immunosorbent Assay
EQ	Equalization
ERDC	US Army Engineer Research and Development Center
EL	Environmental Laboratory
FDEP	Florida Department of Environmental Protection
FY	Fiscal Year
GF/C	Glass Microfiber Filters Type C
H	Hydrogen
HAB	Harmful Algal Bloom
HABITATS	Harmful Algal Bloom Interception, Treatment, and Transformation System
HCL	Hydrogen Chloride
HHV	Higher Heating Value
HTL	Hydrothermal Liquefaction
ISTC	Illinois Sustainable Technology Center
LC-MS/MS	Liquid Chromatography–Dual Mass Spectrometry Instrument
LOEC	Lowest Observable Effect Concentrations
M/V	Mass/Volume
MATC	Maximum Allowable Concentrations
MCE	Mixed Cellulose Ester
MGD	Million Gallons per Day
MHRW	Moderately Hard Reconstructed Water

Term	Definition
MS	Mass Spectrometry
MWL	Midwest Laboratories
N	Nitrogen
NA	Not Applicable
NOEC	No Observable Effect Concentrations
NPDES	National Pollutant Discharge Elimination System
NTC	National Training Center
NYSDEC	New York State Department of Environmental Conservation
O	Oxygen
O&M	Operations and Maintenance
PC	Phycocyanin
PCR	Polymerase Chain Reactions
PNNL	Pacific Northwest National Laboratory
QAPP	Quality Assurance Project Plan
QC	Quality Control
qPCR	Quantitative PCR
RFU	Relative Fluorescence Unit
SCS	School of Chemical Sciences Laboratory
SPC	Specific Conductance
SPE	Solid Phase Extraction
STA	Stormwater Treatment Area
TAE	Tris, Acetic Acid, Ethylenediaminetetraacetic Acid
TE	Tris- ethylenediaminetetraacetic Acid
TGA	Thermogravimetric Analysis
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorous
TPC	Total Pigment Concentration
TS	Total Solid
TSS	Total Suspended Solids
UIUC	University of Illinois–Urbana Champaign
USACE	US Army Corps of Engineers
USEPA	US Environmental Protection Agency
VS	Volatile Solid
VSS	Volatile Suspended Solids
WETT	Whole Effluent Toxicity Testing
YCT	Yeast-Cereal Leaves–Trout Chow Mix

Appendix A: FDEP Multisite 2CS Permit for the Florida Sites

FORM
2CS

WASTEWATER APPLICATION FOR PERMIT TO DISCHARGE
PROCESS WASTEWATER FROM NEW OR EXISTING
INDUSTRIAL WASTEWATER FACILITIES
TO SURFACE WATERS

Facility I.D. Number: N/A

Please print or type information in the appropriate areas.

I OUTFALL LOCATION For each outfall, list the X,Y coordinates and the name of the receiving water.
(latitude/longitude to the nearest 15 seconds)

A. Outfall No. (List)	B. Latitude			C. Longitude			D. Name of Receiving Water
	Deg.	Min.	Sec.	Deg.	Min.	Sec.	
1	28	59	0	-80	37	15	St. Lucie Canal
2	28	50	15	-81	5	15	C-43 Canal
3	28	43	30	-81	15	45	Lake Jesup
4	27	58	45	-81	50	15	Lake Hancock

II OUTFALL DESIGN

A. Outfall No. (List)	B. Design Configuration and Construction Materials	C. Distance from shore	D. Diameter	E. Elevation of Discharge Invert (MSL)	F. Receiving Water Depth at POD (MSL)
1	Temporary Floating Discharge Hose, 6" PVC Suction	5 ft	6 in	12 ft	4 ft
2	Temporary Floating Discharge Hose, 6" PVC Suction	2 ft	6 in	11 ft	4 ft
3	Temporary Floating Discharge Hose, 6" PVC Suction	10 ft	6 in	0 ft	- 4 ft
4	Temporary Floating Discharge Hose, 6" PVC Suction	5 ft	6 in	100 ft	94 ft
	All discharges intermittent and temporary (over 10 days)				
	Additional description provided in Sup. Inf. Section III.F				

Facility I.D. Number: N/A**III RECEIVING WATER INFORMATION**

For each surface water that will receive effluent, supply the following information:

A. Name of Receiving Water	B. Check One		C. Classification (See Ch. 62-302, F.A.C.)	D. Type of Receiving Water (canal, river, lake, etc.)
	Fresh	Salt or Brackish		
St. Lucie Canal (C-44)	☒	☐	Class 3F	Canal
Caloosahatchie C-43 Canal	☒	☐	Class 3F	Canal
Lake Jesup	☒	☐	Class 3F	Lake
Lake Hancock	☒	☐	Class 3F	Lake
	☐	☐		
	☐	☐		

Responses to E, F and G are in Sec. III of *2CS Supporting Information* (attached).

E. Minimum 7-day 10-year low flow of the receiving water at each outfall (if appropriate).

F. Identify and describe the flow of effluent from each outfall to a major body of water. A suitably marked map or aerial photograph may be used.

G. Do you request a mixing zone under Rule 62-4.244, F.A.C.? If yes, for what parameters or pollutants?

IV FLOWS, SOURCES OF POLLUTION, AND TREATMENT TECHNOLOGIES

A. Attach a line drawing showing the water flow through the facility. Indicate sources of intake water, operations contributing wastewater to the effluent, and treatment units labeled to correspond to the more detailed descriptions in Item B.

B. Construct a water balance on the line drawing by showing average flows between intakes, operations, treatment units, and outfalls. If a water balance cannot be determined (e.g., for certain mining activities), provide a pictorial description of the nature and amount of any sources of water and any collection or treatment measures.

B. For each outfall, provide a description of:

1. All operations contributing wastewater to the effluent; including process wastewater, sanitary wastewater, cooling water, and stormwater runoff;
2. The average flow contributed by each operation; and
3. The treatment received by the wastewater.

Use the space on the next page. Continue on additional sheets, if necessary.

Responses to A and B are in Sec. IV of *2CS Supporting Information* (attached).

IV B. Contd.

Facility I.D. Number: N/A

For operations flow diagram please see Figure 5 (attached).

(1) Outfall No. (List)	(2) Operation(s) Contributing Flow		(3) Treatment		
	(a) Operation (list)	(b) Avg. Flow & Units	(a) Description	(b) List Code from Table 2CS-1	
1, 2, 3, & 4	Surface Water Collection	300 gpm	Dissolved Air Flotation and Ozonation	1-H	2-B
	Algal Biomass Dewatering	1.6 gpm	Dissolved Air Flotation and Ozonation	1-H	2-B
	Hydrothermal Liquefaction	0.2 gpm	Bioreactor, DAF & O3	5-A	1-H, 2-B

IV Contd.

Facility I.D. Number:

C. Except for storm runoff, leaks, or spills, are any of the discharges described in Items II-A or B intermittent or seasonal?								
☒ Yes (complete the following table) ☐ No (go to D. below)								
(1) Outfall No. (List)	(2) Operation(s) Contributing Flow(List)	(3) Frequency		(4) Flow				(c) Duration (in days)
		(a) Days per Week (specify avg.)	(b) Months per Yr. (specify avg.)	(a) Flow Rate (in mgd)		(b) Total Volume (specify with units)		
				Long Term Avg.	Max. Daily	Long Term Avg.	Max. Daily	
1,2,3,4	Surface Water Collection	7	0.25		0.4		144,000	7
	Algal Biomass Dewatering	7	0.25		0.002		720 gal	7
	Hydrothermal Liquefaction	7	0.25		0.0002		72 gal	7
	each process operating 8 h/day							

D. Describe practices to be followed to ensure adequate wastewater treatment during emergencies such as power loss and equipment failures causing shutdown of pollution abatement equipment of the proposed/permited facilities.

E. List the method(s) and location(s) of flow measurement.

Responses to D and E are in Sec. IV of *2CS Supplemental Information* (attached).

V PRODUCTION

A. Does an effluent guideline limitation promulgated by EPA under Section 304 of the Clean Water Act apply to your facility?

☐ Yes (complete Item V-B) ☒ No (go to Section VI)

B. Are the limitations in the applicable guideline expressed in terms of production (or other measure of operation)?

☐ Yes (complete Item V-C) ☐ No (go to Section VI)

C. If you answered "yes" to Item V-B, list the quantity which represents an actual measurement of your level of production, expressed in the terms and units used in the applicable effluent guideline, and indicate the affected outfalls.

1. AVERAGE DAILY PRODUCTION			2. Affected Outfalls (list outfall nos.)
a. Quantity per Day	b. Units of Measure	c. Operation, Product, Materials, Etc. (specify)	

Facility I.D. Number: _____

VI IMPROVEMENTS

A. Are you now required by any Federal, State or local authority to meet any implementation schedule for the construction, upgrading or operation of wastewater treatment equipment or practices or any other environmental programs which may affect the discharges described in this application? This includes, but is not limited to, permit conditions, administrative or enforcement order, enforcement compliance schedule letter, stipulations, court orders, and grant or loan conditions.

☐ Yes (complete the following table) ☒ No (go to Item VI-B)

1. Identification of Condition, Agreement, Etc.	2. Affected Outfalls		3. Brief Description of Project	4. Final Compliance Date	
	a. No.	b. Source of Discharge		a. Required	B. Projected

B. OPTIONAL: You may attach additional sheets describing any additional water pollution control programs (or other environmental projects which may affect your discharges) you now have underway or which you plan. Indicate whether each program is now underway or planned, and indicate your actual or planned schedules for construction.

☐ Mark "X" if description of additional control programs is attached.

VII INTAKE AND EFFLUENT CHARACTERISTICS

Responses to A, B and C are in Sec. VII of *2CS Supplemental Information* (attached).

A, B, & C: See instructions before proceeding--Complete one set of tables for each outfall -- Annotate the outfall number in the space provided. NOTE: Tables VII-A, VII-B, and VII-C are included on separate sheets number VII-1 through VII-9.

D. Use the space below to list any of the pollutants listed in Table 2CS-3 of the instructions, which you know or have reason to believe is discharged or may be discharged from any outfall. For every pollutant you list, briefly describe the reasons you believe it to be present and report any analytical data in your possession.

1. Pollutant	2. Source	1. Pollutant	2. Source
Please see Supplemental Information, Section VII D.			

Facility I.D. Number: **VIII POTENTIAL DISCHARGES NOT COVERED BY ANALYSIS**

Is any pollutant listed in Item VII-C a substance or a component of a substance which you currently use or manufacture as an intermediate or final product or by-product?

☐ YES (list all such pollutants below) ☒ NO (go to IX)

--

IX BIOLOGICAL TOXICITY TESTING DATA

Do you have any knowledge or reason to believe that any biological test for acute or chronic toxicity has been made on any of your discharges or on a receiving water in relation to your discharge within the last 3 years?

☐ YES (identify the test(s) and describe their purposes below) ☒ NO (go to Section X)

<p>Acute and chronic toxicity testing has been performed when using the proposed system (DAF + Ozone) with no toxicity observed. A description of these findings is available in the 2CS Supplemental Information, Section IX.</p>
--

X CONTRACT ANALYSIS INFORMATION

Were any of the analyses reported in Item VII performed by a contract laboratory or consulting firm?

☐ YES (list the name, address, telephone number, and certification number of, and pollutants analyzed by each such laboratory or firm below) ☒ NO (go to Section XI)

A. Name	B. Address	C. Telephone (area code & no.)	D. Pollutants Analyzed (list)

Facility I.D. Number: _____

XI CONNECTION TO REGIONAL POTW

A. Indicate the relationship between this project and area regional planning for wastewater treatment. List steps to be taken for this industrial wastewater facility to become part of an area-wide wastewater treatment system.

Please see supplemental information.

XII-A CERTIFICATIONS FOR NEW OR MODIFIED FACILITIES

This is to certify the engineering features of this pollution control project have been designed by me and found to be in conformity with sound engineering principles, applicable to the treatment and disposal of pollutants characterized in the permit application. There is reasonable assurance, in my professional judgment, that the pollution control facilities, when properly maintained and operated, will discharge an effluent that complies with all applicable statutes of the State of Florida and the rules of the Department. It is also agreed that the undersigned, if authorized by the owner, will furnish the applicant a set of instructions for the proper maintenance and operation of the pollution control facilities and, if applicable, pollution sources.

_____ Signature _____ Name (please type) _____ (Affix Seal)	_____ Company Name Address: _____ _____ Florida Registration No.: _____ Telephone No.: _____ Date: _____
--	--

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

Angela Dunn, USACE-Jacksonville District, Enviro. Branch Chief

Name & Official Title (Please type or print)

904.232.2336

Telephone No. (area code & No.)

Digitally signed by

DUNN.ANGELA.E.1300303923

Date: 2020.06.05 09:55:34 -04'00'

Signature

5 June 2020

Date Signed

NOTE: This project was designed under the guidance and oversight of the U.S. Army Corps of Engineers. The initials or signatures of any Corps Employee and any registration designations or Corps individuals that appear on these project documents are within the scope of their employment as required by ER 1110-1-8152 and are not made in their individual capacities.

XII-B CERTIFICATIONS FOR PERMIT RENEWALS

This is to certify the engineering features of this pollution control project have been examined by me and found to be in conformity with sound engineering principles, applicable to the treatment and disposal of pollutants characterized in the permit application. There is reasonable assurance, in my professional judgment, that the pollution control facilities, when properly maintained and operated, will discharge an effluent that complies with all applicable statutes of the State of Florida and the rules of the Department.

Signature	Company Name
Name (please type)	Address:
(Affix Seal)	Florida Registration No.:
	Telephone No.:
	Date:

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

Name & Official Title (Please type or print)	Signature
Telephone No. (area code & No.)	Date Signed

PLEASE PRINT OR TYPE ONLY: You may report some or all of this information on separate sheets instead of completing these pages. Use the same format. SEE INSTRUCTIONS.

Facility ID Number: _____ Outfall No. _____

VII. INTAKE AND EFFLUENT CHARACTERISTICS

PART A - You must provide the results of at least one analysis for every pollutant in this table. Complete one table for each outfall. See instructions for additional details.

1. Pollutant	2. Effluent		3. Unit		4. Intake (optional)	
	a. Max Daily Value (1) Conc. (2) Mass	b. Max 30-day Value (1) Conc. (2) Mass	c. Annual Avg Value (1) Conc. (2) Mass	d. No. of Analyses	a. Long Term Avg Value (1) Conc. (2) Mass	b. No. of Analyses
a. Carbonaceous Biochemical Oxygen Demand (CBOD)	measure estimate	N/A	N/A	4	measure	4
b. Chemical Oxygen Demand (COD)	measure estimate	N/A	N/A	4	measure	4
c. Total Organic Carbon (TOC)	measure estimate	N/A	N/A	4	measure	4
d. Total Suspended Solids (TSS)	measure estimate	N/A	N/A	4	measure	4
e. Total Nitrogen (as N)	measure estimate	N/A	N/A	4	measure	4
f. Total Phosphorus (as P)	measure estimate	N/A	N/A	4	measure	4
g. Ammonia (as N)	measure estimate	N/A	N/A	4	measure	4
h. Flow - actual or projected	Value 300 gpm	Value	Value	10	Value	4
i. Flow - design	Value 300 gpm	Value	Value	1	Value	4
j. Specific Conductivity	Value measure	Value	Value	4	Value	4
k. Temperature (winter)	Value N/A	Value	Value	N/A	Value	4
l. Temperature (summer)	Value measure	Value	Value	1	Value	4
m. pH	Min. 6 Max. 9	Min. Max.	STANDARD UNITS	10		

PART B - Mark "X" in column 2a for each pollutant you know or have reason to believe is present. Mark "X" in column 2b for each pollutant you believe to be absent. If you mark column 2a for any pollutant which is limited either directly, or indirectly but expressly, in an effluent limitations guideline, you must provide the results of at least one analysis for that pollutant. For other pollutants for which you mark column 2a, you must provide quantitative data or an explanation of their presence in your discharge. Complete one table for each outfall. See the instructions for additional details and requirements.

1. Pollutant and CAS No. (if available)	2. Mark "X"		3. Effluent				4. Units		5. Intake (optional)	
	a. bio- prevent	b. bio- harm	a. Maximum Daily Value (1) Conc. (2) Mass	b. Max 30-day Value (if available) (1) Conc. (2) Mass	c. Long Term Avg Value (if available) (1) Conc. (2) Mass	d. No. of Analyses	a. Conc.	b. Mass	a. Long Term Avg Value (1) Conc. (2) Mass	b. No. of Analyses
a. Bromide (24949-67-9)	☐	☒								
b. Chlorine, Total Residual	☐	☒								
c. Color	☒	☐								
d. Fecal Coliform	☐	☒								
e. Fluoride (16984-48-5)	☐	☒								
f. Nitrate-Nitrite (as N)	☒	☐								

: Item VII-B Contd.

Facility ID, Number

Outfall No.

1. Pollutant and CAS No. (if available)	2. Mark "X"		3. Effluent				4. Units		5. Inside (optional)	
	a. Detected	b. Reported absent	a. Maximum Daily Value		b. Max. 30-day Value (if available)		c. Long Term Avg. Value (if available)		a. Long Term Avg. Value	
			(1) Conc.	(2) Mass	(1) Conc.	(2) Mass	(1) Conc.	(2) Mass	(1) Conc.	(2) Mass
g. Nitrogen, Total Organic (as N)	☒	☐								
h. Oil and grease	☐	☒								
i. Phosphorus, Total (as P) (7723-14-0)	☒	☐								
j. Radioactivity										
(1) Alpha, Total	☐	☒								
(2) Beta, Total	☐	☒								
(3) Radium, Total	☐	☒								
(4) Radium 226, Total	☐	☒								
k. Sulfide (as SO ₄) (14808-79-8)	☐	☒								
l. Sulfide (as S)	☐	☒								
m. Sulfide (as SO ₃) (14265-45-3)	☐	☒								
n. Surfactants	☐	☒								
o. Aluminum, Total (7429-90-5)	☐	☒								
p. Barium, Total (7440-39-3)	☐	☒								
q. Boron, Total (7440-42-6)	☐	☒								
r. Cobalt, Total (7440-48-4)	☐	☒								
s. Iron, Total (7439-89-6)	☐	☒								
t. Magnesium, Total (7439-95-4)	☐	☒								
u. Molybdenum, Total (7439-98-7)	☐	☒								
v. Manganese, Total (7439-96-5)	☐	☒								
w. Tin, Total (7440-31-5)	☐	☒								
x. Titanium, Total (7440-32-6)	☐	☒								

VII-2

PART C - If you are a primary industry and this outfall contains process wastewater, refer to Table 2c-2 in the instructions to determine which of the GC/MS fractions you must test for. Mark "X" in column 2a for all GC/MS fractions that apply to your industry and for ALL toxic metals, cyanides, and total phenols. If you are not required to mark column 2a (secondary industries, non-process wastewater outfalls, and non-required GC/MS fractions), mark "X" in column 2b for each pollutant you know or have reason to believe is present. Mark "X" in column 2c for each pollutant you believe is absent. If you mark column 2a for any pollutant, you must provide the results of at least one analysis for that pollutant. If you mark column 2b for any pollutant, you must provide the results of at least one analysis for that pollutant if you know or have reason to believe it will be discharged in concentrations of 10 ppb or greater. If you mark column 2c for acrolein, acrylonitrile, 2,4-dinitrophenol, or 2-methyl-4,6-dinitrophenol, you must provide the results of at least one analysis for each of these pollutants which you know or have reason to believe that you discharge in concentrations of 100 ppb or greater. Otherwise, for pollutants for which you mark column 2b, you must either submit at least one analysis or briefly describe the reasons the pollutant is expected to be discharged. Note that there are 7 pages to this part; please review each carefully. Complete one table (all 7 pages) for each outfall. See instructions for additional details and requirements.

Facility ID, Number: _____ Outfall No. _____

1. Pollutant and CAS No. (if available)	2. Mark "X"		3. Effluent				4. Units		5. Results (optional)		b. No. of Analyses	
	a. Testing required	b. Detected present	c. Detected absent	a. Maximum Daily Value (1) Conc. (2) Mass	b. Max. 30-day Value (if available) (1) Conc. (2) Mass	c. Long Term Avg. Value (if available) (1) Conc. (2) Mass	d. No. of Analyses	a. Conc.	b. Mass	a. Long Term Avg. Value		
										(1) Conc.		(2) Mass
METALS, CYANIDE, AND TOTAL PHENOLS												
1M. Antimony, Total (7440-36-0)	☐	☐	☒									
2M. Arsenic, Total (7723-14-0)	☐	☐	☒									
3M. Beryllium, Total (7440-41-7)	☐	☐	☒									
4M. Cadmium, Total (7440-43-9)	☐	☐	☒									
5M. Chromium, Total (7440-47-3)	☐	☐	☒									
6M. Copper, Total (7440-50-6)	☐	☐	☒									
7M. Lead, Total (7439-92-1)	☐	☐	☒									
8M. Mercury, Total (7439-97-6)	☐	☐	☒									
9M. Nickel, Total (7440-02-0)	☐	☐	☒									
10M. Selenium, Total (7782-49-2)	☐	☐	☒									
11M. Silver, Total (7440-22-4)	☐	☐	☒									
12M. Thallium, Total (7440-28-0)	☐	☐	☒									
13M. Zinc, Total (7440-66-6)	☐	☐	☒									
14M. Cyanide, Total (57-12-5)	☐	☐	☒									
15M. Phenols, Total	☐	☐	☒									
DIOXIN												
2,3,7,8-Tetra-chlorodibenzo-p-Dioxin (1764-01-6)	☐	☐	☒									
GC/MS FRACTION -VOLATILE COMPOUNDS												
1V. Acrolein (107-02-6)	☐	☐	☒									
3V. Acrylonitrile (107-13-1)	☐	☐	☒									

VTL-3

Facility ID. Number:

Outfall No.

1. Pollutant and CAS No. (if available)	2. Mark "X"		c. be- lieved absent	3. Effluent				4. Units		5. Intake (optional)		
	a. . testing required	b. be- lieved present		a. Maximum Daily Value		b. Max. 30-day Value (if available)	c. Long Term Avg. Value (if available)		a. Conc.	b. Mass	a. Long Term Avg. Value	
				(1) Conc.	(2) Mass		(1) Conc.	(2) Mass			(1) Conc.	(2) Mass
GC/MS FRACTION - VOLATILE COMPOUNDS (continued)												
3V. Benzene (71-43-2)	☐	☐	☒									
4V. Bis (Chloromethyl) Ether (542-88-1)	☐	☐	☒									
5V. Bromoform (75-25-2)	☐	☐	☒									
6V. Carbon Tetrachloride (56-23-5)	☐	☐	☒									
7V. Chlorobenzene (106-90-7)	☐	☐	☒									
8V. Chlorodibromomethane (124-6-1)	☐	☐	☒									
9V. Chloroethane (74-00-3)	☐	☐	☒									
10V. 2-Chloro-ethylvinyl Ether (110-75-8)	☐	☐	☒									
11V. Chloroform (67-66-3)	☐	☐	☒									
12V. Dichlorobromomethane (75-24-4)	☐	☐	☒									
13V. Dichlorodibromomethane (75-71-8)	☐	☐	☒									
14V. 1,1-Dichloroethane (75-34-3)	☐	☐	☒									
15V. 1,2-Dichloroethane (107-06-2)	☐	☐	☒									
16V. 1,1-Dichloroethane (75-35-4)	☐	☐	☒									
17V. 1,2-Dichloropropane (78-87-5)	☐	☐	☒									
18V. 1,3-Dichloropropane (542-75-6)	☐	☐	☒									
19V. Ethylbenzene (100-41-4)	☐	☐	☒									
20V. Methyl Bromide (74-83-9)	☐	☐	☒									
21V. Methyl Chloride (74-87-3)	☐	☐	☒									
22V. Methylene Chloride (74-98-2)	☐	☐	☒									
23V. 1,1,2,2-Tetrachloroethane (79-34-5)	☐	☐	☒									
24V. Trichloroethylene (127-18-4)	☐	☐	☒									

Facility ID Number: Outfall No.

VII-4

1. Pollutant and CAS No. (if available)	2. Mark "X"		3. Effluent				4. Units		5. Insolve (optional)	
	a. Testing required	b. Detected	a. Maximum Daily Value	b. Max 30-day Value (if available)	c. Long Term Avg. Value (if available)		a. Conc.	b. Mass	a. Long Term Avg. Value	b. No. of Analytes
			(1) Conc.	(2) Mass	(1) Conc.	(2) Mass	(1) Conc.	(2) Mass	(1) Conc.	(2) Mass
GC/MS FRACTION - VOLATILE COMPOUNDS (continued)										
25V. Toluene (108-88-3)	☐	☐								
26V. 1,2-Trans-Dichloroethane (156-60-5)	☐	☒								
27V. 1,1,2-Trichloroethane (71-55-6)	☐	☒								
28V. 1,1,2-Trichloroethane (79-06-5)	☐	☒								
29V. Trichloroethylene (79-01-6)	☐	☒								
30V. Trichloroethene (75-69-4)	☐	☒								
31V. Vinyl Chloride (75-01-4)	☐	☒								
GC/MS FRACTION - ACID COMPOUNDS										
1A. 2-Chlorophenol (95-57-8)	☐	☒								
3A. 2,4-Dichlorophenol (120-83-2)	☐	☒								
3A. 2,4-Dimethylphenol (105-67-9)	☐	☒								
4A. 4,6-Dinitro-O-Cresol (534-53-1)	☐	☒								
5A. 2,4-Dinitrophenol (51-28-5)	☐	☒								
6A. 2-Nitrophenol (88-75-5)	☐	☒								
7A. 4-Nitrophenol (100-02-7)	☐	☒								
8A. p-Chloro-M-Cresol (99-50-7)	☐	☒								
9A. p-Nitrochlorophenol (67-86-3)	☐	☒								
10A. Phenol (108-95-2)	☐	☒								
11A. 2,4,5-Trichlorophenol (68-06-2)	☐	☒								
GC/MS FRACTION - BASE/NEUTRAL COMPOUNDS										
1B. Acetanilide (63-32-9)	☐	☒								
2B. Acetanilide (206-96-8)	☐	☒								
3B. Anthracene (120-12-7)	☐	☒								
4B. Benzidine (92-87-3)	☐	☒								

Facility ID. Number: _____

Outfall No. _____

VII-5

Facility ID, Number:										Outfall No.		
1. Pollutant and CAS No. (if available)	2. Mark "X"			3. Effluent				4. Units		5. Intake (optional)		
	a. Testing required	b. Detected present	c. Detected absent	a. Maximum Daily Values		b. Max. 30-day Values (if available)		c. Long Term Avg. Values (if available)	d. No. of Analyses	a. Conc.	b. Mass	
				(1) Conc.	(2) Mass	(1) Conc.	(2) Mass					(1) Conc.
1B. Benzene (a) Anthracene (56-55-3)	☐	☐	☒									
6B. Benzene (a) Pyrene (50-32-8)	☐	☐	☒									
7B. 3,4-Benzofluoranthene (205-99-2)	☐	☐	☒									
8B. Benzene (b) Perylene (191-24-2)	☐	☐	☒									
9B. Benzene (b) Fluoranthene (207-08-9)	☐	☐	☒									
10B. Bis (2-Chloroethoxy) Methane (111-91-1)	☐	☐	☒									
11B. Bis (2-chloroethoxy) Ether (111-44-4)	☐	☐	☒									
12B. Bis (2-Chloropropyl) Ether (102-60-1)	☐	☐	☒									
13B. Bis (2-Ethylhexoxy) Phthalate (117-81-7)	☐	☐	☒									
14B. 4-Bromophenyl Phenyl Ether (101-55-3)	☐	☐	☒									
15B. Butyl Benzyl Phthalate (84-68-7)	☐	☐	☒									
16B. 2-Chloronaphthalene (91-58-7)	☐	☐	☒									
17B. 4-Chlorophenyl Phenyl Ether (100-57-3)	☐	☐	☒									
18B. Chrysene (218-01-9)	☐	☐	☒									
19B. Dibenzene (a,h) Anthracene (53-70-3)	☐	☐	☒									
20B. 1,2-Dichlorobenzene (95-50-1)	☐	☐	☒									
21B. 1,3-Dichlorobenzene (541-73-1)	☐	☐	☒									
22B. 1,4-Dichlorobenzene (106-46-7)	☐	☐	☒									
23B. 3,3'-Dichlorobenzidine (92-94-1)	☐	☐	☒									
24B. Diethyl Phthalate (84-66-2)	☐	☐	☒									
25B. Dimethyl Phthalate (131-11-3)	☐	☐	☒									
26B. Di-N-Butyl Phthalate (84-74-2)	☐	☐	☒									
27B. 2,4-Dinitrobenzene (121-14-2)	☐	☐	☒									
28B. 2,6-Dinitrobenzene (804-20-2)	☐	☐	☒									

Facility ID. Number:

Outfall No.

VII-6

1. Pollutant and CAS No. (if available)	2. Mark "X"		3. Effluent				4. Units		5. Embke (optional)		
	a. testing required	b. be-lieved present	c. be-lieved absent	a. Maximum Daily Value		b. Max. 30-day Value (if available)		c. Long Term Avg. Value (if available)	d. No. of Analytes	a. Conc.	b. Mass
				(1) Conc.	(2) Mass	(1) Conc.	(2) Mass				
29B. Di-N-Octyl Phthalate (117-84-0)	☐	☐	☒								
30B. 1,2-Dibenzylhydrazine (for Analysis) (122-66-7)	☐	☐	☒								
31B. Fluoranthene (206-44-0)	☐	☐	☒								
32B. Fluorene (86-73-7)	☐	☐	☒								
33B. Hexachlorobenzene (118-74-1)	☐	☐	☒								
34B. Hexachlorobenzene (87-46-3)	☐	☐	☒								
37B. Heptachloripinates (77-47-4)	☐	☐	☒								
36B. Hexachlorocyclopentadiene (67-72-1)	☐	☐	☒								
37B. Indene (1,2,3-cd) Pyrene (193-39-5)	☐	☐	☒								
38B. Isophorone (78-58-1)	☐	☐	☒								
39B. Naphthalene (91-20-3)	☐	☐	☒								
40B. Nitrobenzene (98-95-9)	☐	☐	☒								
41B. N-Nitrosodibenzylamine (62-75-9)	☐	☐	☒								
42B. N-Nitrosodi-N-Propylamine (621-64-7)	☐	☐	☒								
43B. N-Nitro-sodiumbenzylamine (86-30-6)	☐	☐	☒								
44B. Phenanthrene (85-01-8)	☐	☐	☒								
45B. Pyrene (129-00-0)	☐	☐	☒								
46B. 1,2,4-Trichlorobenzene (120-82-1)	☐	☐	☒								
GOMS FRACTION - PESTICIDES											
1P. Aldrin (509-00-2)	☐	☐	☒								
2P. -BHC (319-84-6)	☐	☐	☒								
3P. -BHC (319-85-7)	☐	☐	☒								
4P. -BHC (36-89-9)	☐	☐	☒								
5P. -BHC (319-86-6)	☐	☐	☒								

VII-7

1. Pollutant and CAS No. (if available)	2. Mark "X"			3. Effluent						4. Units		5. Inlets (optional)			
	a. testing required	b. believed present	c. believed absent	a. Maximum Daily Value		b. Max. 30-day Value (if available)		c. Long Term Avg. Value (if available)		d. No. of Analyses	a. Conc.	b. Mass	a. Long Term Avg. Value		b. No. of Analyses
				(1) Conc.	(2) Mass	(1) Conc.	(2) Mass	(1) Conc.	(2) Mass				(1) Conc.	(2) Mass	
6P. Chloroform (57-74-9)	☐	☐	☒												
7P. 4,4-DDT (50-29-3)	☐	☐	☒												
8P. 4,4-DDDE (72-55-6)	☐	☐	☒												
9P. 4,4-DDDD (72-54-6)	☐	☐	☒												
10P. Dieldrin (69-57-1)	☐	☐	☒												
11P. Endosulfan (115-29-7)	☐	☐	☒												
12P. Endosulfan (115-29-7)	☐	☐	☒												
13P. Endosulfan Sulfate (1031-07-8)	☐	☐	☒												
14P. Endrin (75-29-6)	☐	☐	☒												
15P. Endrin Aldehyde (7421-92-4)	☐	☐	☒												
16P. Heptachlor (76-44-8)	☐	☐	☒												
17P. Heptachlor Epoxide (1024-57-3)	☐	☐	☒												
18P. PCB-1242 (33-469-21-9)	☐	☐	☒												
19P. PCB-1254 (11097-69-1)	☐	☐	☒												
20P. PCB-1221 (11104-28-2)	☐	☐	☒												
21P. PCB-1232 (11141-16-5)	☐	☐	☒												
22P. PCB-1248 (12672-29-6)	☐	☐	☒												
23P. PCB-1260 (11096-82-5)	☐	☐	☒												
24P. PCB-1016 (12674-11-2)	☐	☐	☒												
25P. Toxaphene (8001-35-2)	☐	☐	☒												

Facility ID Number: _____

Outfall No. _____

VII-8

FIGURES
HABITATS 2020
2CS

Site # 1: Port Mayaca Lock and Dam

Address: 18100 SW Conners Hwy, Canal Point, FL 33438

Intake Coordinates	Discharge Coordinates
26°59'05.5"N-80°37'17.7"W	26°59'05.8"N-80°37'15.6"W

US Army Engineer Research & Development Center	Form 2CS Process Flow Diagram <i>2020 HABITATS Research Demonstration</i>	01-MAY-2020 Version 1.4	FIGURE 2CS.1
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Figure 1. Pilot Demonstration Site #1 – Port Mayaca Lock and Dam (S-308)

Site # 3: Lake Jesup

Address: 5951 Sanford Ave, Sanford, FL 32773

Intake Coordinates	Discharge Coordinates
28°43'29.1"N-81°15'15.5"W	28°43'29.1"N-81°15'49.2"W

Figure 3. Lake Jesup Park

Figure 5. Process Flow Diagram for HABITATS pilot field demonstration.

2CS SUPPORTING INFORMATION

HABITATS 2020 Pilot Research Demonstration

Permit to Discharge Process Wastewater from New or Existing Industrial Wastewater Facilities to Surface Water

The following supplemental information is provided in support of the Wastewater Application Form 2CS submitted by the US Army Corps of Engineers and Engineer Research and Development Center to support the HABITATS 2020 Pilot Research Demonstration. The supplemental information is in addition to the information in the application form and is not an independent document. It contains information that is relevant to the permit questions and sections, but for which there was not sufficient space available in the 2CS form.

The Harmful Algal Bloom Interception, Treatment, And Transformation System (HABITATS) is a process for removing algal biomass from natural water bodies, returning improved water to the environment while recovering resources in the form of fuel (biocrude) and agricultural fertilizer (nutrients) and destroying potential algal toxins. It is not an *in-situ* approach, as it operates in a contained environment separate from the water body being treated. HABITATS is designed primarily for temporary deployment. At current design scales, its deployment does not require permanent infrastructure, disruptive land modification, or other construction activities.

III

E. Minimum 7-day 10-year low flow of the receiving water at each outfall (if appropriate).

The effluent discharge rates for the pilot demonstrations are small relative to the receiving water bodies, and the water quality of the effluent is expected to be higher than that of the receiving water bodies. Historical flow data is provided for reference for the cases when the discharges are going into large canals rather than lakes.

St. Lucie Lock and Dam. The St. Lucie Canal area immediately downstream of St. Lucie Lock and Dam is approximately 600'W x 1000'L x 9'D, or ~40 million gallons. Based on a review of flow data at the downstream USGS station, the minimum 7-day average flow during the months of July and August over the last 10 years is greater than 100 cfs (65 MGD). The proposed demonstration flow rate is 0.4 MGD for up to 8 hours per day (effectively 0.14 MGD).

The water flow data for the St. Lucie canal at a gage station near the discharge site is shown in Figure SI.1, which includes historical data over the last 6 years, as well as Figure SI.2, which shows the data from summer 2019 and is expected to be representative of conditions during the demonstration in 2020. There is usually water flowing from the canal into the lake, or from the lake into the canal, ranging from -600 to +800 CFS during July 2019.

Figure SI.1 Historical flow data for the St. Lucie Canal at USGS gage station 02276877.

Figure SI.2 Summer 2019 flow data for the St. Lucie Canal at USGS gage station 02276877.

Moore Haven Lock and Dam. The Caloosahatchee (C-43) canal area immediately downstream of Moore Haven spillway is approximately 200'W x 1000'L x 10'D, or ~15 million gallons. Based on a review of flow data at the downstream USGS station, the minimum 7-day average flow during the months of July and August over the last 10 years is greater than 100 cfs (65 MGD). The proposed demonstration flow rate is 0.4 MGD for up to 8 hours per day, effectively 0.14 MGD. The water flow data for the C-43 canal at a gage station near the discharge site is shown in Figure SI.3, which includes historical data over the last 6 years, as well as Figure SI.4, which shows the data from summer 2019 and is expected to be representative of conditions during the demonstration in 2020. There is usually water flowing from the canal into the lake, or from the lake into the canal, ranging from -500 to +800 CFS during July 2019.

Figure SI.3 Historical flow data for C-43 canal near the discharge location downstream of Moore Haven Lock and Dam (S-77). USGS gage station 02292010.

Figure SI.4 Summer 2019 flow data for C-43 canal near the discharge location downstream of Moore Haven Lock and Dam (S-77). USGS gage station 02292010.

The other two candidate demonstrations are Lake Jesup (~60,000 acre-ft) and Lake Hancock (~18,300 acre-ft). In these cases, direct discharge back to the lake, rather than into canals or tributaries, would be the operating concept. They are both Class III water bodies.

F. Identify and describe the flow of effluent from each outfall to a major body of water. A suitably marked map or aerial photograph may be used.

All of the outfalls proposed will be temporary and be intermittently operated for up to 14 days, including the setup period during which discharges will be minimal. The candidate sites selected for pilot scale demonstrations include the St. Lucie Lock and Dam in Port Mayaca, FL (Figure 1); the Moore Haven Lock and Dam in Moore Haven, FL (Figure 2); Lake Jesup Park in Sanford, FL (Figure 3); and Lake Hancock in Bartow, FL (Figure 4). In all cases, the discharges will occur into Class III F water bodies. The effluent flows will be continuous over an 8-hour period each day of operation. The effluent will be discharged from 6" hoses in a horizontal direction at or just below the water surface so as not to suspend sediment in the area of discharge or cause erosion. The outfall will be tethered at the appropriate height to a single cable with a buoy and anchor to secure and identify their positions in the water. The flow rate of the discharge will be approximately 300 gpm. Each day, approximately 0.14 million gallons of effluent will be discharged between the hours of 0800 and 1600.

G. Do you request a mixing zone under Rule 62-4.244, F.A.C.? If yes, for what parameters or pollutants?

A mixing zone under Rule 62-4.244 is not requested for this work.

IV FLOWS, SOURCES OF POLLUTION, AND TREATMENT TECHNOLOGIES

A. (A larger line diagram with a water balance is provided in Figure 5 in the Figures Section).

B. For each outfall, provide a description of all operations contributing wastewater to the effluent; including process wastewater, sanitary wastewater, cooling water, and storm water runoff.

Operations for all potential demonstration sites and respective outfalls will be identical.

The three operations contributing wastewater to the effluent to be discharged at each site shall include: Surface Water Collection; Algal Biomass Dewatering; and Hydrothermal Liquefaction.

Surface water is collected from a lake or other surface water body at a flow rate of 300 gpm using a floating weir skimmer intake with the weir inlet protected by a 1-inch mesh screen to prevent aquatic organisms such as fish from entering the system while allowing particulates such as cyanobacteria to enter the system. The floating intake will only withdraw water from the top 6" of the water column. A 300 gpm centrifugal suction pump rated for processing 3/8" solids will pull water from the floating skimmer and push the water to the on-shore water treatment system that is designed to remove and destroy cyanobacteria/algae while cleaning the water. The pressurized water will pass through a surge tank to facilitate pressure equalization and reduce pressure fluctuation impacts on downstream processes. The first step in the treatment process will be a Dissolved Air Flotation (DAF) system that includes Flocculation Tubes and a Flotation Chamber. The hydraulic retention time in the DAF system will be approximately 25 minutes. In the DAF process, the water will be dosed with a flotation-

aid chemical that causes the algal cells to aggregate and adhere to bubbles. The flotation-aid chemical will be dosed at a concentration of less than 100 ppm using a variable speed pump that can be adjusted to achieve the correct dose for the water conditions and optimal flotation. The optimal dose will be determined through on-site jar testing performed at a frequency that is appropriate for the feed water variability. The chemically-treated water will then pass into a flocculation chamber that controls sheer forces to promote flocculation. The water will then pass into a flotation chamber and mix with a 75-gpm recirculation stream of pressurized (~80 psi), air-saturated water (ASW). Upon mixing and depressurization of the recirculated water, microbubble formation will occur that presents a high water-to-air surface ratio and allows rapid adsorption of the floc particles. The air-entrained floc particles float to the surface where they concentrate and remain separated from the bulk water. A scraper removes the floating particulates and transfers them to a hopper at a rate of approximately 2 gpm, leaving clarified water remaining in the flotation chamber. The clarified water flows out of the flotation chamber at approximately 375 gpm. Upon exiting, 75 gpm of clarified water is pressurized and saturated with air (ASW) and recirculated back into the chamber to facilitate microbubble generation. In the case that two DAF units are used in parallel, all flows will be halved to maintain the same hydraulic retention times and same total flow.

The remaining 300 gpm of clarified water flows through an ozone contactor (O₃) that oxidizes the water and destroys any potential cyanotoxins that may be present, such as microcystin-LR. The ozone is dosed at a ratio of at least 0.4 relative to the dissolved organic carbon (DOC) concentration in the water, which is expected to be approximately 10 mg/L after DAF treatment. The ozone reacts quickly with the dissolved organic matter in the water and is consumed in the process, producing only water and oxygen, in addition to the transformed and destroyed organic micropollutants. After ozonation, the water is transferred to a holding tank with a retention time of ~50 min. Before entering the tank, the water is tested for ozone concentration and microcystin toxin presence. The ozone testing is continuous and ensures that no ozone residual is remaining. If ozone residual is present, the operation will stop, and ozone levels inside the holding tank will be monitored to confirm the ozone has fully reacted prior to restarting the system. The microcystin testing is conducted every 60 min using FDEP-approved test strips (Abraxis). Each microcystin test takes approximately 20 minutes. If microcystin is detected at concentrations above 1 ppb, there is sufficient time to stop the water flow prior to any discharges occurring. Pending negative results for both the ozone and microcystin tests, the water will proceed to be discharged to the intended surface water.

The algae slurry that is generated by the dissolved air flotation process will be transferred to a compactor press (CP) at a flow rate of 1.6 gpm. A screw compactor or plate compactor shall be utilized, both of which operated under the same principle. Pressure is applied to the algae slurry to push water through a fine screen material. Because the algae is flocculated, it does not pass through the screen and is dewatered on the press. The dewatered algae passes from the system at a flow rate of approximately 0.2 gpm and at a solids concentration of

approximately 15-20%. The press permeate is returned to the influent line at 1.4 gpm so that it can be subjected to DAF and ozone treatment prior to discharge into the environment.

The dewatered algal biomass solids generated at a rate of 0.2 gpm are subjected to hydrothermal liquefaction (HTL) for 30 minutes. The HTL system destroys the algal cells and any toxins through a combination of high heat and pressure. The HTL process generates three waste streams- biocrude oil, inorganic solids, and an aqueous organic solution. The biocrude oil will be generated at approximately 0.04 gpm and stored on-site prior to be transported off-site for fuel upgrading at a laboratory. The inorganic solids precipitate during the process at a generation rate of approximately 0.04 gpm. These solids, comprised largely of benign inorganic materials, will be stored on-site and disposed of in a landfill. Samples will be analyzed to identify the inorganic species present. The aqueous wastewater will be generated at approximately 0.12 gpm and be comprised primarily of water, with dissolved organics and ammonia levels ranging from 0.1 to 1%. This water will be stored on-site and periodically delivered to a local wastewater plant for processing.

All chemicals to be used during treatment have been used previously for wastewater treatment or environmental remediation with direct discharge to surface waters. The chemicals that may be used include a commercially-available cationic starch (Chemical A), Dober GreenFloc 5100; or a cationic polyacrylamide typically used for dewatering applications at wastewater treatment plants (Chemical B, Tramfloc 300, Tramfloc 220, or similar).

Chemical A. The naturally-derived flocculant (GreenFloc5100) is manufactured by Dober Chemical, Inc and is under investigation as an alternative green chemical for DAF applications. It has low charge density and can promote flocculation at doses of around 2-5 ppm. Unlike chitosan products like ClearFloc from Dober, the GreenFloc is available in a highly concentrated form, making it more scalable for large flow applications. To support this permit application, ERDC funded ecological toxicity testing of this chemical at a certified contract lab, and the ecological toxicity endpoints are provided along with the MSDS from the company in Appendix B. In most cases, the chemical would be dosed at levels below the No Observable Effect Concentrations. Given that the chemical will largely adsorb to the biomass as it is removed in the DAF process, it is expected that the residual chemical in the discharge will be far lower than the NOEC levels.

Chemical B. The cationic polyacrylamide (Tramfloc 222 or similar) is under investigation as a potential de-watering aid to be applied upstream of the compactor press, or as a flocculant aid or primary flocculant for the DAF process. If used as a flocculant aid, this chemical will be applied at doses less than 20 G/MIN, about 10-fold lower than the other proposed chemicals. The MSDS are provided in Appendix B. The MSDS provided by Tramfloc is available in Appendix B. Confirmatory ecological toxicity endpoint assays are ongoing and will be provided when available. In most cases, the chemical would be dosed at levels that are orders of magnitude below the LD50 values for this chemical. Given that the chemical will largely adsorb to the

biomass as it is removed in the DAF process, it is expected that the residual chemical in the discharge will be far lower than the NOEC levels.

DAF and dewatering chemical treatment additives will be screened on-site prior to pilot testing using a hybrid bench-scale Platypus Jar Tester-Flotation Apparatus (Sidney, Australia) to identify the most effective regimen and economical dosage. Selection criteria will include ecological considerations and any potential impacts on cyanobacterial cell integrity.

Ozone will be generated on-site using a commercially-available ozone generation system and dosed into the water at a ratio of at least 0.4 times the dissolved organic carbon (DOC) concentration in the water being treated. Based on numerous studies on the destruction of micropollutants in wastewater effluent by ozone, it is expected that this dose will be sufficient for removing microcystin to levels below detection. The rate of reaction of ozone with microcystin is over $10^4 \text{ M}^{-1}\text{s}^{-1}$. Thus, for a DOC of 10 mg/L, an ozone dose of greater than 4 mg/L will be applied, with confirmatory testing to confirm that the ozone is fully consumed prior to discharge, using an inline ozone sensor, and that the microcystin levels are below 1 ppb using Abraxis test strips to test the effluent (prior to entering the hold tank) every 60 minutes.

D. Emergency outages

The systems will be powered on-site by gasoline-powered electrical generators, so they will not be susceptible to power outages on the grid. In the case of a generator failure, the system operations will be stopped.

The use of a 20,000 gallon effluent tank will also provide resilience against failures and limit the potential for environmental release of contaminants in the case of an operational issue.

E. Flow measurement

Influent surface water flow will be measured downstream of the intake pump using a magnetic (or similar) flow meter that is rated for measuring flow of water with high solids content. A similar meter will be installed within the air-saturated water recirculation line. The effluent flow will be measured downstream of the ozone system prior to the hold tank. Instantaneous and cumulative flow data will be recorded every 30 minutes. Flows downstream of the press (permeate flow) and hydrothermal liquefaction system (aqueous wastewater flow) will be measured using magnetic flow meters or similar meters capable of monitoring flows containing solids.

VII. INTAKE AND EFFLUENT CHARACTERISTICS

Table VII-A

The parameters listed in Table VII-A will be collected in accordance with Chapter 62-160 standard operating procedures and analyzed by a National Environmental Laboratory Accreditation Program (NELAP) certified laboratory or measured by a federal laboratory using calibrated instruments and EPA/APHA approved standard methods for water quality testing. A minimum of four influent and four effluent samples will be collected and analyzed for during the ten day pilot demonstration for the parameters listed in Table VII-A. For research purposes, daily samples of most parameters will be taken and analyzed by ERDC. A report of the research sample results will also be provided to FDEP, in addition to the four samples analyzed for compliance purposes.

Table VII-B and VII-C

The influent point of withdrawal the lake source waters for the pilot demonstrations are designated Class I (Potable Water Supplies) or Class III (Fish Consumption, Recreation, Propagation and Maintenance of a Healthy, Well-Balanced Population of Fish and Wildlife). There is no expectation that the influent lake water will contain other than *de minimus* levels of pollutants, if any.

Response to Item D

There is a possibility that intracellular or free microcystin may be present in the source water. FDEP has requested that monitoring of the effluent via the use of test strips for microcystin be conducted. Processed water from the pilot demonstration unit will be containerized and treated with ozone to oxidize microcystin. The water will be tested with the test strips every 30 minutes to assess for the presence of microcystin prior to discharge of the water. These data will be logged on-site. If levels above 1 ppb are detected, the operation will be paused, and water will be re-circulated back through the ozone system until levels are below 1 ppb.

IX. BIOLOGICAL TOXICITY TESTING DATA

Whole Effluent Toxicity Testing will be performed by USACE ERDC as a part of this upcoming demonstration test. It will include both acute and chronic testing for *C. dubia* and *P. promelas* using a composite sample collected during a representative day of operations. These tests will follow *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms* (EPA-821-R-02-012) and *Methods for Measuring the Chronic Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms* (EPA-821-R-02-013), respectively.

In last year's HABITATS demonstration, the effluent water from AECOM's DAF and ozone treatment had no detectable acute or chronic toxicity to either water fleas or minnows when using standard ecological toxicity testing protocols. These data are available in the HABITATS TR 20-1 tech report, published in January 2020.

XI CONNECTION TO REGIONAL POTW

HABITATS is not directly connected to regional POTW but is being studied as one of many tools that regional stakeholders can consider for recreational and source water improvement that would complement existing POTW facilities. HABITATS is focused on removing nutrients (enmeshed in algal biomass) from the environment which may have originated from diffuse and point sources not processed by POTW. Removal of algal biomass in an efficient manner may have complementary benefits for the environment, recreation, and water source protection.

APPENDIX B

Material Safety Data Sheets

GFT 5100**Safety Data Sheet**

according to the Hazardous Products Regulation (February 11, 2015)

Date of issue: 04/18/2017

Revision date: 12/26/2018

Supersedes: 04/18/2017

Version: 2.0

SECTION 1: Identification**1.1. Product Identifier**

Product form : Mixtures
 Trade name : GFT 5100
 Product code : 005100

1.2. Recommended use and restrictions on use

Recommended use : Water Treatment Agent

1.3. Supplier**Manufacturer**

Dober Chemical Corp
 543 Forest Road
 18202 Hazle Township, PA - US
 T 630-410-7300 - F 630-410-7444
regulatory@dober.com - www.dober.com

1.4. Emergency telephone number

Emergency number : 1-800-255-3924 / 1-813-248-0585
 ChemTel

SECTION 2: Hazard identification**2.1. Classification of the substance or mixture**

Classification (GHS CA)
 Not classified

2.2. GHS Label elements, including precautionary statements

GHS CA labelling
 No labelling applicable

2.3. Other hazards

No additional information available

2.4. Unknown acute toxicity (GHS CA)

19.5% of the mixture consists of ingredient(s) of unknown acute toxicity (Oral)
 22.05% of the mixture consists of ingredient(s) of unknown acute toxicity (Dermal)
 19.52% of the mixture consists of ingredient(s) of unknown acute toxicity (Inhalation (Dust/Mist))

SECTION 3: Composition/Information on ingredients**3.1. Substances**

Not applicable

3.2. Mixtures

Comments : There are no ingredients present which, within the current knowledge of the supplier and in the concentrations applicable, are classified as hazardous to health or the environment and hence require reporting in this section.

Full text of hazard classes and H-statements : see section 16

SECTION 4: First-aid measures**4.1. Description of first aid measures**

First-aid measures after Inhalation : Remove person to fresh air and keep comfortable for breathing.
 First-aid measures after skin contact : Wash skin with plenty of water.
 First-aid measures after eye contact : Rinse eyes with water as a precaution.
 First-aid measures after Ingestion : Call a poison center/doctor/physician if you feel unwell.

4.2. Most important symptoms and effects (acute and delayed)

No additional information available

4.3. Immediate medical attention and special treatment, if necessary

Other medical advice or treatment : Treat symptomatically.

12/26/2018

EN (English US)

Page 1

GFT 5100

Safety Data Sheet

according to the Hazardous Products Regulation (February 11, 2015)

SECTION 5: Fire-fighting measures

5.1. Suitable extinguishing media

Suitable extinguishing media : Water spray. Dry powder. Foam. Carbon dioxide.

5.2. Unsuitable extinguishing media

No additional information available

5.3. Specific hazards arising from the hazardous product

No additional information available

5.4. Special protective equipment and precautions for fire-fighters

Protection during firefighting : Do not attempt to take action without suitable protective equipment. Self-contained breathing apparatus. Complete protective clothing.

SECTION 6: Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures

No additional information available

6.2. Methods and materials for containment and cleaning up

Methods for cleaning up : Take up liquid spill into absorbent material.

Other information : Dispose of materials or solid residues at an authorized site.

6.3. Reference to other sections

For further information refer to section 8: "Exposure controls/personal protection"

SECTION 7: Handling and storage

7.1. Precautions for safe handling

Precautions for safe handling : Ensure good ventilation of the work station. Wear personal protective equipment.

Hygiene measures : Do not eat, drink or smoke when using this product. Always wash hands after handling the product.

7.2. Conditions for safe storage, including any incompatibilities

Storage conditions : Store in a well-ventilated place. Keep cool.

SECTION 8: Exposure controls/personal protection

8.1. Control parameters

No additional information available

8.2. Appropriate engineering controls

Appropriate engineering controls : Ensure good ventilation of the work station.

8.3. Individual protection measures/Personal protective equipment

Hand protection:

Protective gloves

Eye protection:

Chemical goggles or safety glasses

Skin and body protection:

Wear suitable protective clothing

Respiratory protection:

Use a properly fitted, particulate filter respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator

SECTION 9: Physical and chemical properties

9.1. Information on basic physical and chemical properties

Physical state : Liquid
 Appearance : Liquid.
 Color : Light to Dark Brown
 Odor : characteristic
 Odor threshold : No data available
 pH : 7.5 - 8.5

GFT 5100**Safety Data Sheet**

according to the Hazardous Products Regulation (February 11, 2015)

Relative evaporation rate (butyl acetate=1)	: No data available
Relative evaporation rate (ether=1)	: No data available
Melting point	: Not applicable
Freezing point	: -2 °C
Boiling point	: No data available
Flash point	: Not Applicable
Auto-ignition temperature	: No data available
Decomposition temperature	: No data available
Flammability (solid, gas)	: Not applicable
Vapor pressure	: No data available
Vapor pressure at 50 °C	: No data available
Relative vapor density at 20 °C	: ≈ 1
Relative density	: No data available
Specific gravity / density	: 1.079 g/ml
Solubility	: No data available
Log Pow	: No data available
Viscosity, kinematic	: No data available
Explosion limits	: No data available

9.2. Other information

No additional information available

SECTION 10: Stability and reactivity**10.1. Reactivity**

Reactivity	: The product is non-reactive under normal conditions of use, storage and transport.
Chemical stability	: Stable under normal conditions.
Possibility of hazardous reactions	: No dangerous reactions known under normal conditions of use.
Conditions to avoid	: None under recommended storage and handling conditions (see section 7).
Hazardous decomposition products	: Under normal conditions of storage and use, hazardous decomposition products should not be produced.

SECTION 11: Toxicological information**11.1. Information on toxicological effects**

Acute toxicity (oral)	: Not classified
Acute toxicity (dermal)	: Not classified
Acute toxicity (inhalation)	: Not classified

Unknown acute toxicity (GHS CA)	19.5% of the mixture consists of ingredient(s) of unknown acute toxicity (Oral) 22.05% of the mixture consists of ingredient(s) of unknown acute toxicity (Dermal) 19.52% of the mixture consists of ingredient(s) of unknown acute toxicity (Inhalation) (Dust/Mist)
---------------------------------	--

Skin corrosion/irritation	: Not classified pH: 7.5 - 8.5
Serious eye damage/irritation	: Not classified pH: 7.5 - 8.5
Respiratory or skin sensitization	: Not classified
Germ cell mutagenicity	: Not classified
Carcinogenicity	: Not classified
Reproductive toxicity	: Not classified
Specific target organ toxicity – single exposure	: Not classified
Specific target organ toxicity – repeated exposure	: Not classified
Aspiration hazard	: Not classified

GFT 5100**Safety Data Sheet**

according to the Hazardous Products Regulation (February 11, 2015)

SECTION 12: Ecological information**12.1. Toxicity**

Ecology - general : The product is not considered harmful to aquatic organisms or to cause long-term adverse effects in the environment.

12.2. Persistence and degradability

No additional information available

12.3. Bioaccumulative potential

No additional information available

12.4. Mobility in soil

No additional information available

12.5. Other adverse effects

GWPmix comment : No known effects from this product.
Other information : No other effects known.

SECTION 13: Disposal considerations**13.1. Disposal methods**

Waste treatment methods : Dispose of contents/container in accordance with licensed collector's sorting instructions.
Ecology - waste materials : None known.

SECTION 14: Transport information**14.1. Basic shipping description**

In accordance with TDG

Transportation of Dangerous Goods

Not regulated for transport

14.2. Transport Information/DOT**Department of Transport**

Not regulated for transport

14.3. Air and sea transport**IMDG**

Proper Shipping Name (IMDG) : Non Regulated

IATA

Proper Shipping Name (IATA) : Non Regulated

SECTION 15: Regulatory information**15.1. National regulations****GFT 5100**

Canada DSL & NDSL Flags	All substances contained in this product are listed on the Canadian Domestic Substance List (DSL) or are not required to be listed.
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15.2. International regulations

No additional information available

SECTION 16: Other information

SDS Major/Minor : None
Date of Issue : 04/18/2017
Revision date : 12/26/2018
Supersedes : 04/18/2017

Indication of changes:

Modified. Hazards identification. Composition/Information on ingredients. First aid measures. Fire fighting measures. Accidental release measures. Handling and storage. Exposure controls/personal protection. Stability and reactivity. Toxicological information. Ecological information. Disposal considerations.

Other information : None.

Abbreviations and acronyms:

IATA	International Air Transport Association
IMDG	International Maritime Dangerous Goods

GFT 5100

Safety Data Sheet

according to the Hazardous Products Regulation (February 11, 2015)

SDS Canada Dober

To the best of our knowledge, the information contained herein is accurate. However, neither the above-named supplier, nor any of its subsidiaries, assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of suitability of any material is the sole responsibility of the user. All materials may present unknown hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards that exist.

SAFETY DATA SHEET

According to Federal Regulation 29 CFR 1910.1200

SECTION 1: Identification of the substance/mixture and of the company/undertaking

Product identifier

Product name: TRAMFLOC® 222 Cationic Granular Powder

Type of product: Mixture

Relevant identified uses of the substance or mixture and uses advised against

Identified uses: Processing aid for industrial applications.

Uses advised against: none

Details of the supplier of the safety data sheet

Company: Tramfloc, Inc.
6046 FM 2920 Rd. #615
Spring, TX 77379-2542
Telephone: 888-929-8973
Telefax: 480-383-6895
E-mail address: water@tramfloc.com

Emergency telephone number:

24-hour emergency number: 800-424-9300 CHEMTREC (CCN 20412), Outside US 703-527-3887

SECTION 2: Hazards identification

According to Hazardous Products Regulations (HPR) (SOR/2015-17) Classification of the product

No need for classification according to GHS criteria for this product.

Label elements

The product does not require a hazard warning label in accordance with GHS criteria.

Hazards not otherwise classified

Very slippery when wet.

Labeling of special preparations (GHS):

This product is not combustible in the form in which it is shipped by the manufacturer, but may form a combustible dust through downstream activities (e.g. grinding, pulverizing) that reduce its particle size.

SECTION 3: Composition/information on ingredients

Component	CAS #	%
Acrylamide Copolymer	69418-26-4	88-92%
Water	7732-18-5	8-12%

Product name: TRAMFLOC® 222

Page: 1

04/20/18

Residual Acrylamide:

79-06-1

999ppm MAX

SECTION 4: First aid measures

Contact with skin:

Wash with plenty of water and soap.

Contact with eyes:

Wash immediately with water for at least 15 minutes. If there is any irritation, OBTAIN IMMEDIATELY MEDICAL ATTENTION.

Swallowing:

Do not induce vomiting. Do not give anything to an unconscious person. Check for breathing and pulse, if present, place in the recovery position and obtain medical attention. If conscious rinse out the mouth with water. Give 3/4 L of water to drink immediately and repeat drinks of water at a rate of a cupful (approx. 250 mL) every 10 minutes.

SEEK A MEDICAL EXAMINATION IMMEDIATELY and present the safety data sheet.

Inhalation:

Ventilate the premises. The patient is to be removed immediately from the contaminated premises and made to rest in a well ventilated area. Should the patient feel unwell, OBTAIN MEDICAL ATTENTION.

SECTION 5: Fire-fighting measures

Extinguishing media

Suitable extinguishing media: dry powder, foam, carbon dioxide

Unsuitable extinguishing media for safety reasons: water jet

Additional information:

If water is used, restrict pedestrian and vehicular traffic in areas where slip hazard may exist.

Special hazards arising from the substance or mixture

Hazards during fire-fighting:

carbon oxides, nitrogen oxides

The substances/groups of substances mentioned can be released in case of fire. Very slippery when wet.

Advice for fire-fighters

Protective equipment for fire-fighting: Wear a self-contained breathing apparatus.

Further information: Dusty conditions may ignite explosively in the presence of an ignition source causing flash fire.

SECTION 6: Accidental release measures

Further accidental release measures:

Avoid dispersal of dust in the air (i.e., clearing dust surfaces with compressed air). Avoid the formation and build-up of dust - danger of dust explosion. Dust in sufficient concentration can result in an explosive mixture in air. Handle to minimize dusting and eliminate open flame and other sources of ignition. Forms slippery surfaces with water.

Personal precautions, protective equipment and emergency procedures

Use personal protective clothing.

Environmental precautions

Do not discharge into drains/surface waters/groundwater.

Methods and material for containment and cleaning up

Nonsparking tools should be used.

SECTION 7. Handling and storage

Precautions for safe handling

Breathing must be protected when large quantities are decanted without local exhaust ventilation. Handle in accordance with good industrial hygiene and safety practice. Forms slippery surfaces with water.

Protection against fire and explosion:

Avoid dust formation. Dust in sufficient concentration can result in an explosive mixture in air. Handle to minimize dusting and eliminate open flame and other sources of ignition. Routine housekeeping should be instituted to ensure that dusts do not accumulate on surfaces. Dry powders can build static electricity charges when subjected to the friction of transfer and mixing operations. Provide adequate precautions, such as electrical grounding and bonding, or inert atmospheres. Refer to NFPA 654, Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids (2013 Edition) for safe handling.

Conditions for safe storage, including any incompatibilities

Unsuitable materials for containers: Aluminum

Further information on storage conditions: Store in unopened original containers in a cool and dry place. Avoid wet, damp or humid conditions, temperature extremes and ignition sources.

Storage stability:

Avoid extreme heat.

Protect from temperatures above: 60 °C

SECTION 8: Exposure controls/personal protection

No occupational exposure limits known.

Advice on system design:

It is recommended that all dust control equipment such as local exhaust ventilation and material transport

systems involved in handling of this product contain explosion relief vents or an explosion suppression system or an oxygen deficient environment. Ensure that dust-handling systems (such as exhaust ducts, dust collectors, vessels, and processing equipment) are designed in a manner to prevent the escape of dust into the work area (i.e., there is no leakage from the equipment). Use only appropriately classified electrical equipment and powered industrial trucks.

Personal protective equipment

Respiratory protection:

Wear a NIOSH-certified (or equivalent) organic vapor/particulate respirator.

Hand protection:

Chemical resistant protective gloves

Eye protection:

Safety glasses with side-shields.

Body protection:

light protective clothing

General safety and hygiene measures:

Handle in accordance with good industrial hygiene and safety practice.

Ensure adequate ventilation. Wearing of closed work clothing is recommended. Wear protective clothing as necessary to minimize contact. Handle in accordance with good industrial hygiene and safety practice. No eating, drinking, smoking or tobacco use at the place of work.

SECTION 9: Physical and chemical properties

Color:	White Granule Powder
Appearance:	Crystalline Powder
Odor:	Odorless
pH:	6-8
Melting Point:	N/A
Boiling Point:	N/A
Flash Point:	N/A
Solid/ Gas Flammability:	As with many organic powders flammable dust clouds may form
Explosive Properties:	N/A
Oxidizing Properties:	N/A
Vapor Pressure:	N/A
Relative Density:	600-900 Kg/m ³
Solubility in Water:	Limited by viscosity

Vapor Density:	N/A
Percent Volatile (% by Wt):	8-10%
Saturation in Air (% by Vol):	N/A
Evaporation Rate:	N/A
Autoignition Temperature:	N/A
Decomposition Temperature:	N/A
Partition Coefficient:	N/A
Odor Threshold:	N/A

SECTION 10: Stability and reactivity

Reactivity

No hazardous reactions if stored and handled as prescribed/indicated.

Corrosion to metals: No corrosive effect on metal.

Oxidizing properties: not fire-propagating

Chemical stability

The product is stable if stored and handled as prescribed/indicated.

Possibility of hazardous reactions

The product is not a dust explosion risk as supplied; however the build-up of fine dust can lead to a risk of dust explosions.

Stable under normal conditions.

No hazardous reactions known.

Conditions to avoid

Avoid extreme temperatures. Avoid humidity.

Incompatible materials

strong acids, strong bases, strong oxidizing agents

Hazardous decomposition products

Decomposition products:

Hazardous decomposition products: No hazardous decomposition products if stored and handled as prescribed/indicated.

SECTION 11: Toxicological information

Primary routes of exposure

Routes of entry for solids and liquids are ingestion and inhalation, but may include eye or skin contact. Routes of entry for gases include inhalation and eye contact. Skin contact may be a route of entry for liquefied gases.

Acute Toxicity/Effects

Acute toxicity

Assessment of acute toxicity: No known acute effects.

Oral

Type of value: LD₅₀

Species: rat

Value: > 5,000 mg/kg (OECD Guideline 401)

Irritation / corrosion

Assessment of irritating effects: Not irritating to eyes and skin.

Skin

Species: rabbit

Result: non-irritant

Method: OECD Guideline 404

Eye

Species: rabbit

Result: non-irritant

Sensitization

Assessment of sensitization: Based on the ingredients, there is no suspicion of a skin-sensitizing potential.

Aspiration Hazard

No aspiration hazard expected.

*Chronic Toxicity/Effects**Repeated dose toxicity*

Assessment of repeated dose toxicity: Based on our experience and the information available, no adverse health effects are expected if handled as recommended with suitable precautions for designated uses. The product has not been tested. The statement has been derived from the properties of the individual components.

Genetic toxicity

Assessment of mutagenicity:

Based on the ingredients, there is no suspicion of a mutagenic effect.

Carcinogenicity

Assessment of carcinogenicity:

The whole of the information assessable provides no indication of a carcinogenic effect.

None of the components in this product at concentrations greater than 0.1% are listed by IARC; NTP, OSHA or ACGIH as a carcinogen.

Reproductive toxicity

Assessment of reproduction toxicity: Based on the ingredients, there is no suspicion of a toxic effect on

reproduction.

Teratogenicity

Assessment of teratogenicity: Based on the ingredients, there is no suspicion of a teratogenic effect.

Other Information

The product has not been tested. The statements on toxicology have been derived from products of a similar structure and composition.

Symptoms of Exposure

The most important known symptoms and effects are described in section

Further important symptoms and effects are so far not known.

SECTION 12: Ecological information

Toxicity

Toxicity to fish

LC₅₀ (96 h) > 100 mg/l, *Oncorhynchus mykiss* (static) (under static conditions in the presence of 10 mg/L humic acid)

Aquatic invertebrates

LC₅₀ (48 h) > 100 mg/l, *Daphnia magna*

Persistence and degradability

Assessment biodegradation and elimination (H₂O)

Not readily biodegradable (by OECD criteria).

Bio-accumulative potential

Assessment bioaccumulation potential

Based on its structural properties, the polymer is not biologically available.

Accumulation in organisms is not to be expected.

Mobility in soil

Assessment transport between environmental compartments

Information on: Anionic polyacrylamide

Adsorption to solid soil phase is expected.

Additional information

Other ecotoxicological advice:

The product has not been tested. The statements on ecotoxicology have been derived from products of a similar structure and composition.

SECTION 13: Disposal considerations

Waste disposal of substance:

Must be disposed of or incinerated in accordance with local regulations.

Container disposal:

Dispose of in a licensed facility. Recommend crushing, puncturing or other means to prevent unauthorized use of used containers.

SECTION 14: Transport information**Land Transport (TDG, Transport Canada):**

Not classified as a dangerous good under transport regulations.

Sea Transport (IMDG):

Not classified as a dangerous good under transport regulations.

Air Transport (IATA/ICAO):

Not classified as a dangerous good under transport regulations.

SECTION 15: Regulatory information

WHMIS CLASSIFICATION: Not WHMIS controlled

United States (USA): All components of this product are included on the TSCA Chemical Inventory or are not required to be listed on the TSCA Chemical Inventory.

Canada: All components of this product are included on the Domestic Substances List (DSL) or are not required to be listed on the DSL.

European Union (EU): All components of this product are included on the European Inventory of Existing Chemical Substances (EINECS) or are not required to be listed on EINECS.

SECTION 16: Other information

The information contained herein is to the best of our knowledge and belief accurate. However, since the conditions of handling and use are beyond our control, Tramfloc, Inc. makes no guarantee for results obtained, and assumes no responsibility for damages incurred by use of this product. It is the responsibility of the user to comply with all federal, state, and local laws and regulations.

Appendix B: New York Quality Assurance Project Plan

NYSDEC DOW and USACE ERDC QAPP

HABITATS Project

Date: August 17, 2020

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QUALITY ASSURANCE PROJECT PLAN

Research Demonstration of USACE ERDC Harmful Algal Bloom
Interception, Treatment, and Transformation System (HABITATS) Project

August 17, 2020

Prepared by:

New York State Department of Environmental Conservation (NYSDEC)

Division of Water (DOW)

Bureau of Water Assessment and Management

Lake Monitoring and Assessment Section

and

US Army Corps of Engineers (USACE)

Engineer Research and Development Center (ERDC)

2902 Newmark Drive Champaign, IL 61822

NYSDEC DOW and USACE ERDC QAPP

HABITATS Project

Date: August 17, 2020

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HABITATS Project QAPP Update Log

Prepared/Revised By:	Date:	Revision No:	Summary of Changes:
Stephanie June	30 April 2020	1.0	Drafted
Martin Page	02 July 2020	1.1	Comprehensive updates throughout
Stephanie June	21 July 2020	1.2	Project task description edits; updated project contact list; added appendices containing chemical and permit review documentation; added project map area and staging at Long Point State Park; updated formatting and grammatical errors.
Stephanie June	07 August 2020	1.3	Edits following comprehensive review including: project organization chart, project personnel responsibilities, addition of introduction, incorporation of USACE edits to field sampling, protocols and tasks, data quality objectives and review, and overall clarity of sampling scheme.

No substantive changes include updating references, correcting typographical errors, and clarifying certain language to make the document more useful and effective.

NYSDEC DOW and USACE ERDC QAPP

HABITATS Project

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I. PROJECT MANAGEMENT

1. Project Introduction

USACE ERDC is deploying its innovative research demonstration project named Harmful Algal Bloom Interception, Treatment and Transformation System in portions of the southern half of Chautauqua Lake later this year. The pilot project uses floating skimmers on the lake to collect surface water laden with harmful algal blooms. Once collected, the blooms are put through shore-based or mobile treatment processes, which detoxify the algae, concentrate it, and convert it into biocrude fuel and fertilizer. During the process, treated water is cleaned, clarified, and safely returned to the lake. Project staging and site access will be coordinated through the Office of Parks, Recreation, and Historic Preservation at Long Point State Park in Bemus Point, New York. The shore-based unit will be operated from the shoreline of Long Point State Park. The mobile treatment will depart from Long Point State Park each day to operate in the open water of the lake. Project duration is estimated at approximately three weeks, and will require boat launch access, boat storage (5 slips), a freshwater source (200 gallons/day), staging area (approximately 18,000 sq. ft), and installation of temporary security fencing.

NYSDEC DOW and USACE ERDC QAPP

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2. Project Title and Approvals

Project Title: Research Demonstration of USACE ERDC Harmful Algal Bloom Interception, Treatment, And Transformation System (HABITATS)

Date of QAPP/Revision number: August 17, 2020, Revision 1.3

USACE ERDC Project Manager: Martin A. Page, Ph.D., Martin.A.Page@usace.army.mil, (217) 373-4541

Approval Signature/Date: PAGE.MARTIN.A.139
2763801

Digitally signed by
PAGE.MARTIN.A.1392763801
Date: 2020.08.19 06:37:43 -05'00'

USACE Aquatic Nuisance Species Research Program (ANSRP) Program Manager: Christine VanZomeran, christine.m.vanzomeran@usace.army.mil, (601) 634-3702

Approval Signature/Date: VANZOMEREN.CHRISTINE.M.1512994543
NE.M.1512994543

Digitally signed by
VANZOMEREN.CHRISTINE.M.1512994543
Date: 2020.08.18 09:49:16 -05'00'

NYSDEC DOW Assistant Quality Assurance Officer: Lewis McCaffrey
lewis.mccaffrey@dec.ny.gov, (315) 426-7514

Approval Signature/Date:

APPROVED
By lpmccaff at 2:40 pm, Aug 19, 2020

NYSDEC Project Coordinator: Karen Stainbrook, karen.stainbrook@dec.ny.gov, (518) 402-8095

Approval Signature/Date: 8/17/2020

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3. Project / Task Organization

a) Martin Page. – Project Manager

ERDC

USACE

C: (217) 418-0957

Martin.A.Page@usace.army.mil

2902 Newmark Drive

Champaign, IL 61822

Specific coordination, oversight and implementation of the HABITATS project as it pertains to site selection, travel, prototype development, technology deployment and operation, water treatment chemical evaluation and selection, water quality monitoring, subcontracting, and cooperative agreement completion.

b) Christopher Veinotte – Field Operations Manager and On-site Safety Manager

New England District

USACE

C: 978-318-8495

Christopher.L.Veinotte@usace.army.mil

696 Virginia Road

Concord, MA 01742

Onsite coordination of the HABITATS project field operations including site mobilization and set-up, research and validation processing, sampling and shipping, and site-break down and demobilization. Responsible for equipment calibration and maintenance, and adherence to health and safety plan of project activities.

c) Catherine Thomas – Manager of On-site Contractors

ERDC Environmental Laboratory (EL)

USACE

C: (601) 634-3797

Catherine.C.Thomas@usace.army.mil

ERDC EL

Vicksburg, MS

Onsite management and coordination of the HABITATS project subcontractors, AECOM and University of Illinois Sustainability Technology Center

d) Bruce MacAllister – Shipboard Treatment System Operator

ERDC

USACE

C: 217-649-7594

Bruce.A.MacAllister@usace.army.mil

NYSDEC DOW and USACE ERDC QAPP

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2902 Newmark Drive

Champaign, IL 61822

Shipboard treatment system design, construction and transport, and deployment and operation of the shipboard treatment system during the HABITATS project.

- e) Clinton Cender – Water Quality Analysis and Data Manager

ERDC

USACE

C: 217-714-7752

Clinton.J.Cender@usace.army.mil

2902 Newmark Drive

Champaign, IL 61822

Responsible for management, security and storage of all data produced or associated with the HABITATS project. Oversee ERDC research sample water quality analysis.

- f) David Pinelli. – AECOM Field Operations Manager

DCS Americas, Algae Solutions Team

C: 828-301-3962

david.pinelli@aecom.com

AECOM

Asheville, NC

Operation and maintenance of AECOM's Algae Harvester Unit onshore system, including field testing, sample collection, compiling project report logs and data evaluation.

- g) Lance Schideman – Hydrothermal Liquefaction Operator

University of Illinois Sustainability Technology Center

C: 217-390-7070

schidema@illinois.edu

1304 W. Pennsylvania Avenue

Urbana, IL 61801

Operation and maintenance of the University of Illinois at Urbana-Champaign, Sustainability Technology Center's Hydrothermal Liquefaction treatment system.

- h) Karen Stainbrook – NYSDEC Project Coordinator

NYS Department of Environmental Conservation

Bureau of Water Assessment Management

625 Broadway, Albany, NY 12233

karen.stainbrook@dec.ny.gov

General oversight and management of the HABITATS project implementation, cooperative agreement, and monitoring program.

NYSDEC DOW and USACE ERDC QAPP

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- i) Stephanie June – NYSDEC Project Manager
NYS Department of Environmental Conservation
Bureau of Water Assessment Management
625 Broadway, Albany, NY 12233
stephanie.june@dec.ny.gov

Coordinate writing of QAPP with USACE (QAPP custodian). Monitoring and onsite project logistics coordination. Assist coordination of waste hauling from project site, water treatment chemical review, and research permit application. Assistance with research design, data quality review, and reporting.

- j) Lewis McCaffrey – NYSDEC DOW Assistant Quality Assurance Officer
NYS Department of Environmental Conservation
Bureau of Water Assessment Management, Finger Lakes Water Hub
615 Erie Blvd. W, Syracuse NY 13204
lewis.mccaffrey@dec.ny.gov

Review the QAPP to verify that those elements outlined in the EPA Requirements for QAPPs (QA/R-5) were adequately discussed.

This QAPP will be approved before any work begins. All the individuals listed above need to receive an electronic copy of the approved QAPP prior to commencement of the project. USACE Program Director and NYSDEC Project Manager will be responsible for obtaining the signatures and the distribution of the QAPP. Personnel organization and line of communication for this project are presented in Figure 1.

In addition to the approved QAPP, all individuals listed above will receive a ZIP file containing:

- o Florida Department of Environmental Protection Standard Operating Procedure FS1000 – General Sampling Procedures
- o Florida Department of Environmental Protection Standard Operating Procedure FS2000 – General Aqueous Sampling
- o USACE ERDC site specific Healthy and Safety Plan
- o USACE Manual EM385-1-1
- o USACE ERDC and NYSDEC CRADA, C-2020-ERDC-3643

NYSDEC DOW and USACE ERDC QAPP
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Figure 1. Project Organization Chart

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4. Problem Definition / Background

Harmful Algal Blooms (HABs) are increasing in both frequency, intensity and duration and have the potential to adversely affect human health, economic prosperity and the water quality of both potable and recreational waters across the nation, including many of those in the State of New York.

In Fall of 2019, New York State Department of Environmental Conservation (NYSDEC) completed a demonstration of the AECOM Algae Harvester Unit in Lake Agawam, NY. The ten-day pilot was informative and identified successes and limitations of the current technology application. The limitations identified included extensive energy requirements and carbon emissions during treatment, the use and discharge of toxic chemicals, and the stationary nature of the technology once established along the shoreline. NYSDEC recognized these limitations require correction prior to future successful optimization of the beneficial outcomes of the Algae Harvester. United States Army Corps of Engineers (USACE) Engineer Research and Development Center (ERDC) also evaluated AECOM's Algae Harvester in summer of 2019 in Florida, with a focus on integrating the technology into their Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS). The HABITATS approach is more scalable than the AECOM Algae Harvester because it includes novel methods for managing the large volumes of potentially toxic algal biomass that is removed from the water. HABITATS aims to remove algae from the water while destroying microcystin toxins, and then convert the resulting algal biomass concentrate into biocrude fuel. USACE ERDC and NYSDEC share the objectives of increasing energy efficiency and deployability of this HAB mitigation technology. Per the authorization of the 2018 Water Resources Development Act, USACE is focused on scalability for mitigating large blooms.

The objective of this project is to demonstrate a more deployable HABITATS prototype while simultaneously addressing the existing technology limitations. The project will consist of two parts: (1) an updated and optimized on-shore HABITATS that uses a green, organic, or less toxic coagulant/flocculant as an alternative to an aluminum based chemical (hereafter referred to as "alternative coagulant/flocculant"), provides a higher rate of algae dewatering, and is integrated with a biomass treatment system that transforms dewatered algae biomass to fuel onsite; and (2) a new shipboard deployable HABITATS unit to intercept and treat algae in the open water, and transport concentrated algal biomass to shore for hydrothermal liquefaction processing and waste management. The result of this collaborative effort will be an optimized on-shore and shipboard HABITATS that will allow for assessing the environmental impact, practical scalability, mobility and economic feasibility of this technology.

The planned HABITATS research studies will have beneficial impacts in the local areas in which they are performed; however, the studies are not expected to have a large impact on the entire lake or areas that are outside of the research demonstration area. The data collected in these studies will help assess scalability, guide full scale designs, and provide a new tool that can be considered as part of a holistic approach to HAB prevention and control.

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To help research and validate HABITATS' ability to mitigate and manage HABs, NYSDEC has established a Cooperative Research and Development Agreement (CRADA) with USACE ERDC to conduct an intensive demonstration over a three-week period that will begin in August 2020. Due to the compressed timeframe, the demonstration will take place seven days a week, with onsite work occurring between approximately 9:00AM and 6:00PM each day. This project is referred to as 'Research Demonstration project for the capture and removal of a HAB on the impacted water body known as Chautauqua Lake.' On-shore and shipboard HABITATS process flow diagrams are presented in Attachment I and II, respectively. The onshore demonstration site location and overall project staging area is depicted in Figure 2.

Figure 2. Site map of Chautauqua Lake (inset A). Project staging and onshore demonstration will occur at Long Point State Park (inset B), including: boat storage (red star) and ~18,000 sq-ft for equipment storage, set-up and onshore demonstration (yellow star). The shipboard demonstration will operate in the southern basin (inset A, blue star).

The Research Demonstration of HABITATS consists of an onshore process (dissolved air flotation unit, Ozone/UV unit, dewatering solids press, hydrothermal liquefaction unit) and a shipboard process (dissolved air flotation unit, Ozone/UV unit, dewatering solids press, ferry to transport solids for on-shore processing). USACE ERDC will collect influent and effluent samples from the Research Demonstration systems to assess algae, toxin, and nutrient removal efficiency, as well as evaluate the use of an alternative coagulant/flocculant and the optimization of dewatering and hydrothermal liquefaction steps.

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Information collected during the Research Demonstration will be used to help assess the effectiveness and appropriateness of the Research Demonstration technology. Assessment of effectiveness for both on-shore and shipboard HABITATS will include, but not be limited to:

- a) Proof of concept of deployment of shipboard HABITATS (Attachment II):
 - i. Safe and successful coordination and operation of lead boats, intake weir, floating dissolved air floatation (DAF), utility barge (dewatering press and Ozone/UV), and solids ferry to harvest and treat in-lake HAB conditions.
 - 1. Start up and validation of algae harvesting skimmers and treatment system flow controls over a one-week period.
 - 2. Optimization of chemical dosing systems and verification of effluent water quality through jar testing and batch testing, to include one Whole Effluent Toxicity Test over a one-week period.
 - 3. Validation of integrated system operations over a one-week period targeting 6 hours of operation per day.
- b) Document treatment efficacy with alternative coagulant/flocculant in onshore and shipboard HABITATS through:
 - i. Documentation of changes in water quality parameter concentrations (Total Nitrogen, Total Phosphorous, Total Suspended Solids, Microcystin) before and after treatment, with intermittent sampling to assess water quality differentials across each treatment step (DAF, Ozone, UV; Compacter Press; Hydrothermal Liquefaction), calculated by percent removal (i.e. percent change between influent and effluent) in relation to volume treated;
 - 1. The DAF and Ozone/UV treatment process is expected to result in a statistically significant reduction and/or a 50%, 75%, 80%, and 95% removal efficiency in Total Nitrogen, Total Phosphorus, Total Suspended Solids, and Total Microcystin, respectively with the use of alternative coagulant/flocculant chemicals.
- c) Document treatment comparability between on-shore and shipboard HABITATS through:
 - i. Evaluation of changes in water quality parameter concentrations (Total Nitrogen, Total Phosphorus, Chlorophyll A, Microcystin) for the onshore and shipboard HABITATS before and after treatment, to assess water quality differentials across each treatment step, calculated by percent removal (i.e. percent change between influent and effluent) in relation to volume treated;
 - 1. The on-shore and shipboard HABITATS are expected to remove nutrients, algal biomass and microcystin at equivalent rates.
- d) Document the 3-D size of the bloom and estimate the potential impact of a full scale HABITATS deployment on a bloom.
 - i. Collect water quality data (phycocyanin concentration and nitrate concentration) via in-situ, boat mounted sondes throughout the southern portion of the water body at the surface (0.25ft) and at depth (3ft) daily during the demonstration.

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- Periodic weekly profiling will be performed at additional depths (1.75 feet and 4.5 feet) to further assess the vertical gradient in bloom density.
- ii. Evaluation of higher throughput algae biomass dewatering step in on-shore HABITATS.
 - iii. Document volume of solids produced in relation to volume of algae biomass dewatered.
- e) Evaluation of resource recovery through on-shore HABITATS hydrothermal liquefaction optimization:
- i. Document amount of biocrude fuel produced per unit volume and mass of algae biomass dewatered.
 - ii. Evaluation of energy usage of DAF and Ozone/UV units, dewatering press, and hydrothermal liquefaction, as a ratio of kW energy expended per gallon of gas produced (kW/gal).
 - iii. Evaluation of the concentration (ug/L) of Total Microcystin in hydrothermal liquefaction by-products (biocrude fuel, solid sludge, and liquid waste) to confirm toxin destruction and understand potential future beneficial uses and fate of those by-products;
- f) Note, the research demonstration is expected to have an effect in localized areas where the treatment takes place. The research demonstration is not expected to have a widespread impact or impact areas that are outside of where the treatment takes place. The intention of the HABITATS project is to demonstrate technology advancements in mobility, test alternative coagulant/flocculant products, and enhance the renewable energy generation process. The HABITATS project is not intended to impart significant water quality improvements in Chautauqua Lake. Therefore, in-lake ambient water quality chemistry and biological monitoring is not a component of this research project.

Site specific coordination, mobilization, demobilization and project details not included in this QAPP are covered under the USACE ERDC and NYSDEC CRADA, C-2020-ERDC-3643. A site plan and any required local permits will be appended to this document with additional details when available. Work shall not proceed without approval of this QAPP. Work shall not proceed without all parties, including the site owner, agreeing to the site mobilization, demonstration execution, and demobilization plans.

All project personnel are to adhere to the site specific Healthy and Safety Plan (HASP) prepared by USACE ERDC, in compliance with USACE Manual EM385-1-1, and those HASPs of their contractors to address the physical hazards that may be present or encountered during sampling, monitoring, or equipment operation. Boat operators will be trained and certified by USACE prior to the demonstration, and certifications will be available for inspection.

Funding Source/Cost Center: This project is being contracted through the USACE ERDC and NYSDEC CRADA, C-2020-ERDC-3643 and will be fully supported by federal funds.

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5. Project / Task Description

a) TIMELINE:

The HABITATS project will begin implementation in August 2020, and will take place over a three-week period:

- Week one: equipment delivery and set-up; characterize water quality; initial flow and control testing of shipboard unit; no treatment
- Week two: perform onshore unit validation and research data collection; shipboard unit startup testing and performance optimization
- Week three: shipboard unit performance validation and research data collection; site breakdown; waste removal; equipment removal

b) TREATMENT SAMPLING DESIGN:

USACE ERDC will collect all influent and effluent samples from the DAF unit and post treatment Ozone/UV system of the shipboard unit. AECOM will collect all influent and effluent samples from the DAF unit and post treatment Ozone/UV system of the onshore unit. The Ozone/UV system is an advanced oxidation process technology (Ozone and/or UV) used to treat final clarified effluent from the DAF. Its purpose is to degrade any microcystin that may be present in the water, not inactivate algal cells. No claims are made for decontamination or disinfection with the Ozone/UV unit.

Samples will be collected daily during operation of the equipment from various sampling points. Samples will be analyzed by Test America and/or USACE ERDC Construction Engineering and Research Laboratory (CERL) and EL for the parameters listed in the attached Table 1. All chemical analyses for performance validation will be done at New York State Environmental Laboratory Approval Program (ELAP) accredited laboratories whenever NYSDOH ELAP certification is available for an analyte. Test America will analyze performance validation samples, hereafter referred to as "validation". All analyses for research purposes, hereafter referred to as "research", will be processed at USACE ERDC CERL and EL, a non-ELAP accredited laboratory. Note, additional details about sample frequency, schedule, and receiving analytical laboratory are included in Section 5C. The samples will also be evaluated onsite for the field parameters listed in Table 2a. A Draft Process Flow Diagram is provided as Attachments I and II. Sample points (SP) are identified as follows:

- SP-1: Source Water directly from Chautauqua Lake; to be monitored via insitu multiparameter sonde by USACE ERDC personnel.
- SP-2: Influent to DAF; to be sampled from a sample port on the DAF and analyzed by Test America (validation) and USACE ERDC (research).
- SP-3: Effluent from DAF; to be sampled from a sample port on the DAF and analyzed by USACE ERDC (research). Periodic analysis by Test America (validation) will be incorporated (see Section 5C).
- SP-4: Effluent from the Ozone/UV unit; to be sampled from a sample port on the Ozone/UV and analyzed by Test America (validation) and USACE ERDC (research).

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- SP-5: By-products (fuel, sludge, liquid waste) from the Hydrothermal Liquefaction Treatment; to be sampled from a sample port on the on the system and analyzed by USACE ERDC (research).

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TABLE 1. Analytical Specifications, QA/QC Requirements and Holding Times

Parameter	Analytic Lab	Standard Method	Precision	Accuracy	Calibration	Blanks	Quantitation Limit	Holding Time
Laboratory Analyses								
pH		150.2	± 0.1	NA	1/day	NA	0.2	< 48 hrs
Conductivity		120.1	Avg Std Dev: ± 64.4	± 6%	1/day	NA	64.4	< 48 hrs
Total Suspended Solids		2540D	± 20%	± 5 mg/L	NA	1/batch	10 mg/L	< 48 hrs
Volatile Suspended Solids		160.4	± 11 mg/L	± 11 mg/L	NA	1/batch	22 mg/L	< 48 hrs
Turbidity		180.1	Avg Std Dev: ± 1.86 NTU	Avg Std Dev: ± 1.86 NTU	2/year	1/batch	1.86 NTU	< 48 hrs
Total Phosphorus		365.4	Avg Range: ± 0.04 mg/L	Avg Range: ± 0.04 mg/L	1/batch	1/batch	0.08 mg/L	< 48 hrs
Orthophosphate	Test America	4500PE, 365.4	± 0.05 mg/L	± 0.05 mg/L	1/batch	1/batch	0.1 mg/L	< 48 hrs
Total Nitrogen		350.1, 351.2, 353.2	± 0.005 mg/L	± 0.005 mg/L	2/year	1/batch	0.01 mg/L	< 48 hrs
Nitrate		353.2	± 0.15 mg/L	± 0.15 mg/L	2/year	1/batch	0.3 mg/L	< 48 hrs
Total Organic Carbon		5310C	± 11 mg/L	± 11 mg/L	1/batch	1/batch	22 mg/L	< 48 hrs
Whole Effluent Toxicity		2000.0, 2021.0, 1000.0, 1002.0	± 3 std dev	± 3 std dev	NA	NA	> 20% mortality	< 48 hrs
Biological Oxygen Demand		5210B	± 20%	± 20%	1/batch	1/batch	18 mg/L	< 48 hrs
Chemical Oxygen Demand		410.4	Avg Std Dev: ± 8.58 mg/L	Avg Std Dev: ± 8.58 mg/L	1/batch	1/batch	8 mg/L	< 24 hrs
Chlorophyll-a		SM 10200	± 0.02 µg/L	± 0.02 µg/L	1/day	1/test	0.06 µg/L	< 24 hrs
Microcystin	BSA Environmental Services	Enzyme-Linked Immunosorbent Assay (ELISA)	± 0.05 ppb	± 0.05 ppb	NA	1/test	0.05 ppb	> 1 month
Microbial ID		SM 10200	± 1 cell	± 1 cell	NA	NA	1 cell	> 1 month
Toxin gene ID		SM 10200	NA	NA	NA	NA	NA	24 hrs
pH		150.2	± 0.1	NA	1/day	NA	0.1	24 hrs
Conductivity		120.1	Avg Std Dev: ± 64.4	± 6%	1/day	NA	64.4	24 hrs
Total Suspended Solids		2540D	± 20%	± 5 mg/L	NA	1/batch	0.5 mg/L	24 hrs
Volatile Suspended Solids		160.4	± 11 mg/L	± 11 mg/L	NA	1/batch	22 mg/L	24 hrs
Turbidity		150.2	± 0.1 NTU	NA	1/day	NA	0.1 NTU	24 hrs
Total Phosphorus	CERL	120.1	Avg Range: ± 0.04 mg/L	Avg Range: ± 0.04 mg/L	1/day	NA	0.08 mg/L	24 hrs
Total Nitrogen		2540D	± 0.005 mg/L	± 0.005 mg/L	NA	1/batch	0.5 mg/L	24 hrs
Total Organic Carbon		160.4	± 11 mg/L	± 11 mg/L	NA	1/batch	22 mg/L	24 hrs
Chemical Oxygen Demand		180.1	Avg Std Dev: ± 8.58 mg/L	Avg Std Dev: ± 8.58 mg/L	2/year	NA	8 mg/L	< 48 hrs

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TABLE 2. Parameters Measured by Field Instrumentation
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Item No.	Description	Analysis Method
2.a. Treatment Water Quality Monitoring (SP-2, SP-3, SP-4)		
1	pH	Thermo pH Probe
2	Turbidity	Milwaukee Field Turbidimeter
3	Dissolved Ozone (DO)	Oxidation Tech Q46H/64 Inline Ozone Meter (SP-4 only)
2.b. Ambient Water Quality Monitoring (SP-1)		
1	Temperature	Aqua TROLL 500 Multiparameter Sonde
2	Phycocyanin	Aqua TROLL 500 Multiparameter Sonde
3	Nitrate	Aqua TROLL 500 Multiparameter Sonde

c) SAMPLING FREQUENCY AND PERFORMANCE VALIDATION:

Three sample sets will be collected daily over a one week period from SP-2, SP-3, and SP-4 sample points of the onshore and shipboard units for either performance validation and/or research purposes (Table 3). One set of performance validation samples will be collected daily from SP-2 and SP-4 sample points for analysis at a certified laboratory for the parameters in Table 1. On four of seven days, one additional performance validation sample will be collected at SP-3 to increase the number of validation samples each day. A total of 18 samples are planned for validation testing ([SP-2 and SP-4 (2 points) X 1 session X 7 days] + [SP-3 (1 point) X 1 session X 4 days] = 14 + 4 = 18 samples). Additional research samples will be collected daily from SP-2, SP-3, and SP-4 for analysis at a USACE laboratory for the parameters in Table 1. The daily validation sample will be collected mid-day to allow ample time to process, package and ship the samples the same day and ensure timely transport to the laboratory.

Due to budgetary constraints, limited certified laboratory analysis is available for this project. USACE CERL and EL have previously demonstrated comparable analytical results to ELAP certified laboratory results in duplicate sampling trials. USACE will collect a duplicate research sample set at the time of the validation sample set to confirm comparability. Field duplicate sample results from different labs run by the same method should be within a 20% difference to be considered comparable. Research results will not be used for regulatory decisions and will be informational only. All other data quality indicator measures are presented in Section 6.

The research samples (USACE CERL) will be collected 1 hr. after the start of treatment system, midway through daily operations, and 1 hr. prior to the shutdown of the treatment

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system. The validation samples (Test America) will be collected midway through daily operations (Table 3). The timing of the samples may be adjusted by the on-site field supervisor as necessary to meet sample shipping schedules for overnight deliveries.

Based on the ecology and limnology of lake systems, the biological and chemical parameters are not expected to change significantly within the *de minimus* time interval it takes to collect samples from SP-2, SP-3 and SP-4, i.e. collect, label, and move to next site. An assumption will be made in the assessment that the water quality at a sampling point is representative of water quality passing at that stage in the treatment and will be used to assess overall treatment performance. The time interval will be no more than five minutes between sampling points; considering this time interval and the hydraulic retention time of the lake system, equivalent water conditions are being compared. Samples will be collected over a 20-minute period to reduce effects of influent or performance variability. Quality control duplicate samples will be collected at the frequency of one sample set per week per installation. An equipment blank will also be collected at the frequency of one sample set per week per installation. Quality control duplicate samples and equipment blanks will be sent to USACE CERL for analysis.

One sample set will be collected daily over a one week period from SP-5, HLT by-products (biocrude fuel, solid sludge, wastewater), for research purposes (Table 3). Samples will be measured to establish volume and/or weight, percent solids (sludge only), and concentration of Total Microcystins. These by-products are not the media for which the ELAP Method is applicable, and therefore all results obtained are for research purposes only.

TABLE 3. Biological and Chemical Water Quality Sampling Scheme – Onshore and Shipboard daily sampling over seven days of operation

Sampling Point	Sample Set 1 (AM)	Sample Set 2* (Mid-Day)	Sample Set 3 (PM)
2	Research	Validation, Research	Research
3	Research	Validation**, Research	Research
4	Research	Validation, Research	Research
5	-	-	Research

*A duplicate research sample set will be collected at the time of the validation sample set to confirm laboratory comparability. This will occur during the mid-day sample session at SP-2 and SP-4.

** On four of seven days, one additional performance validation sample will be collected at SP-3.

De minimus amounts of waste generated from kits or calibration standards will be collected and disposed of in accordance with manufacturer's recommendations on a daily basis.

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d) BENCH SCALE TESTING AND DOSE DETERMINATION:

USACE ERDC and AECOM will perform bench-scale testing during week one, immediately following site set-up, to identify the appropriate coagulant/flocculant doses required at a frequency that reflects the influent water variability and is in compliance with the approved Water Treatment Chemical dosing. The Water Treatment Chemical forms appended to this document describe the maximum dosing allowances for each coagulant/flocculant chemical as well as the ecological toxicity endpoints for each chemical formulation (Attachment III and IV). Based on updated toxicological studies for additional species of concern, the TramFloc222 coagulant/flocculant will not exceed a dose of 0.4ppm, the No Observable Effect Concentration for *Ceriodaphnia dubia*.

On the shipboard system, a Streaming Current Analyzer shall be used to account for influent variability. Representative water samples will be screened for their response to flocculation with a combination of TramFloc 222 (Quaternium-33, low-charge-density cPAM) and GreenFloc 5100 (GFT 5100, low-charge-density cationic starch) using a typical jar test method. Flocculated samples will be visually assessed for floc particle size, strength, and break (apparent clarity between floc particles), as well as flotation and lysis. The bench-scale testing will inform operational conditions for week three of the pilot project.

e) IN-SITU MULTIPARAMETER SONDE AMBIENT WATER QUALITY MONITORING:

One of the HABITATS lead boats will be deployed each morning to survey the algae bloom in the lake for field parameters listed in Table 2b. The boat will be equipped with a cable with two Aqua TROLL 500 Multiparameter Sondes attached: one sonde at the water's surface (0.25ft), and the other sonde three feet below the surface. Each sonde contains temperature and phycocyanin sensors for blue-green algae (cyanobacteria) quantification. One of the sondes also contains a nitrate sensor. The boat operator will take photos and collect GPS coordinates and times during the survey. The data recorded by the sensors will be paired with the logged times and GPS coordinates to generate a depth integrated map of the temperature and cyanobacteria profiles of the lake; a map of nitrate concentrations at a constant depth will be produced as well.

At least one Aqua TROLL 500 Multiparameter Sondes will remain attached to a lead boat to continue to capture surface ambient conditions in the lake throughout the treatment process. This data will be used for overall lake water quality characterization and will be informational in nature only. Due to expected water displacement from the shipboard treatment unit and the anticipated bloom dispersal caused by boating, this probe data cannot be evaluated to determine ambient water quality responses to treatment.

In addition, weekly profiling of the southern basin with the Aqua TROLL Multiparameter Sondes will be performed at additional depths (1.75 feet and 4.5 feet) to further assess the vertical gradient in bloom density.

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f) PERMIT REQUIREMENTS:

NYSDEC has considered appropriate permit requirements for the proposed project pertaining to protection of regulated wetlands and discharges of the treated water. NYSDEC has determined that these permits are not required due to the low doses and non-toxicity of the water treatment chemicals and the distance of the treatment from regulated wetlands. See attached NYSDEC DOW Bureau of Water Permits approved Water Treatment Chemical forms (Attachment III and IV). Office of Parks, Recreation, and Historic Preservation (OPRHP) will require a research permit for the proposed project to occur at Long Point State Park (Attachment V).

The project has been evaluated with the NYS Division of Fish and Wildlife (DFW) staff to make sure that the demonstration does not affect fish. The shipboard treatment will take place in the central portion of the southern basin, and will occupy areas of normal boat traffic. The following actions will be taken to minimize impacts to fish:

- Intake pumps are equipped with 1 inch screens, additional screens will be available for use with the smallest pore size of ½ inch;
- Treatment will avoid early mornings when aquatic life is more active;
- Treatment will occur in August when most fish are large enough to escape entrapment;
- The intake pump zone of influence will be the top 1-4inches of the water column; and,
- Work will cease if an environmental impact (e.g. fish kill) observed and be immediately reported to NYSDEC DFW.

The project will have limited to no impact on the aquatic plant community. The treatment technologies are optimized to target cyanobacteria, and avoid areas of plant debris and sediment. These materials would clog the intake screens and negatively impact the treatment process.

The project will have limited to no impact on critical habitat or freshwater wetlands. The shipboard and onshore treatments will avoid regulated wetland areas by at least 500ft as identified in Figure 3. The onshore treatment hose will be deployed an appropriate distance from the shoreline so as to not impact habitat or cause sediment disturbance. Due to the boat draft, the shipboard treatment will target water depths of 6ft or greater, therefore avoiding critical habitat for aquatic organisms.

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Figure 3. Article 24 Regulated Freshwater Wetlands in the proposed project area of Chautauqua Lake (green polygon). The onshore demonstration area does not have any regulated wetlands within the vicinity. The shipboard demonstration will maintain at least a 500ft distance from regulated wetlands.

g) OPERATING CRITERIA:

HABITATS Operating parameters are as follows:

On-Shore Treatment System (AECOM)

Water Treatment Flow Rate:	100 gpm
TramFloc222 Dose:	0.1 to 0.4 ppm*
GreenFloc5100 Dose:	0.5 to 5 ppm
DAF Retention Time:	25 min
DAF Recirculation Rate:	25-33 gpm
Ozone dose:	2-10 ppm
Screw Compactor Flow Rate:	1-5 gpm
Power:	30 KW

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Shipboard Treatment System (ERDC)

Boat Speed	0-0.5 knots
Flow Rate	200-400 gpm
TramFloc222 Dose:	0.1 to 0.4 ppm*
GreenFloc5100 Dose:	0.5 to 5 ppm
DAF Retention Time:	18 min
DAF Recirculation Rate	50-75 gpm
Ozone dose:	0.4 to 1.0 ppm
Screw Compactor Flow Rate:	1-10 gpm
Power	30 KW (treatment)
	0-10 KW (towing)

On-shore HTL System (solids destruction/transformation)

Flow Rate:	Up to 0.5 gpm
Biocrude Production Rate:	Up to 0.05 gpm
Power:	Up to 30 KW

*Note, updated toxicological studies for additional species of concern indicated a TramFloc222 No Observable Effect Concentration for *Ceriodaphnia dubia* of 0.4ppm. This coagulant/flocculant chemical will not exceed a dose of 0.4ppm for either onshore or shipboard HABITATS treatment systems.

h) PREVENTATIVE MEASURES:

Containment berms will be utilized around fuel storage containers at the onshore staging area to prevent spills. Containment berms will be utilized around chemical storage on the watercraft and onshore. A spill response kit with sorbent materials or pads will be available near the onshore staging area and on the watercraft.

i) PROJECT AREA:

The project area will include the Bemus Bay area on the south side of Long Point State Park as well as the south basin of Chautauqua Lake. Long Point State Park will host the on-shore demonstration, overall staging area, and access point to deploy the ship-board HABITATS technology (Attachment VI). The shipboard system will focus on areas of highest bloom intensity (i.e. within the south basin), with preference given to areas with low boat traffic and away from water supply intake structures. Shallow areas of the lake will also be avoided to reduce disturbance of aquatic habitats.

6. Quality Objectives and Criteria for Measurement Data

The project will utilize lab specific method detection limits (MDL) and QA/QC limits. The data quality indicators of precision, accuracy, representativeness, comparability, completeness, and sensitivity will be measured (when applicable) from data collected from chemical analyses of samples collected.

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Precision will be measured using a duplicate sample. Duplicate samples will be collected once per week, at a single random time during the experiment (either morning, noon or afternoon), at each treatment installation, for each laboratory, using the same sampling equipment and procedures followed for the collection of the other samples. Duplicate samples will be assigned unique sample identification numbers by staff with sampling responsibilities. The data quality objective (DQO) for precision is less than or equal to 20% relative percent difference (RPD) on duplicate samples.

Accuracy will be measured by the use of equipment blanks, which will be assigned unique identifiers by staff with sampling responsibilities. Further, the contract laboratories will undertake their own procedures, typically spiking at least 5% of the samples with a known aliquot of the parameter and carried through the analysis process as a matrix spike. The laboratory will also run the spiked reagent water blank to assess any bias in the analytical system. Sensors and Multiprobes will be calibrated to the manufacturer's specification. The DQO for accuracy is that all equipment blank samples are less than or equal to detection limits.

Representativeness of samples in this project is defined as being able to represent conditions by treatment type and over time. Treatment type representativeness will be accomplished by operating separate units (on-shore vs shipboard) in separate areas of the lake (shoreline vs open water), with sampling points across stages of the treatment train. Time representation will be based on measuring the conditions within a single day (i.e. following start-up, midday, and prior to shut-down) and over three weeks, as well as at the treatment scale by evaluating influent and effluent samples.

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. For this project, comparability will be achieved through using standard field sampling techniques to collect water samples from the same locations of the treatment process, and by obtaining analytical data from those samples following standardized methods for chemical analysis and reporting protocols. Complete field documentation using standardized data collection templates will support the assessment of comparability.

Completeness is defined as a measure of the amount of valid data obtainable from a measurement system compared to the amount that were expected to be obtained under normal conditions. To meet project needs, it is important that appropriate QC procedures be maintained to verify that valid data are obtained. The DQO for completeness is that a minimum of eighty-five percent (85%) of samples at a site are successfully analyzed and reported.

Sensitivity, as it pertains to analytical methods/instrumentation, is defined as the lowest concentration that can be distinguished from background noise. Sensitivity is measured by method detection limit (MDL) determinations, which are performed by laboratories for each analyte and matrix following procedures specified in EPA 821-R-16-006. *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2, December 2016.* The method detection limit is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable

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from method blank results. Instrument detection limits (IDLs) are similar to MDLs although the analytical procedures used for IDL determinations do not include the preparation/extraction procedures that are used for MDL determinations and environmental sample analyses. Therefore, IDLs provide a measure of sensitivity under ideal conditions, and do not take into account effects of sample matrix and/or other factors that may affect sensitivity.

7. Special Training / Certifications

USACE ERDC staff have received boat operator certification training. Additional training is not required for the water treatment systems. The on-site staff are individuals with highly specialized expertise in the operation of HABITATS and collectively have over 20 yrs. of experience in building, testing, and optimizing deployable water treatment systems.

8. Data, Documents, and Records

USACE Project Manager will be the custodian of all records related to the project. Records related to the project that will be retained include the QAPP and the following: All paperwork and electronic records relating to sample collection and submittal to the laboratory (i.e., field sheets, chain-of-custodies, Fed-ex® shipping forms, lab reports and electronic deliverables, or any other documents generated during the project).

Records will be stored in the following locations: Hard copy files will be stored in the on-site tactical operation center and transported to USACE ERDC CERL in Champaign, IL at the conclusion of the project. Electronic files will be stored on the USACE ERDC Secure network with daily electronic backup. Records will be retained for at least 5 years beyond completion of the project

II. DATA GENERATION AND ACQUISITION

1. Sampling Process Design

Influent and effluent sample ports are integrated into the DAF and Ozone/UV units at locations designed to yield representative samples for analysis. Sample locations are depicted on Attachment I and II. USACE ERDC staff will collect water samples from the SP-2, SP-3, and SP-4 locations;

2. Sampling Methods

This document has been prepared to meet the Quality Assurance/Quality Control (QAQC) requirements for the 2020 Research Demonstration of USACE ERDC HABITATS Project. Field data, sample collection methodologies, and laboratory techniques follow USACE modifications of the procedures detailed in the following documents:

- Florida Department of Environmental Protection Standard Operating Procedure FS1000 – General Sampling Procedures

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- Florida Department of Environmental Protection Standard Operating Procedure FS2000 – General Aqueous Sampling

3. Sample Handling and Custody

Samples will be collected directly from sample ports by USACE ERDC personnel wearing the appropriate personal protective equipment (PPE) for the task. All samples will be collected into sample bottles provided by the laboratories. The analytical laboratory will certify that the sample bottles are analyte-free prior to shipping. The sample container will be rinsed with the sample water and then filled. If volatiles are being sampled it is important to minimize the disturbance of the sample by directing water flow toward the inside wall of the sample container. Fill volatile sample containers so no headspace (air bubbles) are present. If containers are pre-preserved, do not overfill sample containers. All sample bottles will be labeled in the field with the sample date and time using a waterproof permanent marker. All samples will be placed on ice in coolers for processing (preservation and packing) prior to shipment to the analytical laboratory. A chain-of-custody record will be initiated (Attachment VII). Samples will be maintained under chain of custody with acceptable preservation until receipt by laboratory. USACE ERDC staff will ship samples to respective laboratories for analysis.

The expected turnaround times upon receipt of the samples for each analytical laboratory are as follows:

Test America (standard testing)	10 business days
Test America (WET testing)	< 1 month
BSA (biological testing)	< 3 months
USACE CERL (standard testing)	2 business days

4. Analytical Methods

Please see Table 1 with parameter and analytical testing listed.

5. Quality Control

The quality portion of the project's quality control methodology is designed to establish and maintain standards that will ensure the validity of the data. ERDC and Test America are responsible for maintaining internal quality control as part of the overall quality control system. Overall quality assurance is achieved by ERDC and Test America implementation of the data quality objectives and the data evaluation measures described below.

All critical chemical analyses for this project will be performed by ERDC and Test America. The majority of samples will be analyzed for research purposes by ERDC's Environmental Laboratory. This laboratory does not hold ELAP certification; however, has been used by USACE ERDC previously on similar projects and exhibited acceptable QC performance. A summary of the typical type of laboratory quality control (QC) samples used by the laboratories mentioned above is presented in Table 4 below. The QC samples which are applicable to each analysis are contained within the individual laboratory method SOP. The data obtained from these QC procedures are used to estimate the quality of analytical data, identify deficiencies, determine

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need for corrective actions for deficiencies, and interpret results after corrective actions were taken.

TABLE 4. Laboratory and field quality control samples.

Laboratory and Field QC Samples			
Name	Use	Frequency	Statistic Tracked in QC Charts
Field Duplicate	Replicate aliquot of the same sample taken through the entire analytical procedure	One per every week of sampling, per lab, per installation	Relative percent difference (RPD) between 1st and 2nd samples
Equipment Blank	Aliquot of deionized (DI)/distilled water collected with sampling equipment after it has been rinsed; analyzed for all analytes	One per every week of sampling	Value
Matrix spike (MS)	A known volume and concentration of the target analyte added to a field sample	One per every week of sampling	Percent recovery
Matrix spike duplicate	Same as MS repeated on a replicate sample aliquot	One per every week of sampling	RPD sample and matrix spike
Method blank	A type II DI water sample free of target analyte that contains all reagents and is subject to all laboratory preparation steps associated with the sample	One per batch where applicable	Value

Sample results that fall within ERDC and Test America acceptance criteria limits allow the data to be categorized as valid or acceptable. If QC rules are broken the analysis is halted, the samples are rerun, or the data may be accepted and flagged appropriately. Some examples of this are: a single measurement outside the control limits, 2-3 measurements between the warning and control limits, 7 consecutive measurements above or below the mean, several consecutive measurements all steadily increasing or decreasing, or an obvious non-random pattern.

6. Instrument / Equipment Testing, Calibration, Inspection, and Maintenance

All equipment necessary for field monitoring (e.g. field equipment, field analysis, laboratory equipment) will be operated according to the applicable method specifications and manufacturer's specifications. USACE Field Operations Manager and On-site Safety Manager

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will be responsible for testing, calibration, inspection, and maintenance of all field equipment, as necessary and per the manufacturer recommendations.

All equipment necessary for on-shore HABITATS (e.g. DAF unit, field equipment, field analysis, field screening instrumentation) will be operated according to the applicable method specifications and manufacturer's specifications. The on-shore treatment system (Intake, DAF, Ozone, Screw Compactor Press) will be operated by AECOM staff trained and experienced in field operations of this equipment. On-site staff will be responsible for HABITATS operation and for testing, calibration, inspection, and maintenance of all field equipment, as necessary and per the manufacturer recommendations. The on-shore DAF treatment unit was designed by AECOM; representatives will be on site for the duration of the Research Demonstration and responsible for its safe and efficient operation. The on-shore ozone system will be similar to a previously demonstrated system by AECOM and will be operated by a trained, experienced operator.

All equipment necessary for shipboard HABITATS (e.g. DAF unit, field equipment, field analysis, field screening instrumentation) will be operated according to the applicable method specifications and manufacturer's specifications. The shipboard harvesting and treatment system (Intake, DAF, Ozone, UV, Screw Compactor Press) will be operated by ERDC (Project Manager and Shipboard Treatment System Operator). Two additional staff will operate the lead boats (USACE Field Operations Manager, and additional certified USACE boat operators). The shipboard HABITATS prototype was designed by USACE ERDC, and assembled by Elastec, Inc.)

The trailer-mounted Hydrothermal Liquefaction (HTL) system was designed and will be operated by the University of Illinois Sustainability Technology Center. The system has been demonstrated successfully and safely for other waste streams in the past. All equipment necessary for the HTL will be operated according to the applicable method specifications and manufacturer's recommendations. University of Illinois Sustainability Technology Center will be onsite for the duration of the Research Demonstration and responsible for its safe and efficient operation.

All actions regarding testing, calibration, inspection, and/or maintenance of equipment during the project will be documented.

7. Inspection / Acceptance for Supplies and Consumables

Bottles and sample containers will be obtained from the contract laboratory for ELAP analytical services, being cleaned and/or tested to contract specifications. USACE will provide bottles and sample containers for research samples to be analyzed by USACE CERL and EL. Field Operations Manager and On-site Safety Manager will be responsible for obtaining and ensuring the integrity of other project consumables.

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8. Data Management

All data obtained for this project will be compiled and placed in a centralized location (USACE ERDC field office on-site). Electronic data will be stored on a secured server which is password protected and accessible to authorized staff only. Electronic backups of the data are made daily and stored at an offsite location. All data will be maintained for at least 5 years beyond completion of the project. USACE ERDC's Project Manager and Data Manager will be responsible for overall data management.

III. ASSESSMENT AND OVERSIGHT

1. Assessment and Response Actions

Due to the limited scope of this project, audits by the QA staff are not required. NYSDEC staff will be present during site setup, site operations, and site deconstruction. At his or her discretion, the NYSDEC Project Manager may conduct random observations and reviews of project staff and the data generated by them. Corrective action letters, when necessary, will be transmitted via email from the NYSDEC Project Manager to the affected staff.

Performance will be in accordance with agreed upon terms specified in the CRADA between USACE and NYSDEC. Deviation from intended plans and procedures should be noted by the person observing the deviation and reported to the USACE Project Manager and/or project staff responsible for the operation in question. The USACE Project Manager shall develop a corrective action plan to ensure that future sampling, analyses, etc. are conducted in accordance with the QA procedures presented in this QAPP. All deviations from intended plans and procedures are to be recorded in the appropriate field or laboratory notes.

Revisions to the Quality Assurance Project Plan are to be approved by the NYSDEC and USACE Project Managers who will notify those on the distribution list of the revision.

2. Reports to Management

All reporting and project deliverables will be compliant with the specifications, timeframes and reporting format outlined in the CRADA between USACE ERDC and NYSDEC. Publications, reports, and or advertisements will be submitted and approved in accordance with the CRADA between USACE ERDC and NYSDEC.

IV. DATA VALIDATION AND USABILITY

1. Data Review, Verification, and Validation

This QAPP shall govern the operation of the project at all times. The NYSDEC and USACE ERDC Project Managers will jointly review data as received by any parties in relation to the field measurements, analytical measurements, and assessment methods, primarily focusing on anomalies and omissions in the data. Problems observed in laboratory data will be brought to the attention of the contract manager and/or QA staff for further review.

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Water Chemistry Parameters and HABs Parameters

Water Chemistry results and HABs results, generated by the analytical laboratories are reviewed at three separate stages. First, analytic laboratory staff will follow specific laboratory protocols to ensure the quality and validity of the data. Data will be sent to the NYSDEC and USACE Project Managers in an agreed-upon electronic format.

Second, the NYSDEC and USACE Project Managers review data results during the input and processing of data files. This review includes confirmation of suspect values and the possible qualification of data results. And third, the Project Quality Assurance Officer evaluates all the quality control data results for the project to quantify the overall precision, accuracy, completeness and validity of the sampling data.

Probe Parameters

Probe (also known as multiparameter sonde) results generated by the project are reviewed at three separate stages. First, the USACE Project and Data Managers review probe data results during the input of the data into an electronic format. This review includes confirmation of suspect values and the possible qualification of data results. Second, the USACE Project and Data Managers evaluate quality control data results for the project to quantify the overall precision, accuracy, completeness and validity of the probe data. Third, the NYSDEC Project Manager will receive, review, and verify the results for validity.

2. Verification and Validation Methods

Data from this project will be verified and validated by the Project Quality Assurance Officer. Data for each of the parameters will be compared with the respective detection limits, precision and accuracy; the analytical laboratory performs these comparisons on results that they generate.

If data validity cannot be verified, these data will be qualified in the database according to [SOP 108-19: Data Validation](#). This information will be noted in the final QA/QC report. Uncertainty in the data allowed for use in the project end product will be limited to that found acceptable in the data verification and validation process.

The methods used to calculate precision, accuracy, completeness, and comparability of the project data are shown below. Acceptable levels of data validation and verification are presented in Section II 6.

- a) Precision: the degree to which two measurements are in agreement. This is evaluated by calculating the relative percent difference (RPD). $RPD = [(reference - observed)/reference] * 100$
- b) Accuracy: the degree of agreement between a sample and an accepted reference (true) value. $Accuracy = observed\ value - true\ value$ (sign of result (+ or -) indicates direction of sample bias where "+" is biased high and "-" is biased low)

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- c) Completeness: the number of valid measurements taken from the number of total measurements taken during the entire project. $\% \text{ completeness} = (\text{valid measurements} / \text{total number of measurements}) * 100$
- d) Comparability: achieved by adherence to routine sampling and analytical methods, sampling handling, holding times, using consistent measurement units, and consistent rule sets for reporting information.
- e) Representativeness: addressed by using standard sampling protocols in regard to sample location within the treatment system and frequency of sampling (for temporal representativeness).

3. Data Usability Assessment

The NYSDEC and USACE ERDC Project Managers will jointly review all data generated by the project to ensure it meets the objectives of the projects. Data that do not meet requirements for precision, accuracy, completeness or comparability will be carefully evaluated by the NYSDEC and USACE Project Managers (in consultation with the contract analytical lab) for deviations from analytical and field and accepted paradigms. Data of questionable usability will be brought forth to the QA staff for further review. If warranted, these data will be removed from the data set with appropriate comments regarding decision process for removal. All data assessed as useable will be used to generate the final decision/outcome of the project. NYSDEC and USACE ERDC will jointly assess the usability of the data, and determine whether the data can be evaluated to measure effectiveness of the treatment unit to remove algae from the source water, and document any impacts to nutrients and/or water chemistry.

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ATTACHMENT I.

Preliminary On-Shore Habitats Process Flow Diagram. Sampling Points identified: SP-1 (ambient), SP-2 (Influent), SP-3 (DAF Effluent), SP-4 (Ozone/UV Effluent). University of Illinois is responsible for Hydrothermal Liquefaction (HTL) System Operation; AECOM is responsible for the organic coagulant addition, DAF and ozone oxidation systems operation; USACE is responsible for all other treatment components identified below.

3/20/2020

DRAFT - FOR OFFICIAL USE ONLY (FOUO)

Note: Solids generation rate assumes
100 mg/L of influent algae

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ATTACHMENT II.
Preliminary Shipboard Habitats Process Flow Diagram. Sampling Points identified: SP-2 (Influent), SP-3 (DAF Effluent), SP-4 (Ozone/UV Effluent). University of Illinois is responsible for HTL System Operation; USACE is responsible for all other treatment components identified below.

Notes:
Solids generation rate assumes 100 mg/L of influent algae.
Solids management will happen at the same site as the on-shore demo.

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3/20/2020

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ATTACHMENT III.

WTC Form Tramfloc222

New York State Department of Environmental Conservation
 Division of Water
 SPDES Permit - **WTC Notification Form** Page 1 of 3 (Rev 2007)

For help completing this form refer to instructions page and to <http://www.dec.ny.gov/permits/93245.htm>.

1.a. Date Signed by Permittee - 18 JUL 2020		1.b. Date Signed by WTC Manufacturer 11 JUL 2020	
2.a. Permittee Name - US Army ERDC		2.b. SPDES No. - NY	
2.c. Contact Name - Martin Page			
3.a. WTC Name - Tramfloc 222			
3.b. WTC Manufacturer - Tramfloc, Inc.			
4.a. WTC Function - Coagulant/Flocculant-Charge Neutralization for Dissolved Air Flotation Treatment			
4.b. If WTC is a biocide is it NYS registered? ☒ Yes ☐ No		4.c. Registration Number - N/A	
5. WTC Point of Addition - Upstream of dissolved air flotation clarifier			
6. Affected Outfall(s) - Mobile shipboard system on Chautauqua Lake, off-shore			
7.a. WTC Daily Dosage: average lbs/day =		1.2, maximum lbs/day = 1.2	
7.b. Dosage Frequency: minutes/day =		360, days/week = 6	
8.a. Outfall Flow Rate: average MGD =		0.144, maximum MGD = 0.576	
8.b. Outfall WTC Concentration: average mg/l =		1, maximum mg/l = 1	
9.a. System Blowdown Flow Rate: average gpm =		0, maximum gpm = 0	
9.b. System Blowdown Frequency: minutes/day =		0, days/week = 0	
10.a. WTC Composition - Ingredients/Impurities (note: ingredients/impurities must total to 100%)	10.b. %	10.c. CAS#	10.d. Outfall Concentration
Cationic Polyacrylamide (cPAM)	92	69418-26-4	0.92 mg/l
Water	7-8	7732-18-5	0.08 mg/l
Acrylamide	< 1	79-06-1	0.01 mg/l
Note: > 90% of cPAM will be removed during the treatment process			
Cationic Polyacrylamide (cPAM)	92	69418-26-4	< 0.092 mg/l
Water	7-8	7732-18-5	0.08 mg/l
Acrylamide	< 1	79-06-1	< 0.01 mg/l
10.c. Intermediate/Final Degradation Products - Biodegradable, Non-harmful hydrolysis products			
11. WTC BOD and COD (lb/lb) - To be determined			

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Division of Water
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(Oct 2013)

1.a. Date Signed by Permittee -		1.b. Date Signed by WTC Manufacturer -	
2.b. SPDES No. - NY			
3.a. WTC Name - Tramfloc 222		7.a. Avg/Max Daily Dosage = 1.2 / 1.2 lbs/day	
12. WTC Toxicity Info (most sensitive species) - Attach description of endpoint for each EC50.			
12.a. Vertebrate Species	Acute LC50	Acute EC50	Chronic NOEC
P. promelas (EPA standard test method)	data pending mg/l	data pending mg/l	data pending mg/l
12.b. Vertebrate Species	Acute LC50	Acute EC50	Chronic NOEC
Oncorhynchus mykiss (manufacturer reported)	> 100 mg/l	mg/l	mg/l
12.c. Invertebrate Species	Acute LC50	Acute EC50	Chronic NOEC
Daphnia magna (manufacturer reported)	mg/l	> 100 mg/l	mg/l
12.d. Invertebrate Species	Acute LC50	Acute EC50	Chronic NOEC
C. dubia (EPA standard test method)	5.4 mg/l	mg/l	data pending mg/l
13. Summarize measures in place to ensure that excessive levels of WTC are not used - Hourly grab samples of effluent water quality; inline streaming current analyzer and proportional gain dosing pump to automate dosing for optimal DAF particle/chemical removal and limit over-dosing; Batch stock feeding (hourly); Pre-dilution of stock prior to dosing; Hourly documentation of chemical consumption			
14. WTCs to be discontinued when use of this WTC begins - N/A new system			

15. Permittee Certification - I certify under penalty of law that this notification and all attachments are, to the best of my knowledge and belief, true, accurate and complete. I also certify that the WTC Usage Requirements and any additional requirements specified on page 3 of this form will be adhered to.

PRINT NAME - Martin Page	SIGNATURE - PAGE, MARTIN A. <small>Digitally signed by PAGE, MARTIN A. 1392763801 Date: 2020.08.17 12:00:06 -05'00'</small>
TITLE/COMPANY - US Army ERDC CERL	
TELEPHONE - 217-373-4541	EMAIL - Martin.A.Page@usace.army.mil

16. WTC Manufacturer Certification - I certify under penalty of law that this notification and all attachments are, to the best of my knowledge and belief, true, accurate and complete.

PRINT NAME - Richard Binkowski	SIGNATURE - <i>Richard Binkowski</i>
TITLE/COMPANY - Tramfloc Inc	
TELEPHONE - 480-459-1695	EMAIL - water@tramfloc.com

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ATTACHMENT IV.

WTC form Greenfloc5100

New York State Department of Environmental Conservation
Division of Water
SPDES Permit - WTC Notification Form Page 1 of 3

(Oct 2013)

For help completing this form refer to instructions page and to <http://www.dec.ny.gov/permits/93245.html>

1.a. Date Signed by Permittee - 18 JUL 2020		1.b. Date Signed by WTC Manufacturer 11 JUL 2020	
2.a. Permittee Name - US Army ERDC		2.b. SPDES No. - NY	
2.c. Contact Name - Martin Page			
3.a. WTC Name - GreenFloc 5100 (GFT 5100)			
3.b. WTC Manufacturer - Dober, Inc.			
4.a. WTC Function - Coagulant/Flocculant-Charge Neutralization for Dissolved Air Flotation Treatment			
4.b. If WTC is a biocide is it NYS registered? ☐ Yes ☒ No		4.c. Registration Number - N/A	
5. WTC Point of Addition - Upstream of dissolved air flotation clarifier			
6. Affected Outfall(s) - Mobile shipboard system on Chautauqua Lake, off-shore			
7.a. WTC Daily Dosage: average lbs/day =		6 , maximum lbs/day = 6	
7.b. Dosage Frequency: minutes/day =		360 , days/week = 6	
8.a. Outfall Flow Rate: average MGD =		0.144 , maximum MGD = 0.576	
8.b. Outfall WTC Concentration: average mg/l =		5 , maximum mg/l = 5	
9.a. System Blowdown Flow Rate: average gpm =		0 , maximum gpm = 0	
9.b. System Blowdown Frequency: minutes/day =		0 , days/week = 0	
10.a. WTC Composition - Ingredients/Impurities (note: ingredients/impurities must total to 100%)	10.b. %	10.c. CAS#	10.d. Outfall Concentration
Proprietary Cationic Starch (details provided separately)	22	TBD	1.2 mg/l
Water	78	7732-18-5	3.8 mg/l
			mg/l
Note: > 90% of OFT will be removed during the treatment process			mg/l
Proprietary Cationic Starch (details provided separately)	22	TBD	0.12 mg/l
Water	8	7732-18-5	0.38 mg/l
			mg/l
10.e. Intermediate/Final Degradation Products - Biodegradable, Non-harmful hydrolysis products			
11. WTC BOD and COD (lb/lb) - To be determined			

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New York State Department of Environmental Conservation

Division of Water

SPDES Permit - WTC Notification Form Page 2 of 3

(Oct 2013)

1.a. Date Signed by Permittee -		1.b. Date Signed by WTC Manufacturer -	
2.b. SPDES No. - NY			
3.a. WTC Name - GreenFloc 5100 (GFT5100)		7.a. Avg/Max Daily Dosage - 6 / 6 lbs/day	
12. WTC Toxicity Info (most sensitive species) - Attach description of endpoint for each EC50.			
12.a. Vertebrate Species	Acute LC50	Acute EC50	Chronic NOEC
P. promelas (EPA standard test method)	20 mg/l	12 mg/l	6 mg/l
12.b. Vertebrate Species	Acute LC50	Acute EC50	Chronic NOEC
	mg/l	mg/l	mg/l
12.c. Invertebrate Species	Acute LC50	Acute EC50	Chronic NOEC
	mg/l	mg/l	mg/l
12.d. Invertebrate Species	Acute LC50	Acute EC50	Chronic NOEC
C. dubia (EPA standard test method)	8 mg/l	6 mg/l	1.5 mg/l
13. Summarize measures in place to ensure that excessive levels of WTC are not used - Hourly grab samples of effluent water quality; inline streaming current analyzer and proportional gain dosing pump to automate dosing for optimal DAF particle/chemical removal and limit over-dosing; Batch stock feeding (hourly); Pre-dilution of stock prior to dosing; Hourly documentation of chemical consumption and system flow rates			
14. WTCs to be discontinued when use of this WTC begins - N/A new system			

15. Permittee Certification - I certify under penalty of law that this notification and all attachments are, to the best of my knowledge and belief, true, accurate and complete. I also certify that the WTC Usage Requirements and any additional requirements specified on page 3 of this form will be adhered to.

PRINT NAME - Martin Page	SIGNATURE - PAGE.MARTINA.1 392763801	<small>Digitally signed by PAGE.MARTINA.129263801 Date: 2020.07.16 11:50:57 -0500</small>
TITLE/COMPANY - US Army ERDC CERL		
TELEPHONE - 217-373-4541	EMAIL - Martin.A.Page@usace.army.mil	

16. WTC Manufacturer Certification - I certify under penalty of law that this notification and all attachments are, to the best of my knowledge and belief, true, accurate and complete.

PRINT NAME - Anthony Weisner	SIGNATURE - <i>Anthony Weisner</i>
TITLE/COMPANY - Dober Inc	
TELEPHONE - 800-323-4983	EMAIL - tweisner@dober.com

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ATTACHMENT V.

Research Permit from OPRHP

**Parks, Recreation
and Historic Preservation**

ANDREW M. CUOMO
Governor

ERIK KULLESEID
Commissioner

**PROJECT PERMIT
#ALL - LP10-01**

Permittee	New York State Department of Environmental Conservation 625 Broadway, 4th Fl, Albany, NY 12233	Region	Allegany
Permittee Contact	Karen Stainbrook, Division of Water Telephone: (518) 402-8095 Email: karen.stainbrook@dec.ny.gov	Site	Long Point State Park
Federal EIN	14-6013200	State Parks Contact	Marla Connolly Telephone: (716) 450-6490 Email: Marla.Connolly@parks.ny.gov
Fee	\$0	Start Date	8/17/2020
		End Date	9/25/2020

*Permittee must provide current proof of compliant workers' compensation and disability benefits insurance upon signing.
Permittee must provide the following environmental review documentation prior to issuance:
If State Parks is not the lead agency: a copy of the SEQRA or NEPA declaration from the lead agency listed in Section 3(c)
If issuance of this permit is a Type II action: (1) written confirmation from State Parks' Division for Historic Preservation that its activity will not impact historic resources, including archeological resources; (2) written confirmation from State Parks' Division of Environmental Stewardship and Planning that its activity will not impact natural resources identified under the New York Natural Heritage Program or impact an area that has received by funding from under the federal Land and Water Conservation Fund*

Required Attachments: ISP/Permit map IS/Copies of required permits (other State agencies, federal)

Upon the following terms and conditions, the New York State Office of Parks, Recreation and Historic Preservation ("State Parks") hereby grants Permittee permission to conduct the following project at the Site as shown on the attached map (the "Project"):

U.S. Army Corps of Engineers' Engineer Research and Development Center is deploying its innovative research demonstration project - named Harmful Algal Bloom Interception, Treatment and Transformation System (HABITATS) - in portions of the southern half of Chautauque Lake later this year. The pilot project uses floating skimmers on the lake to collect surface water laden with HABs. Once collected, the blooms are put through shore-based or mobile treatment processes, which detoxify the algae, concentrate it, and convert it into biocrude fuel and fertilizer. During the process, treated water is cleaned, clarified, and safely returned to the lake. Project staging and site access will be coordinated through the Office of Parks, Recreation, and Historic Preservation at Long Point State Park in Beaman Point, New York. The shore-based unit will be operated from the shoreline of Long Point State Park. The mobile treatment unit will depart from Long Point State Park each day to operate in the open water of the lake. Project duration is estimated at approximately three weeks, and will require boat launch access, boat storage (5 slips), a freshwater source (200 gallons/day), staging area (approximately 18,000 sq. ft), and installation of temporary security fencing.

This Permit does not convey to Permittee any interest other than permission to undertake the Project in accordance with this Permit. Permittee acknowledges that the Site is public non-residential space and that State Parks grants only a right to use "as is/where is" and without warranty.

Section 1. Operations

- Permittee shall conduct its activities only in the locations shown on the attached map (the "Premises"). Permittee shall control access to the work areas and provide safety fencing around all work areas.
- Permittee must obtain all permits required for the Project, and provide copies of such permits to State Parks.
- Permittee shall remove and dispose of all waste and refuse generated by its activities under this Permit.

Section 2. Protection of Park Resources

- Permittee shall take care to protect any existing utilities and structures. At least forty-eight hours before undertaking any operation that would be considered "excavation" as defined in New York State Industrial Code 53, Permittee shall notify the "One-Call Notification System" to ensure that all public utilities are properly marked out; Permittee shall retain the services of a private mark-out company to work with the Park Manager to identify and mark out utility services owned and operated by State Parks.

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(b) Permittee shall take care to protect all existing trees on the Premises. Permittee may only cut or trim trees to the extent permitted by Section 9; if Section 9 contains no provision for the cutting or trimming of trees or shrubs, Permittee shall not engage in such activities.

(c) Permittee shall repair, replace, or rebuild any part of the Premises or Park, or any improvements thereon, damaged or destroyed by the actions or omissions of the Permittee, and shall restore disturbed areas of the Premises or of the Park as near to their original condition as reasonably possible by proper grading, topsoiling, and seeding. Such restoration shall be subject to State Parks' approval.

Section 3. Coordination with State Parks

(a) Permittee shall coordinate the timing of work with Maria Connelly, Park Manager II and give State Parks forty-eight hours advance notice prior to the start of work.

(b) Permittee shall comply with all reasonable requests made by State Parks.

(c) State Parks is the lead agency with respect to the State Environmental Quality Review Act.

Section 4. Indemnification

Permittee agrees to defend, indemnify, and hold harmless the State of New York, State Parks, and their officers, employees, and agents from and against any claims, damages, losses, and expenses that may arise from this Permit or from Permittee's use of the Premises.

Section 5. General Liability Insurance and Proof of Insurance

(a) Permittee shall obtain general liability insurance at its own expense from a company licensed to conduct business in the State of New York. Such insurance policy shall name the State of New York, State Parks, and their officers, employees, and agents as an additional insured; have a liability limit of at least \$1,000,000 each occurrence and \$2,000,000 general aggregate; and be endorsed to provide written notice to State Parks at least 30 days prior to cancellation, non-renewal, or material alteration.

(b) Prior to the start of the term of this Permit, Permittee shall deliver to State Parks an ACORD 25 Certificate of Insurance and the applicable endorsements evidencing the coverage required by this Permit.

(c) Permittee shall require that all its contractors and sub-contractors for the Project meet the insurance coverage requirements of this Section.

(d) Section 8 notwithstanding, State Parks may terminate this Permit without notice if Permittee fails to comply with the insurance requirements of this Permit.

Section 6. Revocation

If at any time during the term of the Permit, State Parks needs the Premises for the performance of its public purposes, State Parks may revoke this Permit by giving Permittee 10 days' notice in writing. Upon the date fixed in such notice, this Permit shall come to an end as if said date were the date originally fixed in this Permit for expiration.

Section 7. Termination

In the event Permittee violates any applicable statute, law, rule, or regulation or does not comply with the terms and conditions of this Permit, State Parks may terminate this Permit by giving Permittee 10 days' notice in writing by regular mail or email of its intention to do so if the violation is not cured.

Section 8. General Conditions

(a) State Parks may inspect the Premises at any time.

(b) State Parks is not required or obligated to make or undertake any repairs, improvements, or maintenance work of any kind.

(c) Permittee shall comply with all applicable federal, State, and local laws, ordinances, rules, and regulations. If Permittee fails to do so, State Parks may enter the Premises and take whatever steps are necessary to achieve compliance and may bill Permittee for the cost of doing so; Permittee shall pay State Parks any amount billed within 30 days of the billing date.

(d) Permittee acknowledges that the waiver by State Parks of any term or condition of this Permit is not a waiver of any other term or condition, nor is it a waiver of the subsequent breach thereof.

(e) Permittee shall not assign or transfer this Permit. State Parks and Permittee understand that Permittee's contractors and sub-contractors are entitled to access and use the Premises for the purposes described herein, subject to the conditions of this Permit.

Section 9. Special Conditions

1. The permittee shall submit a summary of findings to the contact for the Region where the project took place within a year of the research end date (as identified on this permit). State Parks further requires that the researcher(s) provide copies of or otherwise make available to State Parks any material published as a result of this permit.

2. The permittee shall promptly report any and all unusual incidents directly to the Park Manager or Park Police (716) 354-9111. Unusual incidents include, but are not limited to, damage to Park property, accidents, personal injuries, and emergencies involving medical personnel.

3. The permittee is responsible for providing all necessary traffic control devices and flaggers necessary for the safe and successful execution of the project, and must coordinate plans for road closures or other significant interruptions to the normal flow of traffic with State Parks prior to commencement.

Accepted by: New York State Department of Environmental Conservation

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By:
Title: Karen Stainbrook, Research Scientist 4

Date: 8/12/2020

Issued by: THE PEOPLE OF THE STATE OF NEW YORK

Acting by and through the Commissioner of Parks, Recreation and Historic Preservation

By:
Jon G. Butler, Regional Director

Date: 8/15/20

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ATTACHMENT VI.

Map of Long Point State Park Onshore Demonstration, Staging Area, and Site Access

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ATTACHMENT VII. Template Chain of Custody Record

Eurofins TestAmerica, Buffalo		Chain of Custody Record	
10 Hazardous Drive			
Arboret, NY 14225-2223			
phone 716.691.2000 fax 716.691.7091			
Regulatory Program: ☐ Air ☐ MCL ☐ NCL ☐ Other			
Project Manager:			
Client Contact		Date:	
Your Company Name		Carrier:	
Address		COC No.	
City/State/Zip		TALS Project #	
Local 800-800-8000 Phone		Sampler	
Local 800-800-8000 FAX		For Lab Use Only:	
Project Name:		Well-In Client	
Site		Lab Sampling	
P.O.#		Job / SOO No.	
Sample Identification		Sample Specific Notes	
Sample Date	Sample Time	Sample Matrix	Sample Count
Preservation Used: 1= Ice, 2= HCL, 3= H2SO4, 4= HNO3, 5= NaOH, 6= Other _____ Possible Hazard Identification: Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample. ☐ Non-Hazard ☐ Dischargeable ☐ Acidic ☐ Alkaline ☐ Other			
Special Instructions/OC Requirements & Comments:			
Custody Seal Intact:	☐ Yes ☐ No	Custody Seal No.:	
Relinquished by:	Company:	Received by:	Company:
Relinquished by:	Company:	Received by:	Company:
Relinquished by:	Company:	Received in Laboratory by:	Company:
Form No. CH-C-001-002, Rev. 4/04, dated 8/2000			

REPORT DOCUMENTATION PAGE				<i>Form Approved</i> <i>OMB No. 0704-0188</i>	
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				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT	
6. AUTHOR(S) Martin Page, Bruce MacAllister, Marissa Campobasso, Angela Urban, Catherine Thomas, Clinton Cender, Clint Arnett, Craig White, Edith Martinez-Guerra, Ashley Boyd, Elizabeth Gao, Al Kennedy, Tom Biber, Kaytee Pokrzywinski, Chris Grasso, Briana Fernando, Chris Veinotte, Jim Riley, Ashley Gonzalez, Jay Miller, Kathryn Gunderson, Lance Schideman, Yuanhui Zhang, B.K. Sharma, Dan Levy, Bill Colona, David Pinelli, Tammy Karst-Riddoch, and Will Lovins				5d. PROJECT NUMBER	
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14. ABSTRACT Harmful algal blooms (HABs) continue to affect lakes and waterways across the nation, often resulting in environmental and economic damage at regional scales. The US Army Engineer Research and Development Center (ERDC) and collaborators have continued research on the Harmful Algal Bloom Interception, Treatment, and Transformation System (HABITATS) project to develop a rapidly deployable and scalable system for mitigating large HABs. The second year of the project focused on optimization research, including (1) development of a new organic flocculant formulation for neutralization and flotation of algal cells; (2) testing and initial optimization of a new, high-throughput biomass dewatering system with low power requirements; (3) development, design, assembly, and initial testing of the first shipboard HABITATS prototype; (4) execution of two field pilot studies of interception and treatment systems in coordination with the Florida Department of Environmental Protection and New York State Department of Environmental Conservation; (5) conversion of algal biomass into biocrude fuel at pilot scale with a 33% increase in yield compared to the previous bench scale continuous-flow reactor studies; and (6) refinement of a scalability analysis and optimization model to guide the future development of full-scale prototypes.					
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 SAR	18. NUMBER OF PAGES 227	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code)

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